

Characterization of Commercial Synthetic Resins by Pyrolysis-Gas Chromatography/Mass Spectrometry: Application to Modern Art and Conservation

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To characterize a set of synthetic resins, a methodology by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has been developed. The studied reference materials were commercial versions of a wide range of synthetic resins. For each polymer, the pyrolytic and chromatographic conditions were optimized to adequately resolve the fragment mixture in a short time. The proposed analytical method does not require previous treatment of the sample, and due to its high sensitivity, only a small sample quantity in the microgram range can be used. The pyrolysis temperature was found to have little effect on the obtained pyrograms. The summarized data set for the individual polymer materials, especially the characteristic fragments with a structure close to the monomeric unit, was useful to identify commercial synthetic resins. These materials were used in the art and conservation field, as binding media, paint additives, painting varnishes, coatings, or consolidants. Two case studies are introduced where direct Py-GC/MS and thermally assisted hydrolysis and methylation GC/MS were applied on art objects: first, a modern gluing material of a medieval reverse glass painting, and the second example, the binding medium of a painting by Georg Baselitz ("Senta", 1992/1993) from the *Sammlung Moderne Kunst* at the *Pinakothek der Moderne*, Munich.

Synthetic resins are a wide range of materials obtained by polymerization of low-weight hydrocarbons,^{1–5} which were first synthesized during the Industrial Revolution in the 19th century. The history of synthetic polymers for artistic purposes began after the invention of cellulose nitrate by Schönbein and Böttger in 1846. These days, synthetic polymers have tremendous importance in

modern contemporary art objects but also for the conservation/restoration of archeological and art objects due to their excellent physical properties and special functionalities.⁶ Their wide variety of formulations make these materials very useful as binding and retouching media, agglutinants, adhesives, consolidants, coating materials, varnishes, or additions for missing parts of an object. To identify and investigate synthetic resins in art objects is helpful, e.g., in order to propose adequate preventive and active conservation/restoration treatments, to understand aging mechanisms, or to differentiate between artists' products of different manufacturers. Analytical studies dealing with artworks are usually restricted by the low sample amount available and often by the presence of unknown and complex material compositions.

A large variety of synthetic resins have been used in the field of artworks, which can be classified as addition polymers, polycondensates, and polyadducts. In the case of addition polymers, unsaturated monomers are linked with radical reactions to polyolefins, poly(vinyl alcohol), poly(vinyl acetate), polyacrylates, poly(ethylene oxide)s, and poly(vinyl chloride)s.¹ In the group of the polymers also early tar products, like cumaron resin, as well as modern hydrocarbon resins² are included. The polycondensate polymers, such as polyester, alkyds, phenol resins, phenol–formaldehyde resins, aldehyde resin, ketone formaldehyde resins, ketone resins, and cellulose nitrate,^{1,2,4} are formed by chemical reaction between functional groups. The main polyadduct polymers are polyurethanes and epoxide resins.

Fourier transform infrared spectroscopy (FT-IR) is successfully employed to identify synthetic polymers in artworks.^{7,8} This technique allows one to detect characteristic absorption bands of synthetic polymers. However, the overlapping of the absorption bands of the polymeric resins with those of other materials in the sample can make difficult its identification.

As an alternative, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has been used to characterize synthetic materials such as polymers or organic pigments used in art,

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archeology, and conservation.^{9–17} Several methodologies (direct temperature resolved mass spectrometry, Py-GC/MS) have been developed without any derivatization, i.e., pyrolysis can be applied directly to the solid sample, avoiding previous treatments. Py-GC/MS is based on the thermal breakage of the macromolecules of the samples, and the obtained fragments can be separated by gas chromatography and detected by mass spectrometry with high sensitivity. Py-GC/MS provides a high sensitivity using a minimal amount of sample (in the range of ca. 20–100 μg), and its differentiation power allows one to detect fragments from various organic materials in mixtures without interference. The mass spectrometer identifies the compounds by their mass spectrum and allows the differentiation of coeluted fragments. The characterization of the polymers is then made by means of the identified fragments, relating them to the structure of the polymer. Good results with Py-GC/MS were achieved for most of the high molecular weight polymers (e.g., polyacrylates and poly(vinyl acetate)s^{10,13,14}) and also some low molecular weight synthetic resins (e.g., phenol resins,¹⁸ ketone resins,¹⁹ hydrocarbon resins).

The polymer fragments with polar groups can show resolution problems on a nonpolar column; thus, many authors propose a simultaneous derivatization reaction.^{10,15,20} Here a treatment with TMAH (tetramethylammonium hydroxide) was chosen prior to pyrolysis. Upon heating, the TMAH induces hydrolysis and, simultaneously, leads to methylation of acidic compounds. Due to this thermally assisted hydrolysis and methylation reactions with TMAH all organic acids were methylated and good chromatographic separation was achieved. THM-GC/MS is a very sensitive technique and has been successfully applied for identification of alkyd resins and drying oils.^{20–22}

The aim of this work was to develop an analytical methodology to characterize a wide range of synthetic resins. The proposed methodology was based on direct Py-GC/MS and the THM-Py-GC/MS procedure. The temperature of the pyrolysis in the breakage of the macromolecules and the chromatographic condi-

tions were optimized for each kind of resin. The obtained pyrograms were evaluated in order to identify the chromatographic peaks by means of their corresponding mass spectrum, especially from “marker” fragments with a structure similar to the corresponding monomer. The studied standards were recent and historic polymeric resins from the collection of the Doerner Institut, in order to identify them as references for art and conservation materials.

To give practical examples for the application of Py-GC/MS on art objects, binding media analyses were carried out on two samples from a modern painting by the German painter Georg Baselitz, which was supposed to have been painted in acrylic paint. Furthermore, a modern consolidation material from a 16th century reverse glass object (Theodosia altar, Museum Catharijneconvent, Utrecht) was analyzed.

EXPERIMENTAL SECTION

Reference Materials. Twenty-two synthetic resins were selected for this study; their trade names, production date, and characteristic pyrolytic fragments are listed in Table 1. These polymers belong to the collection of artists’ materials of the Doerner Institut, the institution in charge of the restoration, conservation, care, and maintenance of the Bavarian State painting collections. The somewhat arbitrary selection of historic and more recent materials is mainly due to the history of the material collection, but it comprises mainly synthetic resins which are typically applied as binding media or additives, varnishes, retouching materials, consolidants, or coatings in artists’ and conservation materials.

Instrumentation and Measurement Conditions. The analyses were performed using the following instrumentation: a Curie-point pyrolyzer Pyromat V.108 (GSG Mess- and Analysengeräte, Bruchsal, Germany), connected to a gas chromatograph 6890N (Agilent), coupled to a quadrupole mass spectrometer MSD, 5975C inert mass (Agilent). Measurement conditions for the GC were the following: capillary column DB5-ht (5% phenyl)methylpolysiloxane (length, 30 m; internal diameter, 250 μm ; film thickness, 0.1 μm); carrier gas helium running at a constant flow of 1.2 mL min^{-1} (15 cm s^{-1}); splitless injection.

The sample (ca. 50 μg) was introduced in a pyrolysis crucible (Fe/Ni alloy, GSG Mess- and Analysengeräte). Then the crucible was fitted into a hollow glass cylinder, which was set up in the pyrolyzer syringe. Pyrolysis was achieved by Curie-point method. Crucibles for 590, 650, and 764 $^{\circ}\text{C}$ were used.

The pyrolysis chamber was held at 200 $^{\circ}\text{C}$, and the pyrolysis was achieved at a selected temperature for 10 s. Injection temperature was adjusted to 250 $^{\circ}\text{C}$, the initial temperature of the oven was 50 $^{\circ}\text{C}$, maintained for 2 min, then a 10 $^{\circ}\text{C min}^{-1}$ gradient was applied to 320 $^{\circ}\text{C}$ (29 min). Ionization was performed under standard conditions at 70 eV, with a voltage of 200 V. The temperature of the source was adjusted at 250 $^{\circ}\text{C}$, whereas the temperature of the quadrupole was 100 $^{\circ}\text{C}$. The mass spectrometer was scanned in the 42–550 m/z range.

For the alkyd resin and the Baselitz paint samples Py-GC/MS was without derivatization, because the obtained pyrograms have unsatisfactory resolution, mainly by the presence of fragments with polar groups. Then complementary THM-GC/MS analyses were undertaken. For thermally assisted hydrolysis and methylation GC/MS a solution of 2.5% TMAH in methanol was added

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Table 1. Investigated Synthetic Resins with Manufacturer/Date and the Characteristic Fragments Detected through Py-GC/MS (and THM-GC/MS) with Their Most Intense Ions in the Mass Spectrum and the Respective Molecular Weight (MW)

chemical class	product name	manufacturer	date	characteristic fragments after pyrolysis	retention time (min)	most intense ions (<i>m/z</i>)	MW (g/mol)
polyacrylates ^a	Paraloid B-72	Rohm and Haas, probably Frankfurt a. M. (D)	unknown	methylacrylate MA	2.509	55/42/85	86
	Golden Acrylics	Golden Artist Colors, New Berlin, NY	2006	ethylmethacrylate EMA methylmethacrylate MMA	3.598 3.043	69/86/99 41/69/100	114 100
polystyrol ^e	Kraton G1657	Kraton Polymers LLC, Houston, TX	1988	butylacrylate BA isobutylmethacrylate styrene	4.758 5.478 4.868	55/73/85 69/56/87 104/78/51	128 142 104
	Kraton G1650						
poly(vinyl acetate)s ^a	Mowilith 20	Hoechst AG (since 1997 Clariant), Frankfurt a.M. (D)	1984	toluene ethylhexene acetic acid	3.538 3.340 3.863	91/92 55/70/98 45/60	92 112 60
	Mowilith 30						
	Mowilith 40						
	Mowilith 50						
	PVAc AYAA	Union Carbide Corp. (since 1999 Dow Chemical Company), Houston, TX	1987	acetic acid anhydride benzene	2.831 2.939	43/60 78	60 78
	PVAc AYAF						
	PVAc AYAT						
	PVAc AYAT+						
	"Palmer Cement" (contains PVAc AYAB)						
hydrated hydrocarbon resin ^a	Arcon P-90	Union Carbide Corp.	unknown (before ca. 1980)	methylcyclohexane	3.218	83/98/55	98
		Arakawa Chemical Industries, Osaka (Japan)	1998				
early hydrocarbon resins ^a	Cumaron resin	unknown	unknown (at least 40 years old)	hexahydroindene octahydroindene octahydro-methano-indene benzofuran	6.173 6.313 7.086 6.406	79/80/93/122 81/67/96/124 95/67/136/121 118/89/90	122 124 136 118
				allylbenzene indene	5.680 7.136	117/118/91 116/115/89	118 116
				methylbenzofuran	7.966	131/132/104	132
				methylindene	8.717	130/115/129	130
				phthalic anhydride	23.224	104/148	148
				methylphenol	7.318	107/108/77	108
				dimethylphenol	8.703	122/107/77	122
				trimethylphenol	9.499	121/136	136
				oleic acid	19.901	55/69/83	280
				THM-GC/MS			
				methylbenzoate	4.586	105/136	136
				pentacerythritotetramethylether	6.985	75/128	192
				pentacerythritotrimethylether	7.105	75/85/128	178
				dimethylphthalate	12.285	163/194	194
				oleic acid (C18-1)	15.995	55/69/83	296
				palmitic acid (C16)	14.675	74/87/143	270
				stearic acid (C18)	16.185	74/87/143	298
				linoleic acid (C18-2)	15.874	67/81/95	294
				cyclohexanol	4.720	57/82/67	100
				methylcyclohexanol	5.606	71/81/96	114
				methylcyclohexanone	5.679	69/55/112	112
cyclohexanone resins ^b	AW2	BASF, Ludwigshafen (D)	before 1967				

Table 1. Continued

chemical class	product name	manufacturer	date	characteristic fragments after pyrolysis	retention time (min)	most intense ions (<i>m/z</i>)	MW (g/mol)
methylcyclohexene Keton N	3.517 BASF, Ludwigshafen (D)	81/96/67 ca. 1960 to 1979	96 cyclohexanone norbornadienone dimethylcyclohexadienone unknown (at least 40 years old)	4.900 6.107 6.441 methylphenol dimethylphenol methoxybenzaldehyde trimethylphenol styrene diethylbenzene methylphenol dimethylphenol ethylbutanal 4,5-dimethyl-oxazole methyl-2,2-dimethyl-3-hydroxypropionate 2,2-dimethyl-3-hydroxypropionaldehyde butanal benzene	55/42/98 67/110/82 79/94/122 7.318 8.703 13.131 9.499 4.868 7.196 7.318 8.703 3.989 2.783 3.315 5.102 3.926 2.672	98 110 122 107/108/77 122/107/77 136/135 121/136 103/104/78 119/105/134 107/108/77 122/107/77 43/56/72 97/82/54 102/87/73 56/57/72 44/72	108 122 136 136 104 134 108 122 100 72 97 132 102 72 78
phenol resin ^b	unspecified	unknown	unknown (at least 40 years old)				
formaldehyde phenol resin ^b	unspecified formaldehyde phenol resin	unknown	unknown (at least 40 years old)				
aldehyde resins ^b	Laropal A81	BASF, Ludwigshafen (D)	1998				
	Mowital B20H (poly(vinyl butyral resin)	Hoechst AG (since 1997 Clariant), Frankfurt a.M. (D)	ca. 1980				

^a Addition polymers. ^b Polycondensates.

to the samples. After homogenization, the solution was left for 5 min, and then 10 μ L was pyrolyzed under the conditions described above. The derivatization is performed at the same temperature of the pyrolysis.

Case Studies. Samples of the first case study origin from the so-called Theodosia altar in the collection of the Museum Catharjneconvent, Utrecht (inv. no. ABMs 146.01-15). The altar, which dates around 1545, is painted in reverse glass technique, and its 15 glass panels are attached in a wooden frame. The Theodosia altar is currently in the focus of thorough art-technological research,²³ and in this context the conservation materials were analyzed. During previous conservation treatments some parts of the historical cement between the glass panels were replaced by a modern polymer. For the ongoing restoration of the Theodosia altar, this material was characterized by Py-GC/MS to predict its aging behavior and to avoid further damages.

As a second case study two samples from the painting "Senta" (inv. no. HST 1785) by the German painter Georg Baselitz, which dates 1992/93 (see the Supporting Information), were analyzed by Py-GC/MS and THM-GC/MS to identify binding medium components. Georg Baselitz, who was born in Deutschbaselitz (Saxony, Germany) in 1937, is considered as one of the most important representatives of contemporary art in Germany. His painting "Senta" was supposed to be carried out in acrylic paint, but the source of this information found in the collection management system was unclear and needed verification.

RESULTS AND DISCUSSION

Optimization of the Method. The influence of the temperature was studied by analysis of samples from each synthetic resin at three different temperatures (590, 650, and 764 °C) and comparing the fragments (structures and intensity) in the obtained pyrograms. In general, for the majority of the studied synthetic polymers similar results were found at all three temperatures. Only differences were found for the following cases:

- In acrylate polymers, the fragmentation was depending on the pyrolysis temperature. At 590 °C, a larger amount of acrylate fragments was detected, and then this temperature was taken as optimal for acrylic polymers analysis.
- Differences were also found for the Keton N cyclohexanone resin, a BASF product. Pyrograms obtained for Keton N were similar for 590 and 650 °C. At 764 °C a larger amount of ketonic monomer fragments were found. Other compounds with cyclic hydrocarbon-related structure (at retention times from 6.0 to 8.0 min) also showed a higher intensity. Nevertheless, the relative amounts of high-weight fragments, which appear from 13.0 to 17.5 min, were found to be quite similar for the three temperatures. It can be deduced that increasing the temperature to 764 °C favors the fragmentation of the polymer providing compounds helpful for the characterization.^{11,24} These pyrolysis results are coherent with the production of Keton N resin (between ca. 1960 and 1979). The precursor resin AW2 was produced by a mixed condensation of cyclohexanone (1 part) and methylcyclohexanone (3 parts). In contrast, Keton N was a self-condensate of pure cyclohex-

(23) http://www.nike.bam.de/de/kompetenz/themen/kompetenz_themen_hinterglasmalerei-hgm.htm (accessed May 15, 2008).

(24) See ref 20, pp 33–34.

anone.⁴ The self-condensate Keton N seems more stable during pyrolysis (590 and 650 °C vs 764 °C), whereas a pyrolysis temperatures of 590 °C already leads to a good fragmentation of the AW2 mixed condensate. However, a higher pyrolysis temperature provokes an excessive fragmentation so that other authors propose less temperature.¹⁹

The experimental results indicate that the samples containing acrylate should be analyzed by pyrolysis at 590 °C, Keton N at 764 °C, and the other synthetic polymers can be analyzed at the three tested temperatures. Then the use of a unique pyrolysis temperature for the characterization of all the synthetic polymers is not recommended, because the optimal pyrolysis temperature is different in each case.

The temperature of the pyrolysis chamber was fixed to 200 °C. Despite the lower volatility of the fragments with high molecular weight, they are introduced to the column immediately after the pyrolysis into the column by the flow of the carrier gas without significant loss.²⁵

The injection was performed in splitless mode, in order to improve the sensitivity. This allows one to reduce the as much as possible the amount of sample taken and work with micro-samples, which is very important in analysis in samples from artworks.

Several temperature gradients were tested for the resolution of the fragments. The conditions detailed in Case Studies section in the Experimental Section were found to adequately separate all the fragments from the different studied synthetic polymers, using the selected capillary column.

Results on the Reference Resins. The analysis of reference samples all yielded significant and mostly complex pyrograms. Therefore, only the most characteristic fragments as well as the most intense ions in their corresponding mass spectrum are summarized in Table 1 for each resin probe. The obtained fragments provided useful information about the structure of each polymer and, to some extent, the presence of additives. For identification of the resin type, fragments with a structure close to the monomer are most characteristic. Other detected fragments could be considered as oligomers or the result of reorganization of some products formed during the pyrolysis. The most important fragments in each polymeric resin group are described as follows. Traces of the polymers have not been detected, because the pyrolysis reached high yielding, and due to the low volatility of the remaining polymer, the amount of polymeric trace introduced into the chromatographic system would be under the limit of detection.¹⁹

Addition Polymers. One of the most prominent polymers in the art historical field are the acrylics. An unspecified "Paraloid" sample was investigated for identification and classification. The most abundant pyrolysis fragments were methyl acrylate and ethyl methacrylate. These main components indicated a "Paraloid B72" resin, an EMA/MA copolymer frequently used for retouching or consolidation in conservation. Additionally, an antioxidant (butylated hydroxytoluene, BHT) could be detected.

The acrylic-based tube paint from Golden Artist Colors, NY, yielded the following acrylic monomers: methyl methacrylate, butyl acrylate, and isobutyl methacrylate. The antioxidant BHT

was additionally identified. This analysis is in coherence with the Py-GC/MS results on commercial acrylic paints discussed in depth by Learner.²² Py-GC/MS is therefore an adequate method to distinguish between different sorts of acrylics.

Pyrograms of two "Kraton" samples, a styrene–ethylene/butylene–styrene (SEBS) commercial polymer, showed a high amount of styrene, which was considered as the characteristic fragment, as well as toluene and ethylhexene. In the sample from Kraton G1650 and G1657, hydrocarbons were also found, probably additives in the course of production or formed from the ethylene–butylene block.

The pyrolysis products of the various commercial poly(vinyl acetate)s were mainly acetic acid from the polymer side chain and benzene formed by reorganization of the polymer backbone after side-group elimination.⁹ The "Palmer Cement" sample, a former US–American liquid retouching material with a PVAC component equivalent to Mowilith 20,²⁶ contained solvents (ethanol, acetone, methyl isobutyl ketone, toluene) that lead to further pyrolysis products like acetophenone and benzaldehyde. Poly(vinyl acetate) products differing in molecular weight and chain length are indistinguishable by Py-GC/MS.²⁷

Hydrogenated hydrocarbon resins have been recently introduced for use in picture varnishes.²⁸ The characteristic fragments of the saturated hydrocarbon resin "Arcon P-90" were saturated alkylcyclohexanes, such as methylcyclohexane, ethylcyclohexane, 1-ethyl-3-methylcyclohexane, (isopropyl)cyclohexane, and 1-ethyl-4-methylcyclohexane, which derive from the saturated polycyclic structure of the resin.

In the reference collection of the Doerner Institut also an early example of hydrocarbon resins, a brown cumarone resin of unspecified manufacturer and date, is present. It derived from polymerization of cumarone (benzofuran) and indene. The following compounds of the cumarone resin were detected by Py-GC/MS and considered as markers: benzofurane, indene, methylbenzofurane, and methylindene, the monomers of the resin.

Polycondensates and Polyadducts. The term polycondensation (or condensation polymerization) is defined as polymerization by a repeated condensation process (i.e., with elimination of simple molecules). Polyaddition is the agglomeration of functional groups to double bonds or to rings by simultaneous ring opening. In contrast to polycondensation no low molecular weight products emerge during polyaddition.²⁹

The most prominent group of polycondensates are the alkyd resins, or oil-modified polyester resins. The term "alkyd" derives from the polyester component's two main ingredients: a polyhydric alcohol (also called a polyol, such as glycerol or pentaerythritol) and a polybasic carboxylic acid (or polyacid, such as phthalic acid). By incorporating a monobasic fatty acid, the degree of cross-linking is significantly reduced. Often a drying oil is used as the

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Table 2. Pyrolysis Results of a Modern Cement from the Theodosia Altar^a

	characteristic fragments after pyrolysis	retention time (min)	most intense ions (<i>m/z</i>)	MW (g/mol)
rubber-like gluing material (cement)	MMA methylmethacrylate	3.043	69/100/41	100
	EA ethylacrylate	2.785	55/99	100
	DIBP diisobutylphthalate	18.286	149/223/278	278
	BHT butylated hydroxytoluene	13.542	205/220	220

^a Pyrolysis temperature 590 °C.

source of monobasic acids, resulting in an “oil-modified” alkyd resin.

In the here examined alkyd resin type “Alkydharz MM” a large amount of anhydride phthalic acid together with traces of oleic acid, short fatty acids, and carbonyl compounds were identified. According to precedent works,^{20,21,30} especially the alkyd resins require the application of THM-GC/MS. In our case after addition of TMAH the polyol pentaerythritol could be identified, together with the fatty acid content (see Table 1).

Varnishes, paints, and binding media in the field of art include some high-molecular polymers (e.g., acrylics), but the bulk of products is based on low molecular weight condensates. Typical examples are the cyclohexanone resins (e.g., AW2 and Keton N resin). The pyrograms obtained by the analysis of the ketone resin sample from AW2 showed the following characteristic fragments: cyclohexanol, cyclohexanone, and several alkyl derivatives, which clearly derive from a ketone polymer. The characteristic fragments found in the Keton N resin were similar: cyclohexanone and alkylcyclohexanones (see the Supporting Information).

Results on the phenol resins (and unknown dating) were different: The characteristic fragments of an old red-brown, unspecified phenol resin were a wide variety of alkylphenols (2-methylphenol, 2,6-dimethylphenol, 2-methyl-5-isopropyl-phenol, and 4-(1,1-dimethylethyl)-2-methylphenol). In comparison, another brown formaldehyde–phenol resin, also of unknown date and manufacturer, provided a larger amount of phenols (2-methylphenol, 4-methylphenol, 2,2-dimethylphenol, and 2,3,5-trimethylphenol).¹¹

The most relevant fragments detected in the analysis of “Laropal A81”, a ketone resin made by condensation of urea and aliphatic aldehydes,^{31–33} were methyl-2,2-dimethyl-3-hydroxypropionate, ethylbutanal, and isobutanal.

The pyrogram of the poly(vinyl butyral) “Mowital B20H” showed the following characteristic fragments: butanal, obtained from the thermic breakage of the polymer, and benzene, formed by reorganization of other fragments in the same way as in poly(vinyl acetate).

Results on Samples from Artworks. Even if good resolution has been found for the standard synthetic resins, the samples from artworks contain other unknown compounds which can interfere with those from the fragments from the polymers. To avoid these interferences, the mass spectrum is taken for all the points, and not only at the maximum. A strong variation could indicate a coelution.

To identify the peaks in the samples from artworks minimizing the possibility of error, the mass spectrum of the peak in the unknown sample is compared with all the fragments of the standards detected at the same retention time. Then

- if no similarity is found, it was considered that any standard fragment is present;
- if the mass spectrum is similar to one standard fragment (the most important ions are detected at nearly the same ratio and there is not any other intense ion), it was assumed that the fragment is present;
- if the most important ions are present, but the proportion is not the same and/or other intense ions were detected, it was assumed that the searched fragment is present, but there was a coeluting interference.

The identification of the peaks combining the mass spectrum and the retention time would reduce the possibility of mistake.

Case Study 1: Conservation Material from the Theodosia Altar. A soft, rubber-like material was used as modern cement on one of the glass panels of the Theodosia altar. As an acrylic polymer was expected, due to their wide use as restoration of glass artworks,²⁵ the sample was analyzed by the proposed methodology based on Py-GC/MS at 590 °C as pyrolysis temperature. An acrylic resin, namely, a methylmethacrylate–ethylacrylate (MMA–EA) copolymer, together with a low amount of a phthalate plasticizer and BHT antioxidant could be identified (see Table 2) instead of the assumed latex, a polyisoprene. MMA–EA polymers together with additives for stabilization are common trading products of several distributors (e.g., Primal AC-34, Primal AC-634, Primal AC-234 from Rohm and Haas),¹⁴ which are used as adhesives and gluing materials.

Case Study 2: Binding Medium Analyses from a Painting by Georg Baselitz. Two powder samples from a blue and a black part of the unvarnished painting, each weighting ca. 0.1 mg, were taken with a small scalpel. First, the blue sample was pyrolyzed at 590 °C, the optimal temperature for acrylic resins (see the Optimization of the Method section). However, as ketonic markers were in fact detected, the second, black sample was analyzed at 764 °C, the temperature found adequate for Keton N. Both pyrograms, obtained without derivatization, are shown in Figure 1, and the identified fragments are listed in Table 3.

No significant amount of acrylic markers was found in both painting samples. The detection of a small amount of isobutyl

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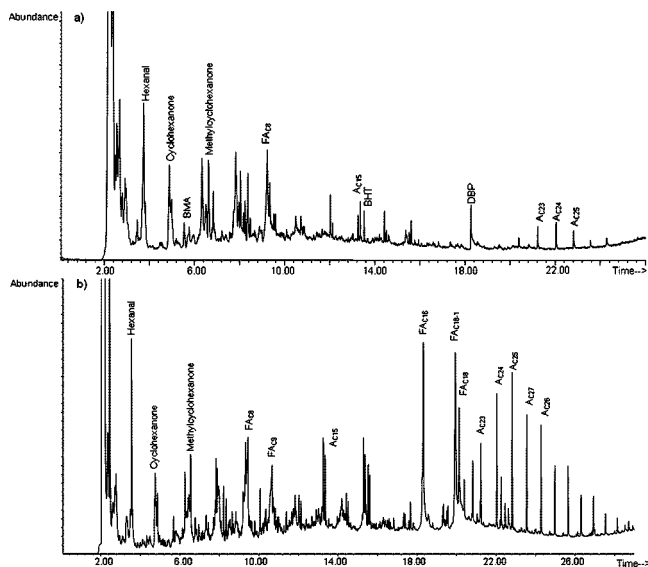


Figure 1. (a) Pyrogram (total ion current, TIC) at 590 °C without derivatization of the blue sample from the Baselitz painting. Characteristic compounds are labeled (see also Table 3). Abbreviations: BMA = butylmethacrylate, FA = fatty acids, BHT = butylated hydroxytoluene, A = alkanes, DBP = dibutylphthalate. (b) Pyrogram (TIC) at 764 °C without derivatization of the black Baselitz paint sample.

methacrylate only in the blue sample was not sufficient to propose the use of an acrylic resin as main binder.

Both pyrograms revealed the presence of cyclohexanone, 2-methylcyclohexanone, and 2-ethylcyclohexanone, all characteristic fragments of cyclohexanone resins. Cyclohexanone resins by themselves are not used as binding medium for artists' paints but are typical additives for alkyd resins¹⁴ or ingredients of paint media. Furthermore, in both samples a wide range of hydrocarbons were detected. A series of linear alkanes with even and odd carbon numbers were identified. This *n*-alkane distribution is typical for paraffin, presumably used as additive to prevent pigment settling in the tube paints.

However, in the blue and black sample also significant amounts of fatty acids were found, and therefore, complementary THM-Py-GC/MS with TMAH was carried out. After methylation the main components of the samples, fatty acids and dicarboxylic acids, could now be detected (Figure 2). Two fatty acids (as their methyl derivatives) were found between 5 and 8 min, an area with poor resolution, by their mass spectrum, including as most intense ions 74, 87, and 55 *m/z*, characteristic from those compounds. Then their specific identification was made in the basis on the retention time, obtained by the study of standards. Finally the fatty acids were characterized as caprylic acid (C₈) at 7.236 min and pelargonic acid (C₉) at 8.405 min.

No typical components of modern alkyds (e.g., phthalic acid or polyols like pentaerythritol) could be identified. However, by the detection of phthalate plasticizer (DBP) (Table 3), it can be assumed that the main binding medium of the Baselitz painting is not a pure drying oil (like linseed oil) but is rather based on an alkyd resin modified with cyclohexanone resins and paraffins.

CONCLUSIONS

The proposed method based on Py-GC/MS is fast and efficient for direct analyses of commercial synthetic resins in microsize

Table 3. Pyrolysis Results of the Dark Blue and Black Paint Sample from "Senta" by Georg Baselitz^a

fragments	retention time (min)	MS fragments (<i>m/z</i>)	MW (g/mol)
Dark Blue Paint: Py-GC/MS			
hexanal	3.603	56/44/72	100
cyclohexanone	4.900	55/98/42	98
BMA butylmethacrylate	5.942	69/87/56	142
methylcyclohexanone	6.402	55/68/112	112
FA _{C8} octanoic acid	9.235	60/73/101	144
AC ₁₅ pentadecane	13.354	57/71/85	212
BHT butylated hydroxytoluene	13.542	205/220	220
DBP dibutylphthalate	18.485	149/223/205	278
AC ₂₃ triacosane	21.226	57/71/85	324
AC ₂₄ tetracosane	22.036	57/71/85	338
AC ₂₅ pentacosane	22.816	57/71/85	352
Dark Blue Paint: THM-GC/MS			
glycerol	4.655	45/58/75/89	102
FA _{C7} heptanoic acid ME	6.145	74/87/143	144
FA _{C8} octanoic acid ME	7.236	74/87/55	158
FA _{C9} nonanoic acid ME	8.405	74/87/55	172
oxo-FA _{C8} methoxy-octanoic acid ME	9.785	45/74/124	188
DA _{C8} suberic acid DME	10.695	74/129/138	202
DA _{C9} azelaic acid DME	11.623	55/74/152	216
FA _{C16} palmitic acid ME	14.675	74/87/143	270
FA _{C18-1} oleic acid ME	15.995	55/69/83	296
FA _{C18} stearic acid ME	16.185	74/87/143	298
Black Paint: Py-GC/MS			
hexanal	3.603	56/44/72	100
cyclohexanone	4.900	55/98/42	98
methylcyclohexanone	6.402	55/68/112	112
FA _{C8} octanoic acid	9.235	60/73/101	144
FA _{C9} nonanoic acid	8.405	60/73/115	158
AC ₁₅ pentadecane	13.354	57/71/85	212
FA _{C16}	18.334	73/60/129	256
FA _{C18-1}	19.901	55/69/83/97	282
FA _{C18}	20.129	73/60/129	284
AC ₂₃ triacosane	21.226	57/71/85	324
AC ₂₄ tetracosane	22.036	57/71/85	338
AC ₂₅ pentacosane	22.816	57/71/85	352
AC ₂₆ hexacosane	23.561	57/71/85	366
AC ₂₇ heptacosane	24.281	57/71/85	380
Black Paint: THM-GC/MS			
FA _{C8} octanoic acid ME	7.236	74/87/55	158
FA _{C9} nonanoic acid ME	8.405	74/87/55	172
oxo-FA _{C8} methoxy-octanoic acid ME	9.785	45/74/124	188
DA _{C8} suberic acid DME	10.695	74/129/138	202
DA _{C9} azelaic acid DME	11.623	55/74/152	216
FA _{C16} palmitic acid ME	14.675	74/87/143	270
FA _{C18} stearic acid ME	16.185	74/87/143	298

^a The table contains the resulting fragments with Py-GC/MS and THM-GC/MS.

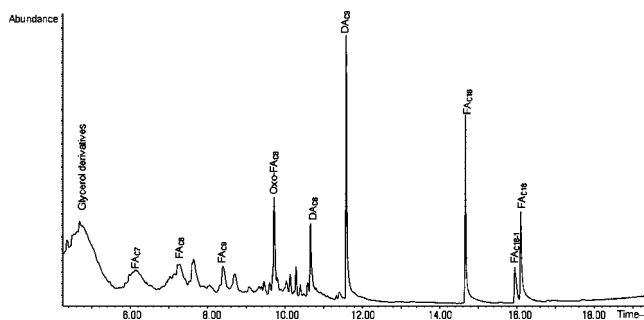


Figure 2. Pyrogram (total ion current, TIC) at 590 °C after THM-GC/MS of the blue Baselitz paint sample. All dicarboxylic acids (DA) and fatty acids (FA) are here detected as methyl esters.

samples. For most polymers identification of the specific resin group can easily be achieved by marker fragments with a structure close to the corresponding monomer(s), but further discrimination is usually limited. Due to its high sensitivity and its high separation power the technique allows one to deal with complex materials

and mixtures, which is highly interesting for analyses involving samples from art, archeology, and conservation.

Applying the developed methodology, the modern rubber-like gluing material on a medieval reverse glass altar could easily be identified as MMA–EA copolymer without further sample treatment. In contrast, the pyrograms obtained from samples of a painting by Georg Baselitz give a good example for the possible complexity of paint samples: Instead of the expected acrylic markers, the measurements hinted toward an alkyd paint with several additives such as ketone resin, paraffin, and plasticizers. In these paint samples THM-Py-GC/MS was necessary for identification of the binding media. Therefore, a combination of different techniques (Py-GC/MS and THM-Py-GC/MS) is recommended for complex paint samples.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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