Jaap J. Boon*, Mark Richter**

Organic Constituents Analysed by DTMS in Grounds, Bole and Transparent Colored Glazes Sampled from Polychrome Works of Art (c. 1620–1780)

Introduction

Coloured glazes on silver leaf presented in this article come from polychrome works of art located in Southern Germany, Austria and Switzerland.[1] They were the main focus of the research project 'The Polychromy of Sculptures and Altarpieces of the Baroque and Rococo Period' funded by the German Research Council (DFG). A more detailed introduction to the technique of polychromy is given elsewhere in this publication.[2] Since almost nothing is known about the organic chemical composition of glazes on polychromy, we have analysed representative samples from a large number of altarpieces made by different painters and polychromers in the period from 1620–1780. The method of direct temperature resolved low voltage electron ionization mass spectrometry (DTMS) was chosen to analyse these samples since this analytical approach was successfully used before in the characterization of blue glazes from altarpieces of the same time period [Van Loon et al. 2004].

Coloured glazes on metal leaf belong to the more striking and complex embellishing techniques in polychromy, which reached a new level of refinement and magnificence in the Baroque and Rococo period. They were executed by various artists and craftsmen (painters, polychromers, gilders and even lacquerers) who often had a perfected and refined repertoire of techniques, achieving a variety of contrasts in colour, surface reflection and texture by using a range of methods. This includes varying the layer structure and composition of the ground, intermediate sizes, preparatory layers (bole, mordant), adhesives, gilding techniques and coatings (coloured glazes, final gloss lacquer). Often this combination of techniques revealed an unforeseen compositional complexity in its multi-layered build-up especially regarding the organic components. Until now a wide range of organic constituents have been identified within the build-up, which not only served as binding media, but also fulfilled other purposes in various layers, above all the preparatory layers and coloured glazes.[3] Analysis of these materials will give us more insight into their use and the artistic intentions.

The composition of binding media and other organic components (coloured resins, additives to these layers) is complex, as seperate layers analysed will be shown to contain different components, extractable as well as cross-linked organic compounds. In many cases it was possible to manually separate or purify specific layers from the polychromed stratigraphy using a binocular stereomicroscope. In this chapter we present the analytical methodology, criteria for interpretation of mass peak patterns and spectra of relevant reference materials, as well as a list of identified materials in the samples from altarpieces and historical interiors. Spectral features will also be mentioned in the chapters of the art works elsewhere in the book.

Analytical DTMS

Direct temperature resolved mass spectrometry, chosen as the principal technique for the analysis of samples from the altarpieces and other polychrome works, can characterise a very broad spectrum of organic materials and even inorganic matter such as carbonates, sulphates, sulphides and elements such as lead, mercury, copper, zinc, arsenic and antimony [Boon 1992; Boon et al. 2007]. The analytical process requires a few micrograms of sample that is placed on an analytical probe equipped with a

* Prof. Dr. emeritus Jaap J. Boon, JAAP Enterprise, Nieuwendammerdijk 79, NL-1025LD Amsterdam, molartadvice@jaap-enterprise.com
** Dr. Mark Richter, Heßstr. 102b, D-80797 München, MarkRichter33@gmx.de

1 The samples were taken during the duration of the DFG research project 'Die farbige Fassung von Skulpturen und Altarretabeln des Barock und Rokoko' between 2005 and 2009.
2 See articles by Michael Kühlenthal and Mark Richter in this publication.
3 Good examples of this are the addition of beeswax and other substances to bole-based preparatory layers beneath the metal leaf, which increase the cushioning effect of this application, making it ideal for polishing. Another example is the admixture of starch to red glazes pigmented with cochineal lake. See articles of various case studies (e.g. Mondsee, Georgenberg, Ering am Inn) and table in the Appendix of this publication, pp. 796–797.

Platinum-Rhodium wire (9:1). This probe is placed inside the ion source of the mass spectrometer via a vacuum lock system. The apex of the platinum-rhodium wire is positioned close to the main extraction field in the ion source. Analysis takes place *in vacuo*. The sample is taken through a thermal ramp by temperature programmed resistive heating of the wire which leads to the appearance of released volatiles, adsorbed compounds, metals soaps, cross-linked substances and inorganics in subsequent temperature windows. Since the compounds are ionized at low voltage, primarily molecular ion information and some fragment ion patterns are detected. The ion patterns are interpreted by mass spectral interpretation, in comparison with reference compounds and with GCMS data if available. The small size of the samples that is required for analysis makes it possible to analyse manually separated layers. For example, samples from some altarpieces could be split into ground, bole, glaze and paint if the size of the sample and layer thickness allowed it. All samples were also analysed routinely in cross-section with light microscopy (VIS and UV-fluorescence) and scanning electron-microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX). Some cross-sections were analysed with imaging FTIR microscopy. These data are discussed elsewhere in the context of the works of art. The main focus of this chapter is the organic chemical composition of the layers applied on the polychrome sculptures, altarpieces or interiors.

Experimental details

The mass spectrometer was a JEOL double focussing mass spectrometer SX102-102A equipped with a JMA-MP7000 data system. Volatile compounds released were analysed under electron ionisation conditions at 16 eV (ion source temperature 160 °C). Ions were post accelerated to 8 kV and separated over a mass range of 20–1000 Dalton at a cycle time of 1 second. The temperature of the probe was kept isothermal in the ion source for 10 seconds and then raised at a ramp of 16 °C/second to reach a final temperature of 800 °C. Data were acquired over a period of 2 minutes.

After preparation and selection of sample under the stereomicroscope (magnification up to 40x), a sample was selected and transferred to a glass mini-mortar for grinding with a glass pestle (5 mm diameter), to a homogenous suspension in ethanol (about 40 microliter). An aliquot of this suspension (about 4 microliter using a SGE microsyringe) was placed as a droplet on the platinum-rhodium (9:1) wire (diameter 100 micron). The ethanol was evaporated *in vacuo* using an oil-free vacuum pump system linked to a vacuum pot equipped with a similar vacuum lock system as present on the mass spectrometer.

The analytical spectrum of materials studied by DTMS

Since the materials used in polychromed works of art (sculpture, altarpieces, architecture) involve such a wide spectrum of chemical compounds, the analysis of standard references potentially used by the artists and artisans is appropriate. The following substances were analysed in the course of the project: Di- and triterpenoid resins (pine resins, Venetian turpentine, sandarac, mastic, frankincense, elemi), vegetable drying oils, egg and collagen proteins, starch polysaccharide, polysaccharide gums, shellac, dragon's
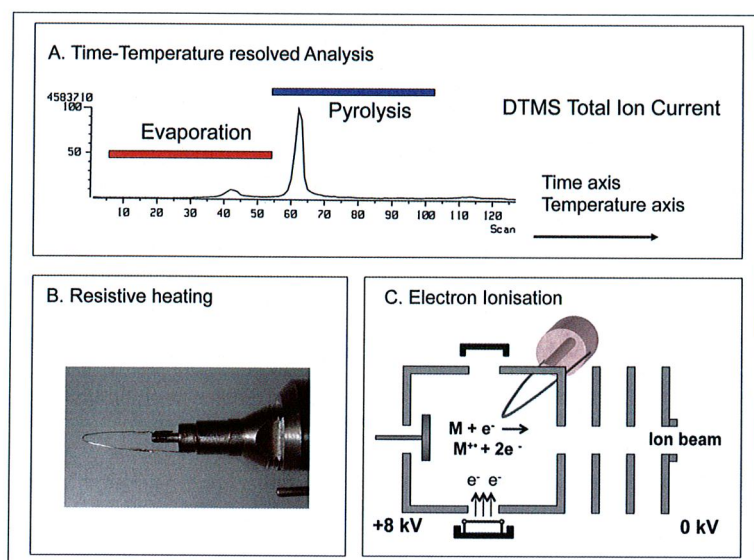

Fig. 1 The low and high temperature parts of the total ion current (TIC) profile during a DTMS measurement correspond with evaporation of compounds (red bar) and pyrolytic dissociation of polymers and cross linked compound networks. The homogenised sample is placed on the loop of the Platina/Rhodium wire. The aspex of the probe wire is placed near the central extraction axis inside the ion source where evolved compounds are ionised by low voltage electrons before extraction into the mass spectrometer.

blood, gamboge, beeswax and related plant waxes, cholesterol and oxidised cholesterols, and even various synthetic resins used in conservation. Table 1 lists these materials and their main characteristic molecular and fragment ions. In many cases they are not single pure compounds but rather mixtures of compounds isolated from natural substances such as tree exudates. This is particularly true for the terpenoid resins [see papers in WALCH/KOLLER 1997]. In the DTMS of sandarac, a volatile and cross-linked fraction is present that will appear with its specific features in subsequent temperature windows (see TIC and MS in Fig. 2c). In that case the mass fragment patterns as well as the appearance temperature windows of the released compounds are taken into account.

Age and conservation treatments also influence the composition. Resins form oxidation products that have been subject of several DTMS and GCMS studies in the past [VAN DER DOELEN et al. 1998; VAN DER DOELEN 1999; VAN DEN BERG et al. 2000; VAN DEN BERG 2003; SCALERONE et al. 2003; THEODORAKOPOULOS et al. 2009] using our instruments. Some of these oxidation processes lead to completely different mass peak patterns and also to differences in the appearance temperature window. Generally oxidation leads to the appearance of compounds in higher temperature windows and a development of cross-linked fractions that also appear as pyrolysis products at a higher temperature. Drying oils change very much in their composition upon drying and ageing [BOON et al. 1997 and 2007; VAN DEN BERG 2002; VAN DEN BERG et al. 2004]. Diacylglyceryl ions like m/z 550, 576 and 604 in DTMS data point to relatively intact glycerol ester carbon skeletons. Triglycerides rarely survive the electron ionisation process since they loose a fatty acyl moiety upon ionisation even at low voltage. Furthermore, ageing leads to hydrolysis of the biological ester bonds and the formation of metal soaps [VAN DEN BERG et al. 2002]. Monocarboxyl lead soaps are unstable under the analytical conditions and lead to appearance of fatty acids in higher temperature windows. Metallic lead is then observed in the highest temperature window. Diacid networks also dissociate but are much more temperature stable [IBIDAPO et al. 1996]. The appearance of lead azelate ions at m/z 348 and 350 points to the presence of free azelate soaps (C9 diacid soaps). These ions are sometimes observed. Azeleic acid itself decarboxylates to a lacton like ion at m/z 152 and a fully decarboxylated compounds with an ion at m/z 98. DTMS analysis of aged drying oils always gives rise to a high abundance of ions forming alkyl-aromatic ion series like m/z 91 (alkyl-benzenes), 105 (alkyl-toluenes) and 119 (alkyl-xylenes) etc. most likely due to the abundance of elimination reactions in the cross-linked substances leading to aromatic radicals that condense into a new more thermally stable substance [VAN DEN BERG 2002]. The peak profiles in the temperature window of compounds related to "cross-linked" oil extend past m/z 500. These compounds are of secondary origin and represent a charred fraction that is (re)pyrolysed at a higher temperature. Since these compounds represent a relatively large amount of the organic matter in a paint sample with oils, we will mark them as abundant in the tables listing the relative concentration of compounds in the samples from works of art. The fatty acid distribution is related to the vegetable or animal origin of the fats and oils relevant to art objects [MILLS 1966; MILLS/WHITE 1987]. Conserved vegetable oil fatty acids generally consist of palmitic (C16:0 FA) and stearic (C18:0 FA) acids because the unsaturated C18 fatty acids cross link and finally oxidise to C9 diacids and related compounds. Myristic acid (C14:0 FA) is found in eggs and animal fats. The ratio of palmitic and stearic acid (P/S ratio) is used as a marker for the origin of the oil from linseed (P/S < 2), walnut (P/S 2.5–3.5) and poppy seed oil (P/S > 3.5). If fatty acids are trapped as soaps at an early stage in the ageing of the artwork, there is a good chance that the P/S ratio is still representative. It is our experience that P/S ratios in DTMS match well with data obtained by GCMS. Proteins are complex molecules with a peptide chain and many different side chains depending on the amino aid composition. DTMS has been used to study proteins in plant matter [VAN ARENDONK et al. 1997]. The DTMS patterns of gelatine or animal glues are very specific and the structure of gelatine appears relatively stable and less prone to ageing. Egg proteins are much more complex and have a less unique peak pattern. Egg proteins are prone to ageing but the aliphatic amino acids appear to be more stable and thus contribute to the spectral features [BOON/DE LEEUW 1987]. Animal glue is rich in proline and thus proline ketopiperazines are relatively abundant. Main mass spectral features in DTMS data are ketopiperazines with m/z 70, 111 and 154 as fragment ions.

The co-occurrence of cholesterol and its oxidation products may be taken as a marker that egg yolk has been used in the artwork. VAN DEN BRINK et al. in 2009 have studied the DTMS features of oxidised cholesterol by MSMS and related the mass peaks to potential structures of the molecules involved.

There are various indications in the historical sources that shellac, gamboge and dragon's blood have been used as colouring matters in coloured lacquers [see table in appendix of this publication]. The DTMS spectra of these compounds give very specific peak patterns and have been recognised in some samples. Dragon's blood could not be discerned, possibly due to the fact that only a very small relative amount is required for a suitable colour effect as in the case of so-called gold lacquers (German: Goldlack) on metal leaf. The peaks of dragon's blood range between 200 and 300 overlap with other compounds and are partly isobaric. Conservation treatments such as cleaning with solvents may result in the loss of volatile and adsorbed compounds or even introduce new materials. Where relevant, such effects will be mentioned. Similarly, in some cases acrylates like B72 (Paraloid) or ketone resins have been detected [LEARNER 2004].
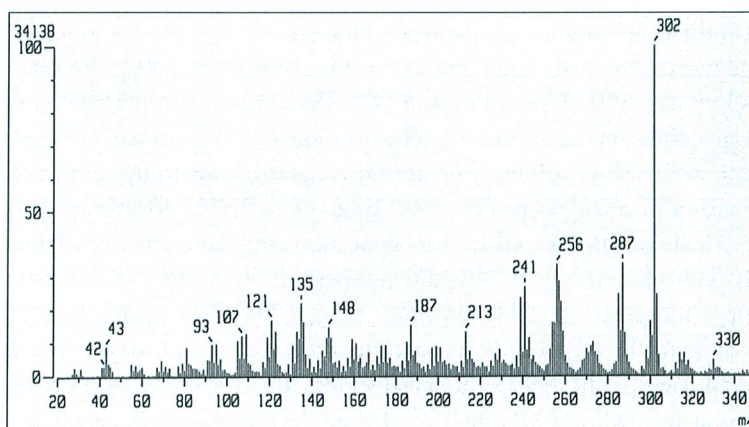

Fig. 2a DTMS of fresh colophonium (commercial product in MOLART collection Amolf 1994).
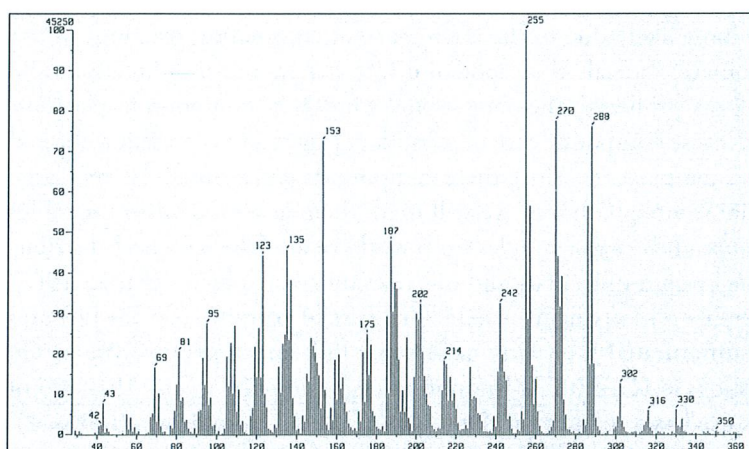

Fig. 2b DTMS of fresh larch resin (Venetian) turpentine (commercial product in MOLART collection Amolf 1994).
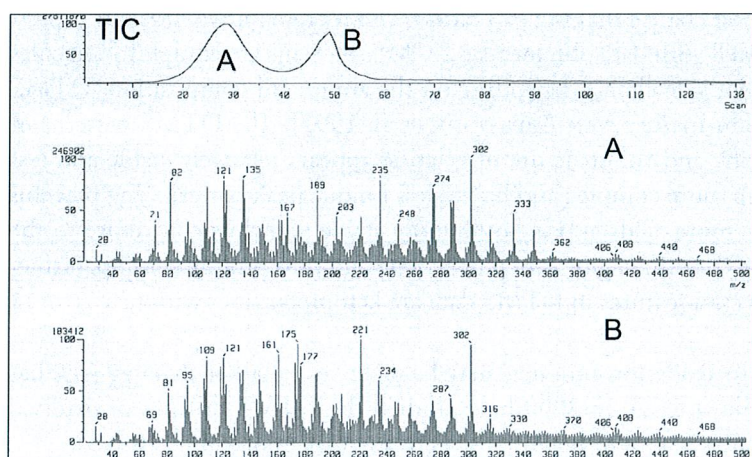

Fig. 2c DTMS of sandarac (600 hrs fluorescent light aged) [SCALARONE et al. 2003].

Fig. 2d DTMS of fresh mastic (commercial product in MOLART collection Amolf 2001).
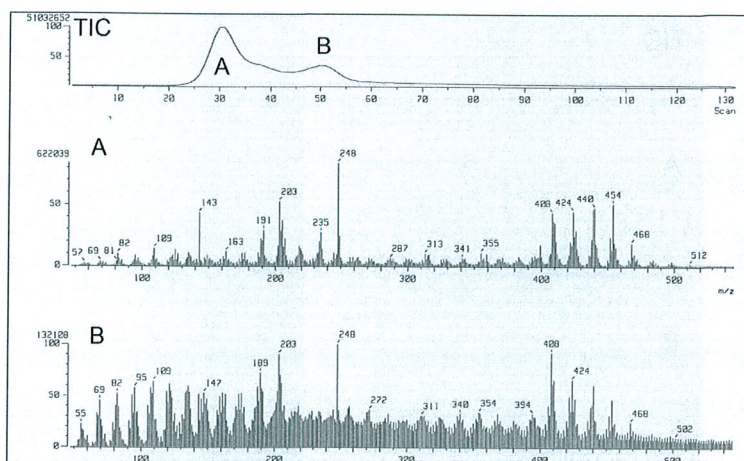

Fig. 2e DTMS of frankincense (from Gerhard Eggebrecht Vegetabilien & Harze, Süderau, Germany) identified as Gum olibanum (Frankincense), origin: Oman, grade: white No. 1. Interpretation of the fragment peaks according to BASAR 2005.
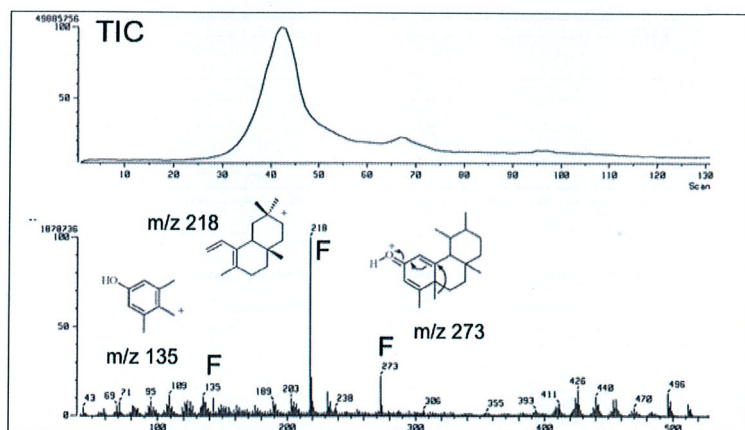
Fig. 2f DTMS of gamboge (from Gerhard Eggebrecht Vegetabilien & Harze, Süderau, Germany), identified as gamboge, origin: Siam (Thailand). Peak A with spectrum A represents the gamboge. Peak B in the TIC is from an associated complex carbohydrate (spectrum not shown).
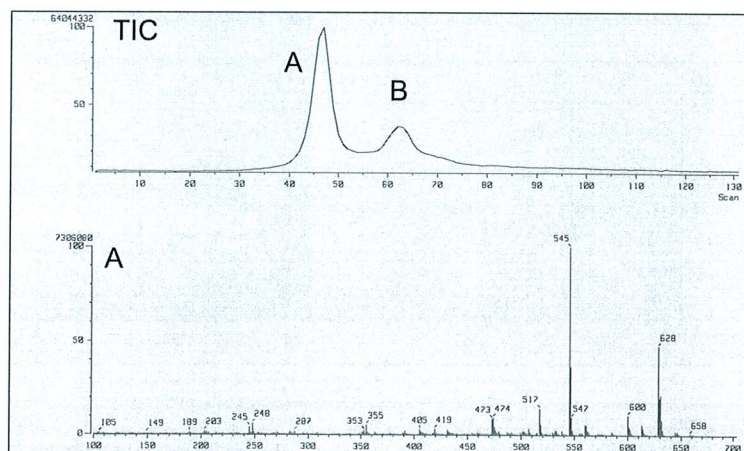
Fig. 2g DTMS of dragon's blood resin from *Dracaena draco* (from a bleed hole in the tree trunk at Tosca on La Palma – sampled by BOON 2009) showing the TIC and mass spectrum summed over the scan range 20–60.
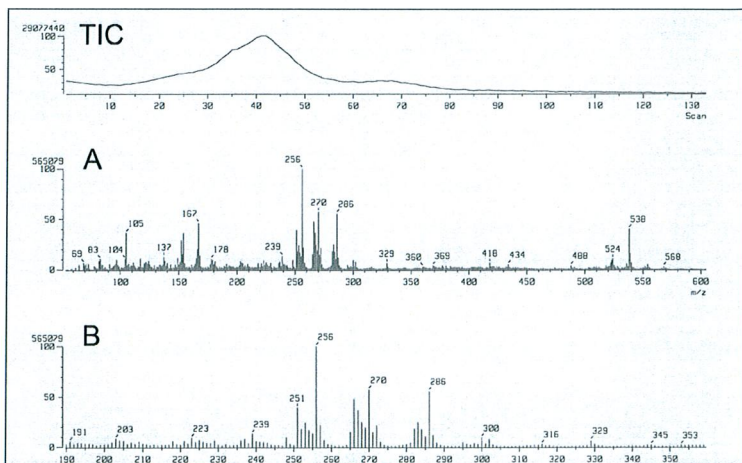
Fig. 2h DTMS of dragon's blood resin from *Daemonorops draco* (1851 Singapore – collection Kew Gardens - sample provided by M.J. Melo Lisbon; see Sousa et al. 2008). Figure B is an expansion of A in the mass range of m/z 190 to 340.
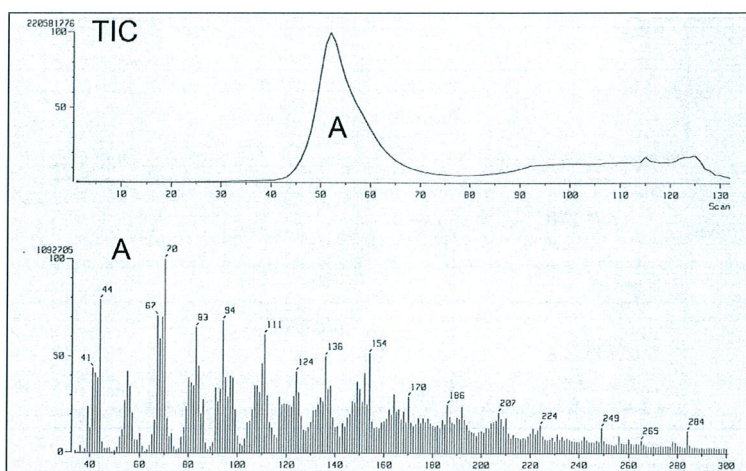
Fig. 2i DTMS of 40 °C water washed cow thigh bone (radius) to remove meat and marrow before pulverizing and homogenisation (source MOLART bone-black pigment project).
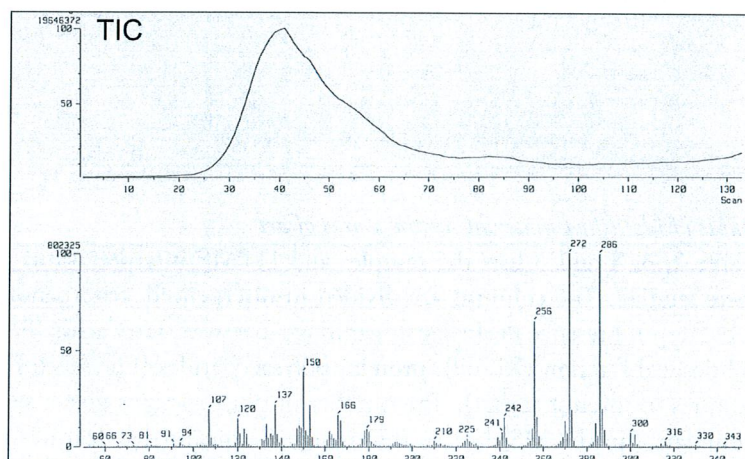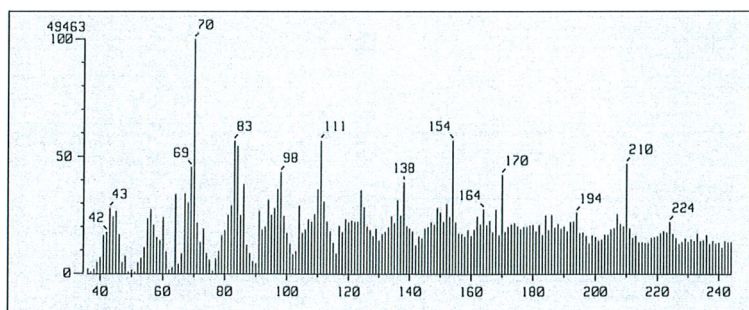

Fig. 2j DTMS of animal glue on silver leaf prepared by Richter in 2000.
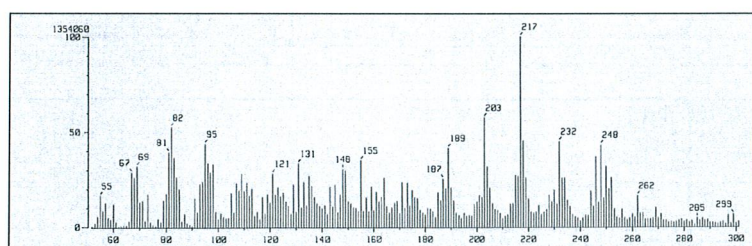
Fig. 2k DTMS of brown shellac (Verfmolen De Kat, Zaandam) showing the mass spectral features of the polymer.

Table of identified materials in the works of art

Table 2, 3, 4 and 5 lists the samples and DTMS interpretations of materials in the works of art that were studied. The columns are divided in diterpenoid, triterpenoids, a cross-linked terpenoid fraction (XL-Terp.), presence of shellac or gamboge, beeswax, fatty acids (FA), acylglycerides (AG), a cross-linked oil derived fraction (XL-oil), protein, polysaccharides (Polysacch.), observed elements (Element), other features of interest (other). The number of plus (+) signs give a semi-quantitative indication of relative abundance in the MS data. A minus sign (-) means that features indicative for the materials were not

observed. The indicator – tr – means trace amount i.e. observable in the DTMS data but not a component that substantially adds to the substance of the material in the sample. A trace amount may modify physical properties during the preparation or application. The relative amount of the materials and their identification is obtained by processing the data in the temperature resolved mode. Summary spectra of the samples are presented in the book, but it should be noted that when one material is present in high abundance, features of other minor materials might be obscured. These compounds are however sometimes very prominent in specific temperature windows.

In the columns, further information is presented. In column DT we indicate C (colophony), Oxy-C (oxidized colophony), S (sandarac), L (Larix derived resins). In column TTP we mention M (mastic) and F (frankincense). In column BWX occasionally oxy-BWX is mentioned when a mass peak series of wax esters with inserted oxygen (observable as a plus 14 Dalton series of ions between the main wax ester molecular ions). In column FA (fatty acids), we mention the ratio of palmitic and stearic acid as P/S. Occasionally long chain fatty acids are mentioned when prominent, and C18 > C16 when stearic acid has a higher intensity than palmitic acid often an indication that other fat sources than oils are present. A P/S less than 1 was indeed observed in a cow bone reference (Fig. 2i) prepared for a bone black reference pigment suggesting that C18 > C16 might indicate an animal origin of the fats. When diacids (mainly C9 diacid) are very prominent it is also mentioned in the FA column. In column AG, we mention the chain length of constituent fatty acyl groups of diglyceride moieties. The release of CO_2, SO_2 and several arsenic compounds points to sources of carbonate, sulphate, arsenates, reduced arsenic and arsenic sulphide clusters such as generated from orpiment. Lead white releases CO_2 at a relatively low temperature, whereas calcium carbonate requires a much higher temperature for decomposition. The lead in lead white is fully reduced due to interaction with the carbon residue on the platinum-rhodium wire. The reduced lead is evaporated and ionized leading to the isotopic signature of lead with peaks at m/z 206, 207, and 208 in the higher temperature range of the DTMS data. Vermilion decomposes into mercury (several isotopic peaks between m/z 199 and 202) and sulphur observable as S_2 at m/z 64. Copper appears at m/z 63 and 65 at the highest scan in the range (usually between scan 120 and 130). Phosphate reduces to P_2 (m/z 62) under DTMS conditions.

Selected Case Studies

Yellow glaze, bole and animal glue

Object:	Polychromed high altarpiece in Georgenberg near Kuchl (Austria)
Site of altarpiece:	Catholic subsidiary church St. George
Dating:	1715–1716
Sculptor:	Johann Georg Mohr
Painter/polychromer:	Simon Jakob Lamberti
Carpenter/joiner:	Johann Pfister
Sampling area:	The sample P6 was taken from the sculpture of St. Rupert, lid of salt vessel, yellow glaze on silver leaf (gold lacquer)

Figure 3 shows a UV fluorescent image of the sample stratigraphy with a thick chalk ground (A), a red coloured bole (B) capped with silver foil and an about 12 micron thick yellow coloured strongly fluorescent glaze on top of the silver leaf. It was possible to separate the sample into three subsamples that were analysed separately by DTMS representing the yellow glaze (Fig. 4), bole (Fig. 5 A) and the ground (Fig. 5 B). The TIC of the yellow glaze shows a lower (A) and a higher (B) temperature release event of compounds in the ion source. Their summation mass spectra of A (scan 40–70) and B (scan 70–100) are presented in figure 4. Mass spectrum A shows fragment ions typical for terpenoid compounds at lower mass, features for diterpenoids from m/z 230–350 and features for triterpenoids from m/z 400–500. The main high intensity mass peaks for diterpenoids at m/z 239, 253, 285, 298, 300, 314, 315 and 316 are representative for colophony with a low degree of oxidation [Van den Berg et al. 2000]. The peaks at m/z 239, 253, 285 and 300 are pointing to dehydroabietic acid. The peaks at m/z 406, 408, 422, 424, 440, 452 and 454 point to triterpenoids in mastic. Mastic also has a release of compounds at higher temperature with many smaller fragment ions released from cross-linked fractions and some peaks in the range from 400–500. Moronic acid is often a compound in aged mastic with a prominent fragment ion at m/z 163. This fragment ion is present but not very prominent in figure 4 A. Since the main mass peaks are from pine resin the relative amount of the diterpenoids (C i.e. colophony) are marked with 3 + signs in table 1. Triterpenoids (M i.e. mastic) and cross-linked terpenoids are marked with 1 +.
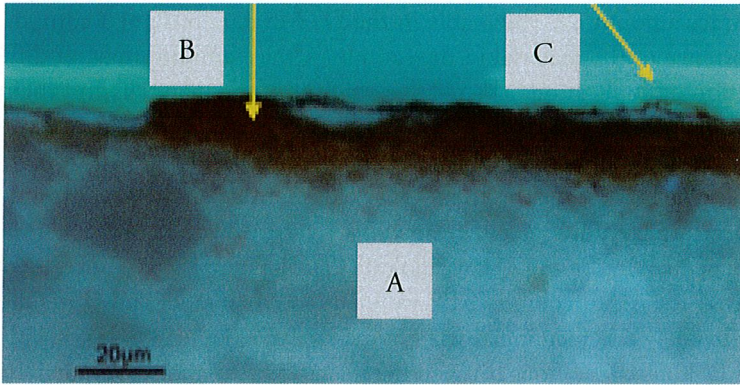
Fig. 3 UV image of the layer structure of a yellow glaze on silver leaf (sample P6) taken from the lid of salt vessel on the sculpture of St. Rupert which is part of the polychromed high altarpiece in Georgenberg near Kuchl, Austria.
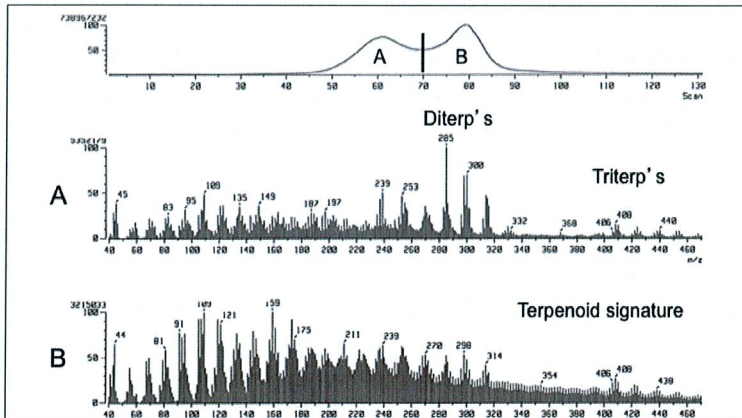
Fig. 4 DTMS of the yellow glaze from the lid of the salt vessel (Fig. 3) showing DTMS spectra from the lower (A) and higher (B) temperature scan range of compound evolution.
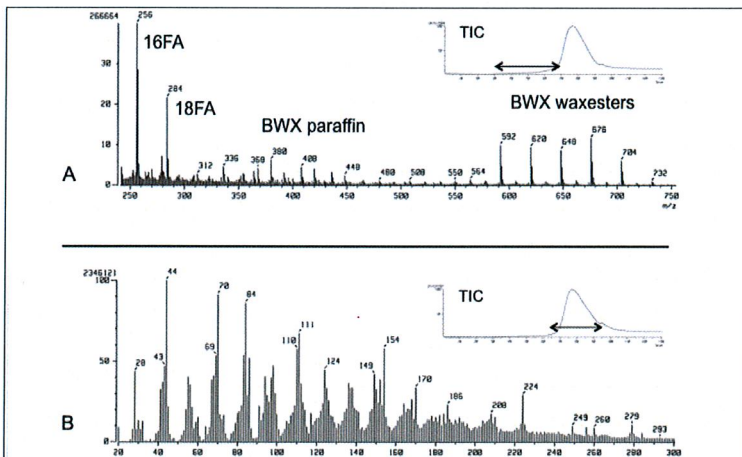
Fig. 5 DTMS of the bole (A) and ground (B) from the lid of the salt vessel (see Fig 3).
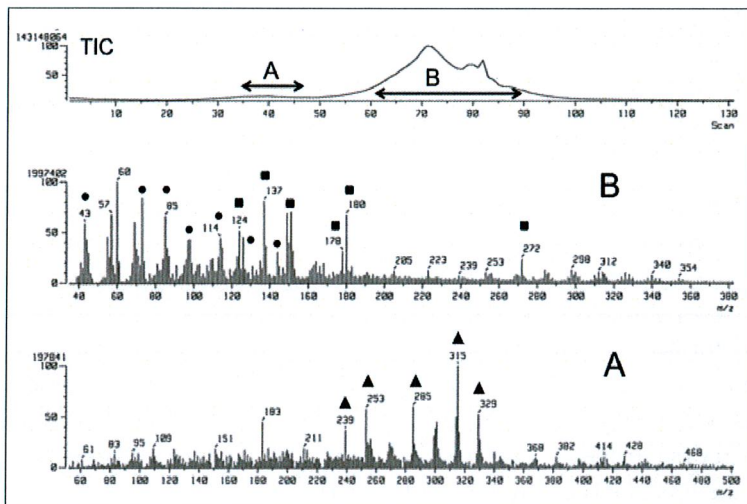
Fig. 6 DTMS of insect wood faecal pellets isolated from wood of the sculpture of St. Rupert which is part of the polychromed high altarpiece in Georgenberg near Kuchl. Mass spectrum B from degraded wood shows features of residual polysaccharides (balls) and guiacyl lignin (squares). The mass spectrum A represent oxidised pine resin (triangles). The same features are marked collectively as oxycolophony in the identification tables (1–5).

Fig. 7 DTMS of the original white gloss lacquer on the marbling of the St. Augustine Altarpiece in the Catholic Parish and Abbey Church St. Alto in Altomünster. The S, L and C represent the identifying features of sandarac, larch resin and colophony in the DTMS spectra. A and B are spectra of evaporated compounds and compounds evolved by pyrolysis of polymeric fractions.
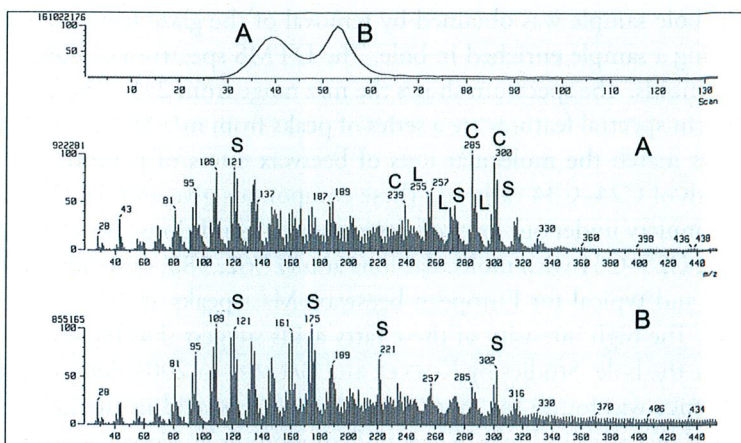
Fig. 8 DTMS of a lacquer reconstruction made with sandarac (S) and larch (L) resins prepared by Richter according to 18th century recipes. Sandarac has an evaporating and polymeric fraction (polycommunic acid).
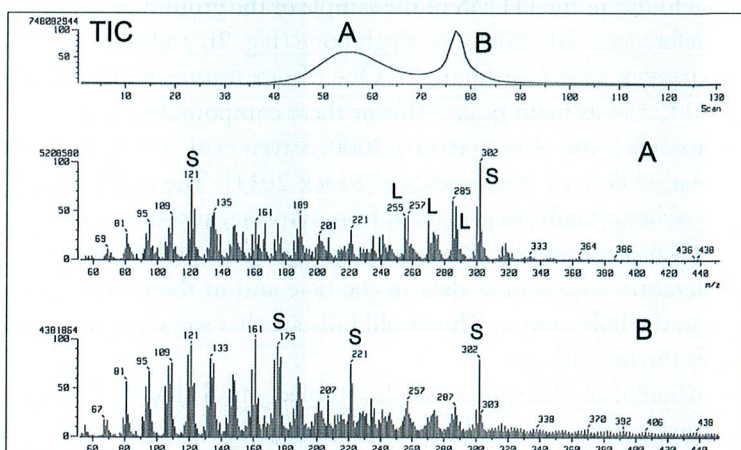
Fig. 9 DTMS data of a sample of red glaze obtained from the Cuvilliés Theatre in the Residenz in Munich showing evaporating (A) and polymeric fractions (B). The F, M, S and oxy-C represent features of frankincense, mastic, sandarac and oxidised colophony.
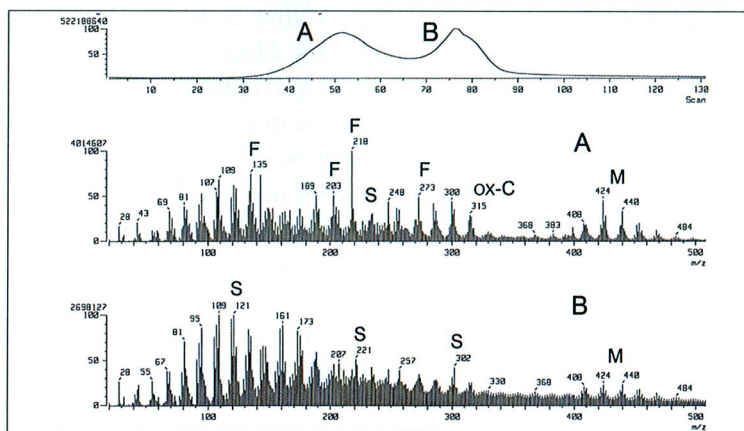
Fig. 10 DTMS of the yellowish brown tortoise shell imitation glaze on silver sampled from the high altarpiece (dated 1673) in Kaisheim showing features of gamboge (G: m/z 628, 545 and 600, 517 – compare Fig 2f) and many mass spectral features generated from arsenosulphides (m/z 150, 225, 300, 321, 396, 428, table 1) present in the glaze.

673
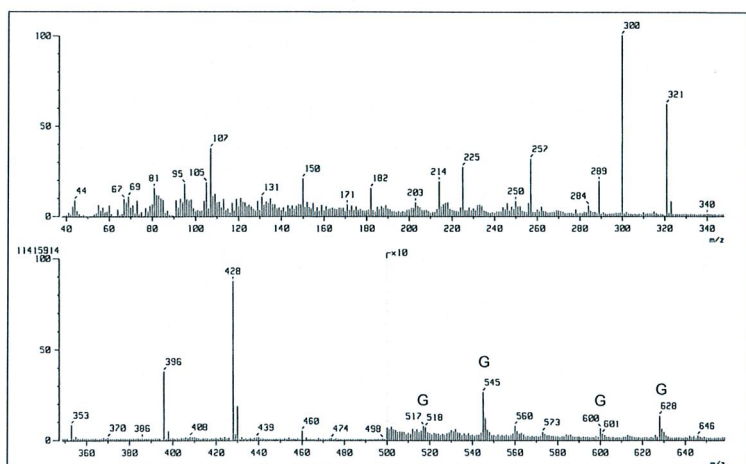
The bole sample was obtained by removal of the glaze from the silver and removal of the white ground leaving a sample enriched in bole. The DTMS spectrum of bole (Fig. 5 A) does not show any peaks for terpenoids. The spectrum shows the m/z range from 245–750 over the TIC scan range from 20–70. Prominent spectral features are a series of peaks from m/z 592 to 732 with a mass off-set of 28 Dalton. These peaks match the molecular ions of beeswax esters of palmitic acid with alcoholic moieties with chain length of C24–C34 carbons. These compounds give an m/z 257 fragment ion representing the palmitic acyl moiety under our low voltage ionisation conditions. Beeswax also contains a series of alkanes ranging from C25–C31 with molecular ions at m/z 362, 380, 408, 436. The peak at m/z 368 is from a C24 fatty acid and typical for European beeswax. Mass peaks at m/z 256 and 284 are from palmitic and stearic acid. The high intensity of these fatty acids suggest that there are other sources of fats that were used to make the bole. Studies by KOLLER and BAUMER in 2001 demonstrate that tallow is a possible source. No evidence was found for myristic acid and lauric acid in the DTMS of the bole however. The bole TIC also shows a second release event of compounds at higher temperature at scan (70–95). This same range is also found in the DTMS of the sample of the ground in figure 8b. The mass peak profile is very similar to a reference made from cow thigh bone (Fig. 2i) and reference of animal glue (gelatine) on silver made by RICHTER shown in figure 2j. One of our feature peaks for animal glue is the compound with m/z 70, 111, 154 as main peaks. This or these compound(s) point to diketopiperazine of proline with other aminoacids [GINZ/ENGELHARDT 2000; SMITH et al. 1988]. The amino acid proline is a main constituent of gelatine derived from collagen [SZPAK 2011]. The m/z 186 is a radical condensation product of two hydroxybenzyl radicals generated from tyrosine, another constituent of gelatine. At a very high temperature CO_2 is released from calcium carbonate, the bulking agent of the ground. Comparison of the high temperature release mass data in the bole and in the ground point to a relatively high contribution of glue in the bole sample. This could indicate that some ground was included during sampling of the bole under the microscope.

The wood of the altarpiece was also studied with DTMS. The wood showed a typical conifer wood spectrum with mass spectral features of guaiacyl lignin, cellulose and hemicelluloses [VAN DER HAGE et al. 1996]. Pellets from wood boring larvae left inside the wood were also analysed. They showed a significant decrease in polysaccharide features, a relative increase in lignin-derived features and an interesting pattern of diterpenoid resin derived features. Figure 6 shows the TIC and two summary spectra. The one for released compounds at low temperature (Fig. 6 A) shows the m/z 239, 253, 285, 299, 300, 301, plus a high intensity m/z 315 and 329. These m/z values point to dehydroabietic acid (DHA) and strongly oxidised DHA from the pine resin in the wood [VAN DEN BERG et al. 2000]. The m/z 178 in the guaiacyl lignin pattern is relatively high relative to m/z 180. The mass peaks are from conferylaldehyde and coniferylalcohol respectively and also point to oxidation of the lignin polymer remains.

Diterpenoid resins

Object:	St. Augustine altarpiece (polychrome side altarpiece) in Altomünster (Bavaria)
Site of altarpiece:	Catholic Parish and Abbey Church St. Alto (main room)
Dating:	1768/69
Sculptor:	Johann Baptist Straub
Painter / polychromer:	Brother Fortunatus Strasser
Sampling area:	The sample E63 (final gloss lacquer of marbling) was taken from the marbling behind the tabernacle

The original white gloss lacquer on the marbling of the St. Augustine altarpiece (1768/69) in the Catholic Parish and Abbey Church St. Alto in Altomünster is a good example of DTMS spectra of mixtures of terpenoid compounds that can still be assigned to specific resin compositions. The same lacquer has been analysed by KOLLER and BAUMER in 1997 using GCMS of the extractable compounds. Indications were found for sandarac and Venetian turpentine. These authors point out in another paper [KOLLER et al. 1997b] that Venetian turpentine is often not pure larch resin but rather a mixture of larch and colophony. Figure 7 shows the TIC and two partial spectra of lower (scan 25–27) and higher (scan 46–65) temperature events in the DTMS analysis of the white gloss lacquer. Sandarac shows two release events of compounds in DTMS with a high intensity molecular ion peak at m/z 302 and fragment ions at m/z 121, 161, 175, 221 and 287 (marked with S). Fragment ions are more intense at the higher T event while

the molecular ion is strong at lower temperature. The difference in release temperature is about 30 mass scans. Sandarac is not the only constituent observable by DTMS. The m/z 255, 257, 270, 271, 273, 286 and 288 are specific features for Larix derived resins (marked with L). Especially the m/z 288 from larixol as rearrangement ions after water loss from m/z 306 (molecular ion) is an indicative feature. Other mass peaks point to some oxidised colophony with m/z 239, 253, 285, 300 and 315 (marked with C). Colophony (observed in oxidised form) appears to be more prominent than what can be concluded from the extractables data obtained by KOLLER and BAUMER in 1997 using GCMS. Sandarac is the main constituent judging from its mass peak pattern and the TIC. The spectra match a reference lacquer made by RICHTER with sandarac, larch resins and turpentine shown in figure 8. The reconstruction was made with Moroccan sandarac (Gerhard Eggebrecht, Süderau) and Tyrolese larch turpentine (Brüder Unterweger, Thal-Assling, Eastern Tyrol). A solid larch turpentine was prepared according to a recipe ('Ein anderer schoener weisser Glanz=Fuernis') found in an anonymous historical source *Grund=mässige und sehr deutliche Anweisung zu der schönen Laccir= und Schildkrotten=Arbeit* (1706). The measures of both solid resins were put in a doubled nylon stocking bag and suspended to dissolve in a glass vessel filled with ethanol. For further instructions and English translations of recipes see KOLLER et al. 1997b 'Turpentine, Larch Turpentine and Venetian Turpentine'. The main peaks in the DTMS are from sandarac (S) and Larix turpentine (L).

The original white gloss lacquer of the marbling in Altomünster has a slightly different composition compared to the red glaze on silver leaf ('Burning Heart' of St. Augustine) on the same altarpiece. This result proved to be important for a better understanding of the lacquer compositions used on this particular altarpiece. It shows that the compositions do vary according to their function. The red glaze also contains gamboge as discussed below.

The mass spectrometry of frankincense has been studied in detail [BASAR 2005; BERGMANN 2004]. The resin contains several isomers of boswellic acid and tirucallic acid with molecular weights of m/z 498 and 456 next to various other triterpenoids like oleanolic acid, ursolic acid, baurenol and lupeol. Gamma-H-rearrangement of boswellic acid derivatives give specific fragment ions at 273, 232, 218 and 135 (Fig. 2e). These fragment ions are also observed under low voltage electron ionisation conditions upon DTMS. Fragment ion m/z 218 is the strongest mass peak in reference samples of frankincense (gum olibanum) from various sources. Samples from artworks with DTMS evidence for frankincense are grouped in table 3.

Frankincense was identified in the red glaze from the Cuvilliés Theatre in Munich (c. 1755), a blue glaze on the small house altarpiece dedicated to St. Michael (eighteenth century) from the Stadtmuseum in Munich and a blue smalt glaze on the ornamental clock with table consisting of lacquerwork and decorations in Chinese style (c. 1725, Inv. No. R3792, Bayerisches Nationalmuseum, Munich). It was also identified in a yellow glaze (gold lacquer) on silver leaf of the polychrome high altarpiece (c. 1710) in the St. Maximilian Chapel of the cathedral in Freising (Bavaria) and a blue smalt glaze (on silver) found in a niche of an altarpiece (1746) in the monastery church of Tegernsee. Frankincense is not the only resinous material in these glazes. It is found mixed together with sandarac, colophony, Venetian turpentine and mastic. Figure 9 shows the DTMS data of a sample of red glaze obtained from the Cuvilliés Theatre. The TIC shows two release events of the red glaze. One at lower temperature (A: scan 35–65) from chemically unbound materials that evaporate and one at higher temperature (B: scan 65–95) where pyrolysis of cross-linked fractions is taking place. The DTMS spectrum of A shows the features of frankincense at m/z 218 (intense) and lower peaks at m/z 235 and 273. The signature of mastic is evident from the peaks at m/z 408, 424 and 440 and related smaller peaks around those masses. Colophony features are present at m/z 315, 300, 285, 253, and 239 pointing to some degree of oxidation and therefore marked as oxy-C in the Table. The DTMS at higher temperature (Fig. 9 B) shows many features of sandarac (m/z 302, 287, 221, 161, 121) and evidence for mastic at higher mass. On closer examination evidence for sandarac are also present in the lower temperature fraction albeit at small relative intensity. Higher molecular weight features of frankincense are less prominent. In the reference materials m/z 426 is a stronger feature but molecular ions peaks at 456 and 498 were not observed. The electron ionization fragment ion peaks mentioned above are therefore the best markers for the presence of frankincense.

In a separate paper, the occurrences of oxidised cholesterols in works of art have been reported [VAN DEN BRINK et al. 2009]. Cholesterol observable in DTMS by its molecular ion m/z 386 and its ion m/z 368 indicative of a loss of water upon electron ionisation is often not an original material when detected. It is a common indicator of hand contact not so much at sampling but rather earlier when the objects were handled with bare

hands. Cholesterol is prone to relative rapid oxidation leading to a number of oxidised cholesterol compounds such as 7-keto-cholesterol (m/z 400 M.W. of 5-cholesten-3-ol-7one) and related compounds [VAN DEN BRINK et al. 2009]. In that paper, the occurrence of cholesterol oxidation products was reported for a red glaze on silver leaf from the inside of a pulpit canopy designed by Dominikus Zimmermann and completed in 1753–1756 present in the Catholic Pilgrimage Church *Die Wies* dedicated to the Flagellated Christ (sample WSK P8), an opaque green glaze on silver leaf on the bust of St. Marinus (c. 1760 belonging to the furnishings of the former Benedictine monastery church in Rott am Inn (sample R4A1), and the Holy Bishop (sample BisP3) presently in the Mainfränkisches Museum Würzburg, dated c. 1505–1510 and thought to be made by Tilman Riemenschneider (1460–1531). Oxidized cholesterols are listed in table II such as the pulpit (c. 1755) of the Wieskirche (sample P8) mentioned above and a red glaze from the altarpiece (1760) in Sünching representing the bole and ground taken from the tabernacle. The presence of these compounds in the bole suggests that egg yolk was used for emulgation.

Gamboge is a resin that can be obtained from the plant family Guttiferae [LANGENHEIM 2003]. The DTMS of a gamboge resin sample (originating from China, material collection at the Technical University of Munich, Chair for Restoration) is characterised by molecular ion peaks at m/z 628, 600 and high fragment ion peaks at m/z 545 and 517 under low voltage DTMS electron ionisation conditions (Fig. 2f). The high peak at m/z 545 together with m/z 628 suggests that gambogic acid is a main compound in the reference material [LIN et al. 1993]. This is also the main feature used as indicative for gamboge resin in the samples from the works of art.

Evidence for the yellow resin dye gamboge was found in a yellow glaze (on gold leaf) from the reliquary retable (dated between 1740 and 1773) in Abwinkl, a red glaze on silver leaf of the St. Augustine altarpiece (dated 1768/69) in Altomünster and a faux tortoiseshell glaze on silver of the high altarpiece (dated 1673) in Kaisheim. The three occurrences of gamboge reported here have in common that they show mainly a resin matrix. The Altomünster sample H1 (c) shows features of sandarac, Venetian turpentine and colophony in almost equal proportions judging from their mass spectral features in DTMS. The yellow glaze from Abwinkl (sample P6c) shows the presence of sandarac, colophony and mastic. The DTMS of the yellowish brown tortoise shell imitation in Kaisheim is shown in Figure 10. Gamboge is present in a matrix of resin (oxidised colophony and mastic) mixed with an unidentified protein and some fats (P/S 1.4). The arsenic features in the DTMS at m/z 75 (As), 150 (As$_2$), 225 (As$_3$) and 300 (As$_4$) are indicative of an arsenic sulphide pigment (present in the mordant). A trace amount of indigo (m/z 262 and 234) [NOVOTNA et al. 2003; GROEN et al. 1998] is also indicated in the DTMS data.

Starch is a hexose polymer that was observed in a number of red cochineal glazes in which it was confirmed by iodine staining. It is recognized in DTMS at a relative high temperature where it released a complex set of compounds by pyrolytic decomposition. Starch and cellulose that are both hexose polymers give approximately the same sets of mass peaks in complex media. Features are electron ionisation m/z values at 43, 55, 57, 60, 73, 82, 84, 96, 97, 98, 102, 114, 126, 144 and 163 [PASTOROVA et al. 1993]. Under chemical ionization condition series of pseudomolecular ions at NH4+ ions can be detected as anhydro-hexose oligomers, but these compounds perish under electron ionization conditions [LOMAX et al. 1991; PASTOROVA et al. 1993; BOON et al. 1994]. Indications for polysaccharides were found in red glazes from the Holy Ghost and Saint Sebastian altarpieces (dated 1679–1681 and 1714) in Mondsee (table 2). Starch granules were observable in cross-sections by SEM and also by staining with KJ-J$_2$ solution (see also article on the scientific examination results of both altarpieces in Mondsee by RICHTER in this publication).

Dragon's blood is a red colorant that occurs in the plant families of Dracaena, Croton, Pterocarpus and Daemonorops [LANGENHEIM 2003]. Dracaena trunk and Daemonorops ectocarps are the main production plant materials. SOUSA et al. in 2008 have identified 4 main components in dragon's blood. Dracorhodin (MW 266), Dracorubin (MW 488), Dracoflavylium (MW 268) and 7,4'-dihydroxy-flavilium (MW 238) occur in different dragon's bloods on the market. Dracorhodin occurs in *Daemonorops draco* while Dracorubin and Dracoflavylium occur in *Dracaena draco*. Samples from many sources of dragon's blood samples provided by Garnier and Melo [including the Kew collection see SOUSA et al. 2008] and collected from trees on La Palma by BOON – were investigated in a comparative DTMS study by Vos et al. in 2010. Various Daemonorops resins analysed by DTMS were found to be mixed with dammar resins. *Dracaena draco* resin was sampled from trees in la Palma and investigated in the young

plant acquired in La palma as a seedling. DTMS features of *Dracaena draco* and *Daemonorops draco* differ. Dracaena has as main DTMS mass peaks 256, 272 and 286 while Daemonorops samples shows two series of correlated mass peaks in DTMS with 203, 256 and 270, and 152, 256, 270 respectively (see Figs 2g, h). DTMSMS showed in addition that the m/z 256 represents different compounds in Dracaena and Daemonorops (Vos et al. 2010). Features indicative for dragon's blood analysed by DTMS were only observed once in the samples from altarpieces and architecture analysed. It was identified in a lacquer on an oak cabinet with mahogany veneer made by Johannes Kroll in 1780. This lacquer was found to contain dragon's blood of the Daemonorops type. This lacquer however was used for restoration and is not original. The reference dragon's blood resin present in the inventory of a nineteenth-century apothecary in Spaichingen, Germany (now part of the material collection of Prof. Dr. Robert Fuchs at the Fachhochschule Köln, The Cologne Institute of Conservation Sciences – CICS) shows a DTMS typical for *Daemonorops draco* (Fig. 11) with the molecular ions in the 200 to 300 range and an unidentified ion at m/z 538 found consistently in Daemonorops reference samples. Indications for dragon's blood were found in a yellow glaze (so-called gold lacquer) on gold leaf from Altomünster as small peaks in GCMS data by Dietemann and Baumer in 2010, which shows that filtering by the chromatographic process prior to mass spectrometry is a better technique than DTMS for minor compounds provided that they are amenable to GC. Contemporary German recipes for gold lacquers on metal leaf often recommend dragon's blood in very small amounts as a colorant [Cröker 1736, Reprint 1982, pp. 236–237].
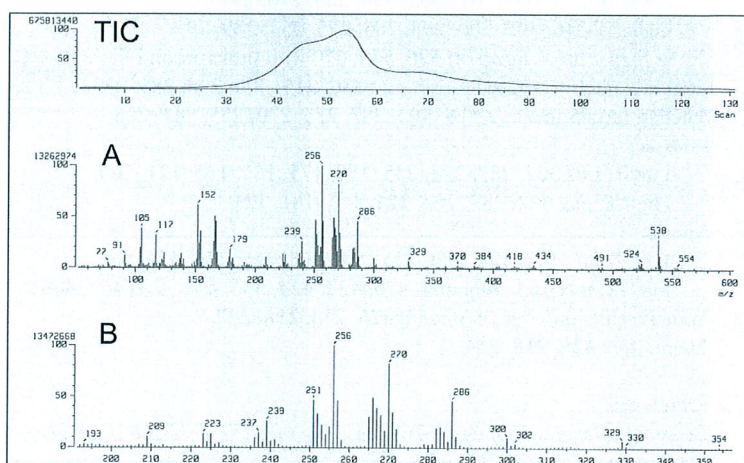
Fig. 11 Dragon's blood resin from the inventory of a 19th apothecary in Spaichingen. The mass spectral features are similar to those of *Daemonerops draco* (see also Fig. 2h).

Concluding remarks

The methodology of DTMS used here to characterise microgram amounts of complex substances has proved its value since it can point to and tentatively identify chemical substances from a broad range of materials used by artists and artisans. DTMS is a survey technique. The temperature resolution of DTMS does add additional information. DTMSMS is certainly a further way to add identifying information if the collisional induced fragmentation pattern of compounds is known or can be obtained from reference compounds. The wide mass range used in this study offers advantages over GCMS, which is generally limited by the filtering of the chromatographic column and mass range. In this way evidence for gamboge could be found in some of the samples. Also the higher molecular weight fraction of beeswax can be observed directly. In general more specific target analytical methods are necessary to fully identify the complex mixtures on the compound level if the compounds can be dissolved for further chromatographic and/or mass spectrometric processing. Other chapters in this book are good examples of this approach. This study gives a first glimpse into the many different materials that have been used by polychromers and painters. Why they were chosen depends on availability, price and intended effect. In some cases, the ageing effects may have been taken into account such as yellowing of oils in the case of green glazes or the darkening of resins such as colophony in gold lacquers. The further correlation with workshop practice will require studies of specific workshops and their choice, preparation and use of organic materials. We believe that materials were chosen carefully with a good understanding of the physical properties during the production of works of art.

Table 1   Criteria for assignment of mass peaks and mass peak patterns.

---

1. Time-temperature domain of the peak pattern

   Overall scan range 0-130 under the experimental conditions used.

   Volatile compounds (< scan 20 scan), adsorbed compounds (scan 20-50), metal soaps (scan 50-60), polymers and cross linked-linked materials (scan 60-80), inorganic compounds at high temperature (> scan 80).

---

2. Specific peaks assigned to identifiable compounds

   Palmitic acid (m/z 256) and stearic acid (m/z 284)

   Azeleic acid (C9 diacid) m/z 152, 98

   Indigo m/z 262, 234

   Ocotillone in dammar m/z 125, 143, 205, 399

   Moronic acid in mastic m/z 163

   DHA m/z 239, 285, 300

   7-oxo-OH-DHA in oxidised pine resins m/z 315

   Larixol in larch resin and Venetian turpentine m/z 288 (M-H_2O)

---

3. Specific peaks assigned to materials (numbers in bold are high abundance peaks)

Natural resins

   Colophonium fresh: m/z 302, **300**, 287, 285, 239

   Oxy-Colophonium: m/z **315**, **300**, 285, 239

   Root colophonium:

       low T m/z 226 and 316, 302, 300, 285, 270, 239

       higher T 316, 302, 300, 298, 285, 273, 253, 239, 237

       at higher mass: m/z 374, 526, 556, 570 with peaks around those masses

   Burgundy pitch (Oxidised form): m/z 330, **315**, 300, 298, 285, 253, 237, 239

   Venetian turpentine: m/z 316, **302**, 287, 273, 270, 255, 241, 288

   Sandarac:

       Low T: m/z 302, 287, 274, 235, 189, 175, 161, 135, 121, 109

       High T: m/z 302, 287, 257, **221**, 175, 161, 121

   Mastic:

       Low T: m/z 143, 191, 203, 235, 248, 408, 424, 440, 454, 468.

       High T: m/z 163, 406, **408**, 410, 422, **424**, 436, 438, 452, 454, 468

   Frankincense: m/z 496, 470, 440, 426, 273, **218**, 232

   Elemi: m/z 426, **218**, 234.

Fatty substances

   Beeswax: m/z 592, 620, 648, 676, 704, 732; m/z 257; m/z 368 (C24 FA)

   Oxidised beeswax: m/z 606, 634, 662, 718

   Oxy-Cholesterols: m/z 400, 382, 384, 402 [cholesterol m/z 386, 368]

   Fatty acids:

       Oils-linseed P/S < 2, walnut P/S > 2 and < 3.5, poppy > 3.5,

       Tallow m/z 228 (C14 FA), m/z 256 (C16 FA), 284 (C18 FA), 298 (C20 FA)

       Oil Diacylglycerides: m/z 550 (C16-C16), m/z 576/8 (C16-C18 [:1; :0]), m/z 602-606 (C18-C18 [:0; :1; :2])

       Prepolymerised oil also m/z 278, **280**, 292

       Cross-linked oil fraction (XL) m/z 91, 105, 119, (continuous profile of peaks up to m/z 600)

   Shellac: m/z 203, **217**, 232, 246

Synthetic resins

   Acrylate m/z 55, 69, 86, 99, 114 (B72)

Protein
   Animal glue: always m/z 208, 224 plus m/z 70, 111, 154; m/z 186, 94
   Other protein: egg with m/z 124, 138, 152,166, and a high m/z 84

Polysaccharide
   Hexosan (cellulose or starch): m/z 43, 55, 60, 73, 98, 114, 126, 144, 163
   Gum Arabic: m/z 114 (pentose), m/z 126 (hexose), m/z 128 (deoxy-hexose)

Other natural materials
   Gamboge: m/z 644, **628**, 600, 545, 517, (scan area 55-60)
   Dragon's blood:
      Dracaena draco m/z 242, 256, **272**, **286**, 300
      Daemonorops draco m/z **256**, 266, 270, 286, 300, 524, 538

4. Specific peaks assigned to certain inorganic materials:
   Carbonates: CO_2 (m/z 44)
   Sulphates: SO_2 (m/z 64), SO (m/z 48)
   Sulphides: S (m/z 32 and 34), H_2S (m/z 34 and 36), HSSH (m/z 66)
   Phosphate: P_2 (m/z 62), P_4 (m/z 124) at highest temperature
   Arseno sulphides (like Orpiment): m/z 107 (AsS), m/z 182 (As_2S), m/z 214 (As_2S_2), m/z 289 (288)
      (As_3S_2), m/z 321 (320) (As_3S_3), m/z 352 (As_3S_4), m/z 396 (As_4S_3), m/z 428 (As_4S_4)
   Arsenic clusters: m/z 75 (As), 150 (As_2), 225 (As_3), 300 (As_4)
   Metals: Pb (m/z 206, 207, 208), Hg (m/z 199, 200, 201, 202), Cu (m/z 63)
   Alkali: K (m/z 39), Na (m/z 23)

Table 2 Constituents in selected art work samples identified by mass spectrometry (DTMS).
(C: colophonium; S: sandarac; M: mastic; L larch turpentine; F: frankincense; Tr: trace; hT: high temperature; P/S: palmitin/stearin ratio)

Sample (layer)	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac, Gamboge	Beeswax
Abwinkl, reliquary retable, sample P5d, red glaze on silver leaf (red glaze)	++ S, C	++ M	+	-	Tr
Abwinkl, reliquary retable, sample P6c, yellow glaze on gold leaf (yellow glaze)	++ C, S	+ M	+	+ Gamb.	Tr
Ering am Inn, high altarpiece, sample P38, green glaze on silver leaf (green glaze and some of the overpaint)	-	-	-	-	-
Ering am Inn, high altarpiece, sample P45, green glaze on silver leaf (ground and bole)	-	-	-	-	+
Ering am Inn, high altarpiece, sample P45, green glaze on silver leaf (green glaze)	-	-	-	-	-
Ering am Inn, high altarpiece, sample P54A, red glaze on silver leaf (red glaze + blue overpaint)	-	-	-	-	-
Ering am Inn, high altarpiece, sample P54B, red glaze on silver leaf (blue overpaint)	-	-	-	-	-
Ering am Inn, high altarpiece, sample P54C, red glaze on silver leaf (red glaze)	-	-	-	-	+
Sünching, altarpiece, sample Sue1, red glaze on silver leaf (red glaze)	++ C > L > S	+ M	+ S, M	-	-
Sünching, altarpiece, sample Sue2, blue smalt glaze on silver leaf (blue smalt glaze)	++ C > L > S	+ M	+ S, M	-	-
Sünching, altarpiece, sample Sue2, blue smalt glaze on silver leaf (ground)	-	-	-	-	-
Sünching, altarpiece, sample Sue2, blue smalt glaze on silver leaf (bole and ground)	Tr C	-	-	-	Tr
Mondsee, Holy Ghost altarpiece, sample G2, green glaze on silver (green glaze)	+ Oxy-C	+ M	-	-	++
Mondsee, Holy Ghost altarpiece, sample G3, red glaze on silver (red glaze)	-	-	-	-	+
Mondsee, St. Sebastian altarpiece, sample P2, red glaze on silver (red glaze)	-	-	-	-	+
Mondsee, St. Sebastian altarpiece, sample P3a, green glaze on silver leaf (green glaze)	+++ Oxy-C	-	++	-	+
Mondsee, St. Sebastian altarpiece, sample P3c, green glaze (ground, bole, glaze)	+ C	-	+	-	+
Cuvilliés Theatre, drapes, sample P3, red glaze on silver leaf (red glaze)	++ S, oxy-C	++ M, F	+	-	-
Cuvilliés Theatre, drapes, sample P3, red glaze on silver leaf (red glaze)	++ S, oxy-C	++ M, F	+	-	-

680

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	-	-	-	-	++ Hg	Vermilion
-	-	-	-	-	+ Hg	Some vermilion and cochineal lake
Tr	+	+ p/s 1.5	-	+	+ Pb	+ Sulphates (HT) + Carbonates + Carboxylates
-	+ p/s 5 C16 & C24 from bwax	-	++ Animal glue			++ Carbonates
-	+ p/s 6.5	-	? Not animal glue	-	++ K	Tr cholesterol + Carboxylates
+	++ p/s 2.2	++	-	-	++ Pb	Lead / carbonates from overpaint PEG contamination (44 dalton offset peaks) Antioxidants (m/z 662, 647)
-	++ p/s 2	++	-	-	+ Pb	Lots of lead /carbonate from overpaint + m/z 59, 103 (tripropylene glycol?) + m/z 662, 647 = antioxidant
-	+ p/s 2.1	++	-	-	+ Pb	Trace of unknown (m/z 410 and 428) + Carbonate
-	+ ?	+	-	-	-	+ Carboxylates
-	-	-	-	-	+ As	+ Smalt
-	-	-	+++ Animal glue	-	-	+++ Sulphates HT + Carboxylates + Carbonates = limestone
-	+ p/s 2.1	-	+++ Animal glue	-	-	+++ Sulphates HT + Carboxylates + Carbonates = limestone + Cholesterol and Oxo-cholesterols
Tr	++ p/s 1.2	++	-	-	+ Pb + Sb-ox	Naples yellow + Petroleum paraffins C21-35
-	+ p/s 1.5	+	-	++ Hexosan (starch)	-	+ Petroleum paraffins C23-C33 (layer on original red glaze) + Carbonates = limestone
+ C16–16; C16–18; C18–18	++ p/s 1.1 C20–28	++	-	+ Hexosan (starch)	Tr Pb	-
-	-	-	-	-	-	-
-	++ p/s 1.6	+	++ Animal glue	-	Tr Pb	-
-	-	-	-	-	-	-
-	-	-	-	-	-	-

Sample (layer)	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac, Gamboge	Beeswax
Kaisheim, St. Joseph sculpture group, sample P1, red glaze on silver (bole, red glaze and top transparent layer)	+ Oxy-C	+ M aged	+ M	-	+
Kaisheim, St. Joseph sculpture group, sample P1A, red glaze on silver (glaze and top layer)	+ Oxy-C	+ M	-	-	Tr
Kaisheim St. Joseph sculpture group, sample P2, tortoiseshell imitation, yellow glaze on silver leaf (yellow glaze)	++ Oxy-C	-	-	-	-
Kaisheim, high altarpiece, sample H1, yellow-ish-brown glaze on silver leaf (yellow-brown glaze)	+ Oxy-C	+ M	-	+ Gamb.	-
Würzburg Residence, Green-lacquered Room, sample P3a, green glaze on silver leaf (ground and mordant)	-	-	-	-	-
Würzburg Residence, Green-lacquered Room, sample P3b, green glaze on silver leaf (white mordant)	-	-	-	-	Tr
Würzburg Residence, Green-lacquered Room, sample P3c, green glaze on silver leaf (green glaze)	-	-	-	-	-
Rheinau, right side altarpiece (J. T. Sichelbein), sample B1, blue glaze on silver (blue glaze)	++ Oxy-C, L, S	Tr M	++ Diterp.	-	-
Rheinau, right side altarpiece (J. T. Sichelbein), sample R5, yellowed varnish with blue glaze (random sample)	++ 0xy-C, S	-	+	-	+
Rheinau, high altarpiece, sample Z1, yellow glaze on silver leaf (yellow glaze	++ S ++ Oxy-C	+ M	+	-	-
Rheinau, high altarpiece, sample Z2, yellow glaze on silver leaf (yellow glaze	+ S +++ Oxy-C	+ M	+	-	-
Rheinau, high altarpiece, sample Z3, green glaze on silver leaf (green glaze)	+ C ++ oxy-C	+ M	-	-	
Rheinau, high altarpiece, sample Z5, red glaze on silver leaf (red glaze)	+++ Oxy-C	+M	+	-	-
Georgenberg, high altarpiece, sample P1, A, red glaze on silver leaf (red glaze)	-	-	-	-	-
Georgenberg, high altarpiece, sample P1, B, red glaze on silver leaf (orange bole)	-	-	-	-	+
Georgenberg, high altarpiece, sample P2, A, green glaze on silver leaf (green glaze)	-	-	-	-	+
Georgenberg, high altarpiece, sample P3, A, green-blue glaze on silver leaf (green-blue glaze)	-	-	-	+ Shellac (later glaze 19th century)	Tr
Georgenberg, high altarpiece, sample P5, A, yellow glaze on silver leaf (yellow glaze)	+ Oxy-C	-	+ Diterp.	-	-
Georgenberg, high altarpiece, sample P6, A, yellow glaze on silver leaf (ground)	-	-	-	-	-
Georgenberg, high altarpiece, sample P6, B, yellow glaze on silver leaf (bole)	-	-	-	-	++
Georgenberg, high altarpiece, sample P6, C, yellow glaze on silver leaf (yellow glaze)	+++ C	+ M	-	-	Tr

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	++ p/s 1.7	++	-	-	Tr Pb	+ Carbonate = limestone + Carboxylates + m/z 104+148 = phtalic acid (Alkyd paint)
-	+ p/s 1.3	++	-	-	-	+ Carbonate = limestone + Carboxylates + m/z 104 and 148 = phtalic acid (Alkyd paint)
-	+ p/s 1.9	+	+ Not animal glue	-	++ As	++ Arsenic sulphide pigment (AASP)
-	+ p/s 1.4	+	+ Not animal glue	-	+ As	+ Arsenic sulphide pigment (AASP), Tr indigo
+ C16–16; C16–18; C18-18	++ p/s 2	++	++ Animal glue	-	+ Pb	+ Carbonate as limestone + PbAzelate
+ C16–16; C16–18; C18–18	+++ p/s 1.8 ++ C9 diacid	++	-	-	++ Pb	+ PbAzelate Lead soaps! m/z 44
+ C16–16; C16–18; C18–18	+++ p/s 1.6 ++ C9 diacid	++	-	-	++ Pb	+ PbAzelate
-	-	++	-	-	+ Pb	-
-	-	++	-	-	++ Pb	+ m/z 192 Synthetic resin (later yellowed varnish on top) Unknown: m/z 271
-	C18 > C16 p/s 0.8	?	-	-	-	-
-	Tr C18 > C16 p/s 0.8	?	-	-	-	-
-	-	-	-	-	-	+ Paraloid B72 p-EMA-MA resin + m/z 135&150
-	-	-	-	-	-	+ Unknown m/z 135 and 150 + Synth. acrylate resin Paraloid B72
-	+	++	-	+ Hexosan (starch)	+ Pb	+ Synth. acrylate resin Paraloid B72
+	+ p/s 2	-	-	+ Hexosan (starch)	-	+ Synth. acrylate resin Paraloid B72
+	++ C14 –C24 18:1 p/s 1.8	+++	-	-	+ Pb + Cu	+ Carboxylates +Carbonate
-	Tr	-	+	++ Hexosan (starch)	+ Pb + Cu	++ Carboxylates + Carbonates + Sulphate + Indigo (m/z 262)
-	-	+	-	-	-	+ Carboxylates + Carbonate Limestone
-	-	-	+++ Animal glue	-	-	++ Carbonates > limestone
+	+ p/s 1.9	+	+ Animal glue	-	-	+ Carbonates = limestone + Organic sulphonates in proteins
-	-	-	-	-	-	-

683

Sample (layer)	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac, Gamboge	Beeswax	
Georgenberg, high altarpiece, sample P7, A, yellow glaze on silver leaf (yellow glaze)	+ C	-	-	-	tr	
Freising, altarpiece, sample M1 (Episcopal chapel), blue smalt glaze with overpainting (blue smalt glaze, 18th century) on white mordant, further overpainting	+++ S, L	-	+ S	-	-	
Altomünster, left side altarpiece, sample H1c, red glaze on silver leaf (red glaze)	+++ S, C, L	Tr M	-	+ Gamb.	-	
Wieskirche, pulpit, sample P1, yellow glaze on silver leaf (yellow glaze)	Tr C	Tr M	-	-	tr	
Wieskirche, pulpit, sample P4, yellow glaze on silver leaf (yellow glaze)	++ Oxy-C	++ M	-	-	+	
Wieskirche, pulpit, sample P6, yellow glaze on silver leaf (yellow glaze)	++ Oxy-C	++ M	+	-	+	
Wieskirche, pulpit, sample P8, red glaze on silver leaf (red glaze)	-		-	-	Tr	
Wieskirche, pulpit, sample P9a, blue glaze on silver leaf (blue glaze)	tr Oxy-C	+ M	-	-	+ Also plus oxy-bwx series	
Wieskirche, pulpit, sample P9b, blue glaze on silver leaf (ground)	-	-	-	-	-	
Wieskirche, pulpit, sample P11, brownish-red glaze on silver leaf (brownish-red glaze)	-	-	-	-	+++	
Wieskirche, pulpit, sample P12, brownish-red glaze on silver leaf (brownish-red glaze)	-	-	-	-	+++	
Marienberg, Hochaltar, P1b, yellow glaze on gold leaf (yellow glaze)	+++ S, C (S>C)	Tr M	+ S	-	-	
Marienberg, Hochaltar, P2, yellow glaze on gold leaf (yellow glaze)	+++ S, C (S>C)	Tr M	+ S	-	-	
Marienberg, Hochaltar, P4a, yellow glaze on gold leaf (yellow glaze)	+++ S, oxy-C (S>C)	Tr M	+ S	-	-	
Marienberg, Hochaltar, P4b, yellow glaze on gold leaf (bole)	++ S, C	+ M	+ S	-	++	
Muljava (Slovenia), altarpiece, sample P1, red glaze on silver leaf (red glaze)	-	-	-	-	Tr	
Muljava (Slovenia), altarpiece, sample P2, green glaze on silver leaf (green glaze with later coating)	-	-	-	+ Shellac (later glaze)	Tr	
Nemski Root (Slovenia), altarpiece, sample P1, faded red glaze on silver leaf (red glaze)	+ L (aged)	-	+ Diterps	-	Tr	
Nemski Root (Slovenia), altarpiece, sample P2, green glaze on silver leaf (green glaze)	+ L fresh	-	-	-	-	
Nemski Root (Slovenia), altarpiece, sample P3, reddish-orange glaze on silver (glaze)	+++ C, L	-	+	-	-	
Nemski Root (Slovenia), altarpiece, sample P4A, red glaze on silver leaf (red glaze)	-	-	-	-	-	
Nemski Root (Slovenia), altarpiece, sample P4B, red glaze on silver leaf (bole and some ground)	-	-	-	-	-	
Nemski Root (Slovenia), altarpiece, sample P5, green glaze on silver leaf (green glaze)	+++ L > C	-	+	-	-	

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	-	-	-	-	-	+ Carbonates + Carboxylates
-	Tr p/s 1.8	-	-	-	+ Pb	+ Carbonates + Carboxylates + Sulphate (HT) Unknown m/z 348, 333, 274, 235 m/z 288 larixol-H_2O
-	-	-	-	-	-	++ Unknown m/z 134, 135
Tr C16–16; C16–18; C18–18	+ p/s 1.1	+ linseed	++ Animal glue	-	+ Pb	High temp. sulphate source (BaSO4?) Pb-Azelate
-	-	+	-	-	+ Pb	-
-	+ p/s 1.9	+	++	-	+ Pb	+ Sulphates (hT) + Carboxylates + Carbonate = limestone
-	+ C14, 16, 18 p/s 1.5	-	++ Not animal glue	-	-	Cholesterol and oxycholesterols, Tocopherol (530)
+ C16–16; C16–18; C18–18	+ p/s 1.5	+	++ Animal glue	-	++ Pb	+ Pb-Azelate + Carboxylates + Sulphates (hT)
-	Tr p/s 2.3	-	+++ Animal glue	-	-	++ Sulphate (hT) Tr Pb-Azelate
-	+ p/s 3.5	-	++ Animal glue	-	+ Pb	+ Sulphates (hT) + Carboxylates
+ C16–16; C16–18; C18–18	+ p/s 2.2	-	++ Animal glue	-	+ Pb	+ Sulphate (hT)
-	-	-	-	-	-	Unknown m/z 107, 108, 135, 150
-	-	-	-	-	-	Unkown m/z 107, 108, 135, 150
-	-	-	-	-	-	Unkown m/z 107, 108, 135, 150
-	-	-	+ Animal glue	-	-	Sulphate carbonate
Tr	++	+	-	-	+ Pb	+ Sulphate (LT) + Carboxylates
-	++ p/s 1.2 Az	+	-	-	Tr Pb	+ Sulphate (LT & HT) ++ Carboxylates
Tr C16–16; C16–18; C18–18	+ p/s 1.2	++	-	+	Tr Pb	Tr sulphates
-	-	-	-	-	Tr Cu	m/z 288 larixol
-	-	+	-	-	-	m/z 288 larixol
-	++ p/s 1.2	++	-	-	+ Pb	+ Carboxylates
-	+ p/s 1.4	+	?	-	+ Pb	+ Carboxylates
-	-	-	-	-	+ Cu	m/z 288 larixol

Table 3 Glazes with frankincense

Sample	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac Gamboge	Beeswax	
Cuvilliés Theater, drapery, sample P3, red glaze on silver leaf (red glaze)	++ S, oxy-C	++ M,F	+	-	-	
Munich, Stadtmuseum, house altarpiece, sample E28, blue glaze on silver leaf (blue glaze)	+ L, C	++ F	+++	-	+	
Munich, Bayerisches Nationalmuseum, orna-mental clock (Inv. No. 3792R), sample P8, blue smalt glaze on silver leaf (blue glaze)	+ S, C	++ F, M	-	-	-	
Tegernsee, side altarpiece (niche), sample P1b, blue glaze on silver leaf (blue glaze)	++ L, oxy-C	+ F,M	+	-	-	
Munich, sculpture (*Pietà*), sample P1 Mu B, blue smalt glaze on silver leaf (blue smalt glaze)	+ C	+ F,M	+	-	-	
Freising, high altarpiece, sample P7b, yellow glaze on silver leaf (yellow glaze	+ oxy-C	+ F		+ Shellac (later glaze)	tT	

Table 4 Glazes with gamboge

Sample	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac Gamboge	Beeswax	
Kaisheim, high altarpiece, sample H1, yellow-ish-brown glaze on silver leaf (yellow-brown glaze)	+ Oxy-C	+ M	-	+ Gamb.	-	
Abwinkl, reliquary retable, sample P6c, yellow glaze on gold leaf (yellow glaze)	++ C, S	+ M	+	+ Gamb.	Tr	
Altomünster, left side altarpiece, sample H1c, red glaze on silver leaf (red glaze)	+++ S, C, L	Tr M	-	+ Gamb.	-	

Table 5 Ground and preparatory layers (e.g. bole or mordant)

Sample	Diterpeniod resin	Triterpenoid resin	XL-terp.	Shellac Gamboge	Beeswax	
Georgenberg P6, A, ground	-	-	-	-	-	
Georgenberg P6, B, bole	-	-	-	-	++	
Ering am Inn, high altarpiece, sample P45, green glaze on silver leaf (ground and bole)	-	-	-	-	+	
Sünching, altarpiece, sample Sue2, blue smalt glaze on silver leaf (ground)	-	-	-	-	-	
Würzburg, Residence, Green-lacquered Room, sample P3a, green glaze on silver leaf (ground and mordant)	-	-	-	-	-	
Wieskirche, pulpit, sample P9b, blue glaze on silver leaf (ground)	-	-	-		-	

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	-	-	-	-	-	-
-	+ 16, 18 p/s 2.2	+	-	-	+ As	m/z 288 larixol !! + Sulphate (LT) + Carbonates + Carbopxylates
-	-	-	-	-	+ ++ As, As2 (from the smalt)	-
-	-	-	++ Animal glue	-	Tr As	+ Sulphate (HT) + Carbonate Arsenic from green over-painting m/z 396 and 289
-	-	-	-	-	-	* m/z 150, 225 and 300 = arsenicoxide = smalt
	++ p/s 0.80 18:1 p/s	+	-	-	++ Pb	

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	+ p/s 1.4	+	+ Not animal glue	-	+ As	+ Arsenic sulphide pigment (AASP), Tr indigo
-	-	-	-	-	+ Hg	Some vermilion and red lake
-	-	-	-	-	-	++ Unknown m/z 134 , 135

AG	FA	XL-oil	Protein	Polysaccharide	Element	Other
-	-	-	+++ Animal glue	-	-	++ Carbonates > limestone
+	+ p/s 1.9	+	+ Animal glue	-	-	+ Carbonates = limestone + Organic sulphonates in proteins
-	+ p/s 5 C16 & C24 from bwax	-	++ Animal glue	-	-	++ Carbonates
-	-	-	+++ Animal glue	-	-	+++ Sulphates HT + Carboxylates + Carbonates = limestone
+ C16–16; C16–18; C18–18	++ p/s 2	++	++ Animal glue	-	+ Pb	+ Carbonate as limestone + PbAzelate
-	Tr p/s 2.3	-	+++ Animal glue	-	-	++ Sulphate (hT) Tr Pb-Azelate

Literature

- ANONYMOUS: *Grund=mässige und sehr deutliche Anweisung zu der schönen Laccir= und Schildkrotten=Arbeit / Und zu allerley erdencklichen horn und fürtrefflichen holz=Arbeiten. Vermittelst welcher diese schöne Kunst leicht und ohne Lehrmeister von sich selbsten zu erlernen und zu begreifen. Zusamt allerley erdencklichen und geheimen Fürnis=Künsten auf allerley Sachen / worbey man dergleichen gebrauchen mag. Wie auch von mancherley ersinnlichen Verguldungen und Versilberungen auf was man nur selbsten will / nebenst Zubereitung der schönsten und raresten Farben und Mahler=Künsten. Nebst einen Anhang der Schreib=Kunst. Absonderlich für Mahler, Bildhauer, Kupferstecher, Schreiner und andere Künstler / dergleichen noch niemahln also an das Tage=Licht gekommen / und heraus gegeben worden,* Zufinden bey Johann Christoph Lochner / Gedruckt bey Christian Sigm. Froberg, Nürnberg 1706
- BASAR, S.: *Phytochemical Investigations on Boswellia Species - Comparative Studies on the Essential Oils, Pyrolysates and Boswellic Acids of Boswellia carterii Birdw., Boswellia serrata Roxb., Boswellia frereana Birdw., Boswellia neglecta S. Moore and Boswellia rivae,* unpublished PhD Thesis, Institute of Organic Chemistry, University of Hamburg, Hamburg 2005, available under http://www.boswellness.com/sites/default/files/pdfs/DissertationBasar.pdf
- BAUMER, U./DIETEMANN, P.: *Identification and differentiation of dragon's blood in works of art using gas chromatography/mass spectrometry,* in: *Analytical Bioanalytical Chemistry,* 397, 2010, pp. 1363–1376
- BAUMER, U./DIETEMANN, P./FIEDLER, I.: *Nicht nur Leim-Analyse der Binde- und. Klebemittel der Muenchner Boulle-Moebel',* in: RENATE EIKELMANN (ed.): *Prunkmöbel am Muenchner Hof – Barocker Decor unter der Lupe,* Bayerisches National Museum, Munich 2011
- BERGMANN J. H.: *Untersuchungen zum Harz des Weihrauchbaums (Boswellia spp.) unter besonderer Berücksichtigung der Säurefraktion,* PhD thesis, Technische Universität München, Munich 2004, available under http://tumb1.biblio.tu-muenchen.de/publ/diss/ch/2004/bergmann.pdf
- BOON J. J./DE LEEUW, J. W.: *Amino acid sequence information in proteins and complex proteinaceous material revealed by pyrolysis-capillary gas chromatography-low and high resolution mass spectrometry,* in: *Journal of Analytical and Applied Pyrolysis,* 11, 1987, pp. 313–327
- BOON, J. J.: *Analytical pyrolysis mass spectrometry: new vistas opened by temperature-resolved in-source PYMS,* in: *International Journal of Mass Spectrometry and Ion Processes,* Vol. 118/119, 1992, pp. 755–787
- BOON J. J./PASTOROVA, I./BOTTO, R. E./ARISZ P. W.: *Structural studies on cellulose pyrolysis and cellulose chars by PYMS, PYGCMS, FTIR, NMR and by wet chemical techniques,* in: *Biomass & Bioenergy,* 7, 1994, pp. 25–32
- BOON, J. J./PEULVÉ, S./VAN DEN BRINK, O. F./DUURSMA, M. C./RAINFORD, D.: *Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films,* in: T. BAKKENIST/R. HOPPENBROUWERS/H. DUBOIS (eds): *Early Italian Paintings: Techniques and Analysis,* Symposium, Maastricht, 9–10 October 1996, Maastricht 1997, pp. 35–56
- BOON J. J./HOOGLAND, F. G./VAN DER HORST, J.: *Mass spectrometry of modern paints,* in: TH. J. S. LEARNER (ed.): *Modern Paints Uncovered,* Proceedings from the Modern Paints Uncovered Symposium organized by the Getty Conservation Institute, Tate, and the National Gallery of Art, Tate Modern, London, 16–19 May 2006, Los Angeles 2007, pp. 85–95
- CRÖKER, J. M.: *Der wohlanführende Maler,* Jena 1736, Reprint Mittenwald 1982
- GINZ, M./ENGELHARDT, U. H.: *Identification of Proline-Based Diketopiperazines in Roasted Coffee,* in: *Journal of Agricultural and Food Chemistry,* 48, 2000, pp. 3528–3532
- GONZALEZ, A. G./LEON, F./HERNANDEZ, J. C./PADRON, J. I./SANCHEZ-PINTO, L./BARRERA, J. B.: *Flavans of dragon's blood from Dracaena draco and Dracaena tamaranae,* in: *Biochemical Systematics and Ecology,* 32, 2004, pp. 179–184.
- GROEN, K. M./VAN DER WERF, I. D./VAN DEN BERG, K. J./BOON, J. J.: *The scientific examination of Vermeer's Girl with a Pearl Earring,* in: I. GASKELL/M. JONKER (eds): *Vermeer Studies,* Symposium XXXIII Center for Advanced Study in the Visual Arts, Washington 1998, pp. 168–183
- IBIDAPO, T. A.: *The characterization of the halatopolymers: a review,* in: *Polymer Engineering and Science,* 35, 1996, pp. 1920–1927
- LIN, L.-J./LIN, L.-Z./PEZZUTO, J. M./CORDELL, G. A./RUANGRUNGSI, N.: *Isogambogic acid and Isomorellinol from Garcinia Hanburyi,* in: *Magnetic Resonance in Chemistry* 31, 1993, pp. 340–347
- KOLLER J./BAUMER, U.: *Baroque and Rococo Transparent Gloss Lacquers II. Scientific Study of Lacquer Systems,* in: K. WALCH/J. KOLLER (eds): *Lacke des Barock und Rokoko,* Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, Vol. 81, Munich 1997
- KOLLER, J./BAUMER, U./GROSSER, D./WALCH, K.: *Turpentine, Larch Turpentine and Venetian Turpentine,* in: K. WALCH/J. KOLLER (eds): *Lacke des Barock und Rokoko,* Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, Vol. 81, Munich 1997
- KOLLER, J./BAUMER, U.: *Ein Beispiel norddeutscher Leinölmalerei,* in: KULTURBEHÖRDE HAMBURG/DENKMALSCHUTZAMT (eds): *Die vier Flügel des Hochaltars aus dem Hamburger Dom,* Ein deutsch-polnisches Restaurierungsprojekt, Berichte aus der Restaurierungswerkstatt St. Jacobi, Vol. 1, Hamburg 2001, pp. 96–110
- LANGENHEIM, J. H.: *Plant Resin. Chemistry, Evolution, Ecology, Ethnobotany,* Cambridge 2003
- LEARNER, T. J. S.: *Analysis of Modern Paints,* Los Angeles 2004
- LOMAX, J. A./COMMANDEUR, J. M./BOON, J. J.: *Pyrolysis mass spectrometry of polysaccharides,* in: *Biochemical Society Transactions,* 19, 1991, pp. 935–940
- MILLS, J. S.: *The gas chromatographic examination of paint media. Part I: Fatty acid composition and identification of dried paint films,* in: *Studies in Conservation,* 11, 1966, pp. 92–107
- MILLS, J. S./WHITE, R.: *The Organic Chemistry of Museum Objects,* Oxford 1987
- NOVOTNÁ P./BOON, J. J./VAN DER HORST, J./PACÁKOVÁ, V.: *Photodegradation of indigo in dichloromethane solution,* in: *Journal of Coloration Technology,* 119, 2003, pp. 121–127
- PASTOROVA, I./OUDEMANS, T. F. M./BOON, J. J.: *Experimental polysaccharide chars and their "fingerprints" in charred archaeological food residues,* in: *Journal of Analytical and Applied Pyrolysis,* 25, 1993, pp. 63–75

- SCALARONE, D./VAN DER HORST, J./BOON, J. J./CHIANTORE, O.: *Direct-temperature mass spectrometric detection of volatile terpenoids and natural terpenoid polymers in fresh and artificially aged resins*, in: *Journal of Mass Spectrometry,* 38, 2003, pp. 607–617
- SMITH, G. G./SUDHAKAR REDDY, G./BOON, J. J.: *Gas chromatographic–mass spectrometric analysis of the Curie-point pyrolysis products of some dipeptides and their diketopiperazine*, in: *Journal of the Chemical Society, Perkin Transactions,* 2, 1988, pp. 203–211
- SOUSA, M. M./MELO, M. J./PAROLA, A. J./SEIXAS DE MELO, J. S./CATARINO, F./PINA, F./COOK, F. E. M./SIMMONDS, M. S. J./LOPES, A.: *Flavylium chromophores as species markers for dragon's blood resins from Dracaena and Daemonorops trees*, in: *Journal of Chromatography A*, Vol 1209, 2008, pp. 153–161
- SZPAK, P.: *Fish bone chemistry and ultrastructure: implications for taphonomy and stable isotope analysis, Journal of Archaeological Science*, 38, 2011, pp. 3358–3372
- THEODORAKOPOULOS, C./BOON, J. J./ZAFIROPULOS, V.: *Direct temperature mass spectrometric study on the depth-dependent compositional gradients of aged triterpenoid varnishes*, in: *International Journal of Mass Spectrometry* ,284, pp. 98–107
- VAN ARENDONK J. J. C. M./NIEMANN, G. J./BOON, J. J.: *The effect of enzymatic removal of proteins from plant leaf material as studied by pyrolysis-mass spectrometry: detection of additional protein marker fragment ions*, in: *Journal of Analytical and Applied Pyrolysis,* 42, 1997, pp. 33–51
- VAN DEN BERG, J. D. J.: *Direct temperature resolved mass spectrometry of oil paint constituents and aged oil paints.* In: Analytical studies on traditional oil paints. PhD thesis at the University of Amsterdam. With atlas of mass spectra. MOLART Report 6, Amsterdam 2002, downloadable from www.amolf.nl
- VAN DEN BERG, J. D. J./VAN DEN BERG, K. J./BOON, J. J.: *Identification of non-cross-linked compounds in methanolic extracts of cured and aged linseed oil-based paint films using gas chromatography-mass spectrometry*, in: *Journal of Chromatography A*, 950, 2002, pp. 195–211
- VAN DEN BERG, J. D. J./VERMIST, N. D./CARLYLE, L./HOLCAPEK, M./BOON, J. J.: *The effects of traditional processing methods of linseed oil on the composition of its triacylglycerols*, in: *Journal of Separation Science*, 27, 2004, pp. 181–199
- VAN DEN BERG, K. J./BOON, J. J./PASTOROVA, I./SPETTER, L. F. M.: *Mass spectrometric methodology for the analysis of highly oxidised diterpenoid acids in Old Master paintings*, in: *Journal of Mass Spectrometry*, 35, 2000, pp. 512–533
- VAN DEN BERG, K. J.: *Analysis of diterpenoid resins and polymers in paint media and varnishes*, Review and collated papers. Molart Report 10 with atlas of mass spectra, 2003, downloadable from www.amolf.nl and www.rce.nl
- VAN DEN BRINK, O. F./FERREIRA, E. S. B./VAN DER HORST, J./BOON, J. J.: *A direct temperature-resolved tandem mass spectrometry study of cholesterol oxidation products in light-aged egg tempera paints with examples from works of art*, in: *International Journal of Mass Spectrometry*, 284, 2009, pp. 22–34
- VAN DER DOELEN, G./VAN DEN BERG, K. J./BOON, J. J.: *Comparative chromatographic and mass-spectrometric studies of triterpenoid varnishes: Fresh material and aged samples from paintings*, in: *Studies in Conservation*, 43, 1998, pp. 249–264
- VAN DER DOELEN, G.: *Molecular studies of fresh and aged triterpenoid varnishes.* PhD thesis, University of Amsterdam, Amsterdam 1999. With atlas of mass spectra. MOLART Report 1, downloadable from www.amolf.nl
- VAN DER HAGE, E. R. E./MULDER, M. M./BOON, J. J.: *Structural characterization of lignin polymers by temperature-resolved in-source pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography/mass spectrometry*, in: *Journal of Analytical and Applied Pyrolysis,* 25, 1993, pp. 149–183
- VAN DER HAGE E. R. E./WEEDING, T. L./BOON, J. J.: *Mass spectrometry of natural and synthetic lignin polymers: on the detection of coumaryl units by in-source pyrolysis mass spectrometry'*, in: R. P. NEWTON/T. J. WALTON (eds): *Applications of Modern Mass Spectrometry in Plant Science Research,* Oxford 1996, pp. 117–138
- VAN LOON, A./BOON, J. J./KEUNE, K./VAN DER HORST, J.: *Binding Medium Analysis of Seventeenth- and Eighteenth-Century Blue Coloured Glazes on Silver Leaf Gildings*, in: M. KÜHLENTHAL/S. MIURA (eds): *Historical Polychromy. Polychrome Sculpture in Germany and Japan,* Munich 2004, pp. 352–379
- VOS, N./GORIS, K.: *Drakenbloed*, Student project for Mass spectrometry supervised by H. PEETERS, C. DE KOSTER and J. J. BOON, unpublished 2nd year research project at the Chemistry Faculty of the University of Amsterdam, Amsterdam 2010.
- WALCH, K./KOLLER, J.: *Lacke des Barock und Rokoko*, Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, Vol. 81, Munich 1997