Gas Chromatography-Mass Spectrometry Study of a Painting That May Contain Asphaltum Pigment

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Abstract

A painting held within the Marietta College archives was chemically analyzed to determine whether asphalt based paint, known as asphaltum, was used in its creation. Asphaltum paint was popularly used by artists for a period during the nineteenth century, but quickly fell out of use when it became associated with causing wrinkling, cracking, and other detrimental effects on paintings. Some of the damage to the brown and black areas of the painting being studied is consistent with what has been reported as asphaltum related damage, warranting investigation. This study utilized gas chromatography-mass spectrometry to analyze raw asphaltum pigment and a paint made from this pigment in an effort to gauge the effect the paint making process has on the chemistry of the sample, an search for any characteristic compounds in samples from the painting. Ultimately, instrumental limitation impeded gathering interpretable data for this study.
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Summary

Marietta College has, in its achieves, a heavily damaged and poorly cared for painting, shown in Figures 1 and 2, hereafter referred to as the Marietta College Portrait. One possible explanation for the deteriorated state of the Marietta College Portrait, as seen in Figure 3, is the presence of asphaltum paint in the brown and black areas of the painting. For a period during the nineteenth century it was highly popular among artists to use asphalt as a pigment to prepare a brownish-black paint known as asphaltum, but popular artistic opinion eventually turned against asphaltum, and it was blamed for extensive age-related damage to the paintings in which it was used.

Figure 1. Front of The Marietta College Portrait
**Figure 2.** Damage to The Marietta College Portrait, as seen from the front

**Figure 3.** Wrinkling and cracking in a brownish black paint area of The Marietta College Portrait
Previous research has been conducted in analyzing characteristic marker and biomarker compounds in raw asphalt samples, but research concerning the identification and characterization of marker and biomarker compounds in asphaltum paint remains scarce. However, what limited research has been performed in this area of study indicates that a limited range of marker and biomarker compounds can survive the paint making process, suggesting that it may be possible to chemically identify the presence of asphaltum paint.

The proposed research would work to analytically identify asphaltum paint by characterizing the marker and biomarker compounds in raw asphaltum pigment, determining which of these compounds can survive the process of turning the pigment into paint, then investigating as to whether these compounds are present in the brownish-black areas of the Marietta College Portrait.

**Introduction**

To better understand both the role that asphaltum and asphalt-based pigments play in the deterioration of paint, and the ways in which the presence of these pigments can be chemically detected, it is necessary to consider several key areas; the actual use of asphalt as an artistic material, the chemical nature of asphalt and asphaltum pigment, the effect the presence of asphalt has on the drying process of paint, and the chemical detection of asphalt in painting samples.

**A. The use of asphalt as an artistic material**

Asphalt has been used for protective coatings and other technical uses since prehistoric times, because of its durability and water, acid, and alkali-resistant qualities\(^1,2\). Its use as a pigment began with the growth of oil painting in the seventeenth century, during which time asphalt was extensively used for glazing, due to its rich blackish-brown color\(^1\). Because asphaltum permits the artist to apply the paint in a sketchy and free painting style, some artists
used it in the underpainting of a piece (applying one layer of asphaltum to a canvas, then painting with other pigments on layers overtop the asphaltum layer)\textsuperscript{3}. Other artists preferred to use it for glazing, shading, and conveying shadows in flesh tones\textsuperscript{4}. To recreate the tinted, aged look of the paintings of the old masters, some artists would add a brown pigment, in some cases asphaltum, to the varnish layer, although this proved to be a near fatal choice for the durability of the painting, as witnessed in “Duncan Gray” by Sir David Wilkie, seen in Figure 4, which quickly and extensively cracked, requiring extensive crack-filling and in some areas complete re-painting (nonetheless, cracks reappeared after the restoration)\textsuperscript{4}.

\textbf{Figure 4.} Duncan Gray, 1819, by Sir David Wilkie. Heavy cracking, especially in upper right hand corner, attributed to asphaltum\textsuperscript{5}. 
Surprisingly, liquid asphaltum was sometimes mixed with other paints to assist in the drying process\textsuperscript{4}. Due to asphaltum’s poor drying ability, artists would mix in large quantities of driers; eventually, this mixture of asphaltum and drier began to be used as a drier in its own right\textsuperscript{4}.

Broadly, asphalt is classed as a variety of bitumen, a group term for long chain hydrocarbons (22 to 50 carbon atoms present, according to Eastaugh), and can fall into two broad categories of natural asphalts or artificial asphalts, and artists encountered both as the raw material for pigment\textsuperscript{6}. Asphalts can be found in naturally occurring sedimentary rock formations and as an artificial by-product of the petroleum and coal industries. Asphalt from the distillation of petroleum products first became available in 1860, and the first mention of asphaltum coming from a coal-tar derivative came in 1841 from George Field’s \textit{New Edition Chromatography: or, A Treatise on Colours and Pigments, and of their Powers in Painting}\textsuperscript{4}. In his 1901 \textit{The Chemistry of Paint and Pigments}, 3\textsuperscript{rd} Ed., Sir Arthur Church notes that the coal-tar derivative based asphaltum is exceptionally bad for painting, even by general asphaltum standards, because it is particularly attractive to artists an account of the ease with which it can be turned into a paint and it is particularly prone to staining and bleeding into other layers of paint\textsuperscript{4}. Before this, artificial asphalt was obtained as a by-product from the production of coal-tar and lamp black, although the naturally occurring asphalt was preferred by artists. The best asphalt for pigment manufacturing came from the Dead Sea, known as \textit{lacus asphaltites}, and floated on the surface of the water and could be easily collected from the shoreline, and due to its semi-solid nature was more transportable\textsuperscript{6,7}. The conclusion that the Dead Sea was a source of asphalt for artistic uses agrees with the long history of blocks of Dead Sea asphalt being traded throughout Europe, which dates at least to 50 A.D. from records by Diodorus of Sicily, although recent archeological evidence indicates that other locations, such as the Gulf of Suez at Gebel Zeit or Abu Durba,
may have also been utilized as a general source of natural asphalt. However, the specific definition of what constitutes asphalt or asphaltum is rather blurry, especially when considering 19th century artists’ handbook. In regards to painting, asphaltum could refer to bitumen, true natural asphalts, and rock asphalts.

It is readily apparent why asphaltum fell out of use as an artist’s material. Mayer mentions that as soon as the oil film begins to dry, surface defects are encountered, especially when it is mixed with linseed oil. These defects eventually result in wrinkling and cracking, and these problems are exacerbated when the asphalt is mixed with another pigment. For example, Van Dyke Brown is composed of clay, iron oxide, decomposed vegetation, and asphalt, and it is one of the worst-drying pigments to be used in oil. Carlyle notes that the earliest reference to asphaltum being the cause of cracking in paint, rather than any other component or practice the artist may have employed, can be found in 1866, where in A Century of Painters of the English School; with Critical Notices of Their Works, and an Account of the Progress of Art in England, (Vol I 137), Richard and Samuel Redgrave postulated that the deterioration of asphaltum paint was not due to the presence of wax, a ingredient some artists included with their paints, but to the use of asphaltum. The defects of asphaltum were more detrimental when the paint was used in an improper way. For example, the use of asphaltum in underpainting would result in the upper layers of paint developing deep and extensive cracking, then the asphaltum would press through. If a coat of asphaltum was applied too heavily, it’s incredibly long drying time resulted in the paint layer literally sliding off the canvas, and exposure to sunlight resulting in the decomposition of the paint.

Another factor that contributed to the diminished use of use of asphaltum pigment is the fact that the pleasing color of asphaltum could be imitated by mixtures of stable and permanent
pigments. For example, Vibert brown, a mixture of lithanthrax and oxide of iron on an aluminum base, contributed to the disuse of asphaltum\textsuperscript{4,6}. But even before adequate substitution paints had been developed, suggestions as to suitable alternatives had been made, such as charcoal black, raw umber, and oxide of iron\textsuperscript{4}. Even before asphaltum paint began to be attributed to painting damage, other materials were introduced as being superior to asphaltum as a result of their ease with which to work and color quality. One such paint was the brown earth Cappagh brown, which was described as being a particularly well-drying paint that produced a transparent, deep, and rich color, and was first mentioned in 1840 and became commercially available from Winsor & Newton in 1846\textsuperscript{4}. Another popular pigment, produced from burning Prussian blue, was Prussian brown, which was described as having all of asphaltum’s advantages with none of its disadvantages, could be worked in both water and oil, had a transparent quality that would not diminish with time, and dried well\textsuperscript{1,4}. One artist described Prussian brown in that “it closely resembles Asphaltum in tint, as well as in transparency; so that it is preferable to it in every point of view,” demonstrating quite clearly the preference towards Prussian brown as opposed to asphaltum\textsuperscript{4}.

Another interesting note can be made in the modern usage of the term “asphaltum.” The paint company Gamblin Artist Colors offers Asphaltum in their Earth collection, describing it as a transparent brownish-black recreation of the 18\textsuperscript{th} century material that is true to the original compound’s working properties, but with better drying time and light stability\textsuperscript{9}. Clearly, this pigment is not actually made from asphalt, it is in fact a mixture of transparent Mars Red with Bone Black in linseed oil, but the naming of this pigment is in itself an over the shoulder reference to the once admired working quality of asphaltum\textsuperscript{9}. 
Although the use of asphalt as an artistic material has fallen out of favor with artists, its extensive use through the seventeenth to nineteenth centuries resulted in a wide variety of recipes and recommendations concerning its use, ranging from painting with the tar-like substance itself, to heavily adulterating it with a variety of solvents, oils, dries, or other materials. However, the multitude of recipes can be generally divided into two categories: those where the asphalt is burnt then ground into the drying oil, and those where the asphalt is dissolved in heated turpentine. These differences are furthered by the fact that “asphalt” may refer to either the natural form or the artificial form, as outlined above. The general method of preparation of asphaltum involving burning the asphalt consisted of pulverizing the asphalt, then melted in hot oil before other materials, such as oil mediums or other pigments were added. For instance, Antwerp brown was a form of asphaltum modified with lead acetate, or in which a drying oil was included rather than turpentine. Carlyle notes that J. Wilson Neil, in his 1833 article *The Art of Making Copal and Spirit Varnishes*, identifies the reason for boiling the asphalt was to make it soluble in turpentine and oil. Additionally, large amounts of oil, about 150% of the amount as asphalt used, were required in the preparation of asphaltum. Artists were somewhat aware that asphaltum greatly extended the drying time of the oil that it was mixed with, so artists added considerable drying medium to their paints to counteract the influence of the asphalt. Also, some of the recipes call for the boiling of the oil itself, a step that involves exposing the raw oil to intense sunlight or heat, often in the presence of lead salts, which leads to more extensive carbon to carbon bonding between the molecules of the mixture and results in an oil that has better drying properties, an increased refractive index, and a reduced light-scattering effect at the oil-pigment interface, which allows for a more saturate paint color.
B. The chemical nature of asphalt and asphaltum pigment

Chemically, asphalts are semi-solid emulsions of cross-linked organic groups\(^6\). In asphalts, layers of asphaltenes, or polycyclic aromatic and heterocyclic hydrocarbons, are dissolved in maltenes, of lower molecular weight aliphatic and alicyclic hydrocarbons, shown in Figure 5\(^{11,12}\). The polyaromatic centers that compose the asphaltene layer are bound together by carbon chains, which vary in length from two carbon atoms to forty, and additional asphaltene layer interactions result from \(\pi-\pi\) stacking between the aromatic systems of the layers\(^{12,13,14}\). Carbon-13 NMR (nuclear magnetic resonance) analysis shows that 40 to 50% of the carbons in asphaltene fractions are found in the polyaromatic centers, and the hydrogen to carbon ratio is approximately 1 to 1, or one hydrogen atom to one carbon atom\(^{13}\). Another common (but not universal) feature of asphalt is an abundance of sulfur compounds\(^{12}\), occurring as “hard, bright, and lustrous masses” or as viscous semi-solids\(^6\).
Figure 5. The maltene fraction (left) and the asphaltene fraction (right) of a raw asphalt sample. In a sample, the polycyclic asphaltene centers in the lower right would be bound together by varying length alkane and alkene chains, seen at the right\textsuperscript{15}.

Asphalt originates with the organic components of cell membranes of ancient plankton, algae, chlorophyll, and bacteria, along with compounds from plant sources\textsuperscript{8}. These heterocyclic compounds serve as the building blocks for asphalt. As these forms of organic debris settled at
the bottom of lakes, seas, and other bodies of water, they were exposed to higher pressures with
an absence of oxygen, resulting in the elimination of oxygenated functional groups,
disproportionation (a particular reaction involving the transfer of a hydrogen atom from one
molecule to another), and cleavage of methylene (a carbon atom bonded to two hydrogen atoms)
units from side-chains. The end result of these processes is the formation of aromatic
heterocyclic compounds, along with isoprenoid fragments, that make up the asphalt sample. Comparing the starting biological material to the ending geochemical material, it is apparent that
the compounds undergo significant forms of degradation, such as the loss of functional groups,
structural modifications and rearrangements, stereochemical changes, and aromatization, all
degradations that make charting the pathways of chemical degradation challenging

Both fractions of asphalt, the maltene and the asphaltene, each contain unique chemical
markers and biomarkers. Molecular markers and biomarkers can be thought of as the molecular
remnants of the living organisms that the asphalt is derived from, composed primarily of carbon,
hydrogen, and other elements, and show some structural differences from the biomolecules from
which they originated. Markers and biomarkers are typically encountered as individual
compounds, but can also appear as homologous series of compounds linked together. This is
important to note because both of these forms of markers and biomarkers are encountered in
asphalt. The biomarkers of the maltene fraction consist of aromatic steroids, such as sterane,
C-ring monoaromatic sterane, and hopanes, while the markers of the asphaltene fraction consist
of long-chain alkanes and alkenes, alkylbenzenes, alkylnaphtalenes, alkylanthracenes,
alkylphenanthrenes, alkylbensothiophenes, and alkyl dibenzothiophenes. The carbon
structures that are present in these markers and biomarkers are remnants of the original algae and
bacteria compounds that compose the asphalt.
The preparation of asphalt compounds into paint, as noted in section A, consisted of exposing the asphalt to extreme sheer stresses and temperatures, which would affect the chemical composition of the sample. Additionally, the paint layer will spend significant amounts of time under strongly oxidizing conditions, along with potential exposure to solvents if the painting has undergone cleaning, conservation, or restoration treatments. Specifically, heating the samples resulted in the near complete disappearance of the long-chain alkanes and alkenes, the reduced presence of hopanes and steroids, and an overall reduction of aromatic compounds, of whom alkylbenzene remains the most well-preserved.

Of particular note among markers and biomarkers are hopane and hopanoid compounds, shown in Figure 6, five membered polycyclic carbon compounds consisting of four cyclohexane rings and one cyclopentane ring. Hopanoids are one of the most abundant categories of organic compounds found in sedimentary samples, since these compounds are incorporated into the molecular structure at an early digenetic stage, and are thought to contribute to membrane integrity and stress tolerance. Previous research has indicated that hopane and hopanoids are a very resilient biomarker in the preparation of asphaltum paint. It appears that the more highly cross-linked aromatic compounds are the most likely to survive the paint-making process, although they will be present in a lower concentration that what would be found in the unadulterated asphalt samples, and the pentacyclic carbon structure of hopanoids also strengthens resistance to degradation.
C. The chemical effect of asphalt on the drying process

Although artists have used oils from a variety of sources, such as linseed, walnut, and poppyseed, chemically all these oils are tri-esters of glycerol and unsaturated fatty acids, that can be thought of as three fatty acids attached together\textsuperscript{25,26}. The principle fatty acids that are present in drying oils are palmitic acid, stearic acid, oleic acid, and linolenic acid, and the differences between the various kinds of drying oils originate from differences in the relative ratios of these acids to one another in triglycerides within the oil, and this ratio remains unchanged by the aging of the sample\textsuperscript{10,27,28}. During the drying process, the oils will undergo oxidation through hydroperoxide formation, followed by polymerization, which results in cross-linkage between the compounds, to consume any double bonds within the mixture, upon prolonged exposure to light and oxygen\textsuperscript{22,25,27}. Since unsaturated fatty acids are consumed as the oil dries, it is possible to monitor the drying of the oil be tracking the loose of the unsaturated compounds\textsuperscript{22}.

Asphalt has been noted to have antioxidant properties, meaning that it inhibits the oxidation of compounds around it. This has obvious implication when considering the drying time of oil, because asphalt theoretically would prevent the unsaturated fatty acids from undergoing oxidation, the faster and preferred method to achieve drying, and instead forces these
compounds to undergo cross-linking, a process that takes more time\textsuperscript{22}. However, even though the presence of asphalt forces the linseed oil to undergo an unfavorable mechanism to achieve drying, the end products of both unsaturated fatty acid oxidation and cross-linkage are identical, meaning that the oil in asphaltum paint just uses a different, longer mechanism to produce the same end product\textsuperscript{22}.

**Review of Literature**

With an understanding of both the role that asphaltum and asphalt-based pigments play in the deterioration of paint, and the ways in which the presence of these pigments can be chemically detected, it is now possible to consider past writings and research on this topic. This consideration can be broken down into three areas on discussion; the actual use of asphalt as an artistic material, the chemical nature, analysis, and detection of asphalt in painting samples.

**A. The use of asphalt as an artistic material**

Since the discontinuation of the use of asphaltum in the 1800’s, the majority of writings regarding historical artistic materials have simply noted asphaltum’s poor reputation and advised against its use, with only limited notes regarding how artists prepared and used the paint, as witnessed in Doerner’s 1934 *The Materials of the Artist and Their Use in Painting with Notes on the Techniques of the Old Masters*, Mayer’s 1940 *The Artist’s Handbook of Materials and Techniques*, and Eastaugh’s 2008 *Pigment Compendium: A Dictionary of Optical Microscopy of Historical Pigments*. As a results, the majority of these writings only introduce the reader to the topic of asphaltum pigment, without provide suitable information for the reader to study the pigment’s use, let alone work with the pigment themselves. An important exception to this observation is Carlyle’s 2002 *The Artist’s Assistant: Oil Painting Instruction Manuals and Handbooks in Britain 1800-1900 With Reference to Selected Eighteenth-century Sources*. This
study is an extensive review of oil painting catalogs, instruction manuals, and handbooks produced during the 19th century, and contains formulas and recipes for the creation and use of asphaltum paint. An important inclusion in Carlyle’s book is Appendix 15, which gives an overview of a number of documented recipes for the preparation of asphaltum, ranging from 1758 to 1855, noting the original literature source of the recipe, name of the recipe, a list of materials, and a brief excerpt concerning its preparation. This is valuable information when making a recreation of asphaltum paint, and will be further discussed in the Asphaltum Paint Recipe section.

While writings that deal specifically with the use of asphalt as a painting material may be limited, the study of the general historical use and trade of asphalt is valuable to archaeologists. As a result, a larger body of research exists documenting the historical aspects of asphalt. Given the significance of asphalt from the Dead Sea, some writings, such as that provided by Nissenbaum, deal specifically with Dead Sea asphalt, while others take a broader look at the historical trade of asphalt, such as Connan and Harrell. Consideration of these sources is relevant to the study of asphalt as a painting material, because the source of asphalt has been thought to play a role in determining the degree to which a paint layer degrades. Eastaugh provides information regarding the origins of the asphalt that an artist in the 1800’s would have encountered, and Carlyle references a number of historical works that demonstrate artists’ views on the relation between the quality of an asphaltum paint and the source of the asphalt (these sources are discussed in detail in the Introduction).

B. Chemical studies of asphaltum painting material

One of the earliest studies of asphaltum pigment from a chemical perspective was provided by White in his 1986 article *Brown and Black Organic Glazes, Pigments, and Paints.*
After reviewing some historical accounts of the use of asphalt in painting, White explains briefly how raw asphalt was turned into a pigment, the chemical structure of asphalt, the origins of asphalt, and the possible forms of chemical analysis that could have been used to chemically characterize asphalt. While the simultaneous discussion of the artistic use of asphalt and the chemical nature of raw asphalt provides a good background to begin the chemical study of asphaltum pigment, the article does not specifically discuss the chemical nature of the painting material itself, only the raw material used to make it.

The most comprehensive study of asphalt specifically as a paint pigment is provided by Georgiana Languri et al. in the form of a PhD thesis and a number of related journal articles. The 2004 PhD thesis *Molecular Studies of Asphalt, Mummy, and Kassel Earth Pigments: Characterization, Identification and Effects of the Drying of Traditional Oil Paint*, is an extensive study of three obsolete paint pigments, and provides numerous insights about the chemical nature of asphaltum and the effect it has on the painting process. For example, Languri determined the precise reason why the presence of asphaltum causes drying oils such as linseed oil to dry in an extended period of time; the antioxidant effect of the asphaltum prevents the fatty acids from undergoing oxidation to achieve polymerization, the chemically preferred drying process, forcing the fatty acids to undergo the longer and less preferred cross-linking to achieve polymerization. To provide experimental support for this reasoning, Languri monitored the induction time necessary for the unsaturated fatty acids to transition from the natural cis conformation to the trans conformation (the trans conformation favors the chemical interactions necessary to achieve the reactions necessary for drying), and found that linseed oil alone has an induction time of 80 hours, linseed oil mixed with the smalt pigment has an induction time of 60 hours, while the linseed oil and asphaltum mixture has an induction time of 160 hours, an
indication that the asphaltum paint dries at a distinctly slower rate than regular paints or linseed oil\textsuperscript{22}. However, it is important to note that just because asphaltum paint significantly affects the drying time of oil, this effect may not be the result of the asphalt compounds in the paint itself. In the same study, Languri notes that factors such as the method of paint preparation and the presence of other poorly drying compounds may play a more significant role in the observed poor-quality drying\textsuperscript{22}.

Languri’s PhD thesis also provides and extensive analysis on how the presence of markers and biomarkers characteristic of asphalt are affected by the process of turning the raw material into paint, but also on how their presence is affected by other factors such as the drying of the oil. A detailed description of the effect that paint preparation has on the markers and biomarkers (particularly hopanes and hopanoids) present in asphalt is given in the Introduction.

An important topic to consider is the effect that drying has on the presence of asphalt markers and biomarkers, since modern recreations of asphaltum paint will not be able to dry, even under accelerated conditions, to the degree that would replicate a finished painting. In the PhD research performed by Languri, known layers of asphaltum paint were analyzed by pyrolysis GC-MS, allowed to dry for approximately four months under accelerated condition, and then were analyzed again through pyrolysis GC-MS. It was found that the full range of markers and biomarkers that had been characterized immediately after the paint layer had been produced were present after the drying period, although the concentration ratios of the markers and biomarkers in relation to one another had been altered. For example, the amount of aliphatic compounds had reduced in comparison to the hopanoids, and the hopanoids reduced in comparison to the monoaromatic steroids\textsuperscript{22}. This indicates that, although the drying process may affect the quantitative aspects of the marker and biomarker compounds in the paint, the simple
qualitative presence of the compounds remains preserved, meaning that the degree of drying is not of major concern when considering the presence or absence of asphalt marker and biomarker compounds.

In a 2002 Journal of Analytical and Applied Pyrolysis article, Languri analyzed a 19th century asphaltum paint sample from the Hafkenscheid collection of painting materials, from the Teylers Museum in the Netherlands, and determined the biomarker compounds present are in agreement with what would be expected for asphalt, particularly asphalt samples from the Dead Sea\textsuperscript{12}. This study proves that marker and biomarker compounds can be located in a sample that is upwards of 200 years old. Additionally, solvent sensitive compounds, usually found in the maltene fraction, can be extracted upon exposure to solvents used in cleanings or other restorative treatments\textsuperscript{12}. This means that if the painting has undergone certain types of restorative treatments, the markers and biomarkers found in the maltene fraction may not be reliable indicators of the presence of asphalt. However, the compounds of the asphaltene layer are more resistive to the solvent effects, and still are a viable source for identification\textsuperscript{12}.

In another article, from 2005 in Studies in Conservation, Languri studied mummy pigment from the Hafkenscheid collection, a paint pigment made from ground Egyptian mummies. The chemical identification of asphalt was of significance in this study, because Egyptians soaked bandages in asphalt-resin mixtures during the mummification process to stop bacterial growth, meaning that if characteristic marker and biomarker compounds for asphalt were found in the pigment sample, then the sample was likely authentic mummy pigment\textsuperscript{15}. Here, the presence of biomarkers such as hopanoids and (di)benzothiophenes suggested that asphalt was present and that the sample did contain mummy, but the absence of the compound gammacerane, which is abundant in asphalt from the Dead Sea, suggested that Egyptian mummy
was not present, since Dead Sea asphalt was commonly used by the Egyptians for mummification\(^\text{15}\). Once again, this article demonstrates the identification of asphalt markers and biomarkers in a paint pigment, although the asphalt was not the primary component of the pigment.

Interestingly, unpublished studies performed by Languri indicate that the poor drying capabilities of asphaltum paint may be over stated. After preparing three samples of asphaltum paint according to 19\(^\text{th}\) century recipes, specifically William’s Antwerp brown method, Merimee’s English method, and Merimee’s Other method, without the addition of other components such as vermillion, beeswax, or megilp, the presence of saturated 18 fatty acid in oil was used as an internal standard to monitor the progression of the oil’s drying. After 12 weeks of exposure to light-aging, equivalent to 40 years of exposure under museum conditions, it was found that the recreated asphaltum paint had dried to a similar extent as acceptable oil paints\(^\text{21}\). This surprising result may indicate that the notion held for nearly a century and a half, that asphalt is inherently a poor pigment, may not be as readily acceptable as previously thought.

**C. Chemical studies of raw asphalt and related markers and biomarkers**

Although literature concerning the specific chemical study of asphalt-based painting materials may be limited, more the research regarding raw asphalt and its related markers and biomarkers is more extensive, given the prevalence of asphalt in the fields of petroleum and geochemistry, and considering this literature can provide a background when studying asphaltum pigment.

In 1984, Behar et al. reviewed the information that had been gathered from previous research regarding asphaltenes, research that used methods such as infrared spectroscopy, nuclear magnetic resonance, and x-ray spectroscopy, and applied pyrolysis gas chromatography
to the study of asphaltenes. The information reviewed in and provided by this study supports the asphaltene structure described in the Introduction, of a series of polyaromatic centers bound together by alkane and alkene carbon chains of varying length\textsuperscript{13}.

Research has also been conducted to explore the solubility of asphaltenes and maltenes. 2003 research by Spiecker et al. discusses the interaction that the asphaltene layers have with one another, and how this results in the asphaltene fraction’s solubility in polar and aromatic solvents, and its insolubility in organic solvents\textsuperscript{14}. On the other hand, Sharma et al. demonstrate in a 2007 article that maltenes are soluble in organic solvents\textsuperscript{11}. This information regarding the solubility of asphaltenes is of particular note to this study given the significance of solvent extractions in separating the fractions from one another, and is further explained in the experimental section.

An overview of the field of petroleum geochemistry was produced in 2002 by Hunt et al., and recounts the development of instrumental methods such as GC-MS and pyrolysis GC-MS, and there application to geochemical samples\textsuperscript{19}. Also, Hunt describe the development of biomarker identification in the field of geochemistry, which utilized the molecular remains of living organisms that had been incorporated into sedimentary samples, as a means of analyzing and identifying geochemical compounds\textsuperscript{19}. Hunt’s review provides a good introduction to both GC-MS techniques and biomarker identification, both important areas of consideration in the investigation of asphaltum pigment.

An additional factor that can be noted in regards to the resilience of hydrocarbons is the effect of aging. In a study performed by Shiea evaluating the effect of aging on asphalt pavement mixes, it was found that as the sample ages, the size of the most prevalent hydrocarbons decreases; specifically, at two years a prevalence of C16 to C20 is observed by
FTIR analysis, and after 5 years a prevalence of C14 to C18 is observed by FTIR analysis. Although this study was performed on asphalt compounds in pavement as opposed to a prepared paint sample, it still suggests that in the case of an asphaltum paint, which could date from the 1800’s given the time frame when asphaltum use was at its highest, aging may have an impact on what hydrocarbon compounds remain present in the sample.

Languri’s research notes that hopanes and hopanoid based compounds can be identified in asphaltum paint layers, so a consideration of the literature regarding these compounds is warranted. Research conducted by Damste et al. in 2004 and later Welander et al. in 2010 describes the role that hopanes and hopanoids play in membrane strength and integrity for bacteria, and how after the organism’s death they can become degraded and are incorporated into sedimentary compounds. Further research into the incorporation of hopanoids into geochemical compound was published by Farrimond et al. in 2003, wherein hopanoids were chemically released from their bound state in kerogen samples in an effort to better understand how they were bound in the samples. Finally, chemical and instrumental studies of free, polyfunctionalized, and bound hopanoids were performed by Shunthirasingham et al. in 2006 and Sessions et al. in 2013, providing information regarding the analysis and characterization of hopanoid compounds in the geochemical state. These studies provide a better understanding of the origins of hopanes and hopanoids in asphalt, suggest reasons for the resilience of these compounds throughout the paint making process, and demonstrate techniques that can be used in their isolation and identification from within a larger sample.

**Experimental Methods**

The experimental methodology used in this study can be organized into three sections: the preparation of the asphaltum paint from Kremer Asphaltum Pigment, the extraction used to
A. Asphaltum paint recipe
   a. Background

   As can be concluded from the Introduction, it is impossible to identify a single “correct” method of preparing asphaltum paint, since factors such as the type of asphalt being used, the degree to which it has been processed, and the particular needs of the artist all affect the manner in which the paint will be prepared. Making matters even more difficult is that almost all artist’s manuals or handbooks from the mid to late 1800s to today simply note asphaltum’s detrimental qualities and advise against its use, with little constructive information about how the paint was prepared.

   However, the overview given in Appendix 15 of Carlyle’s *The Artist’s Assistant* documents a number of recipes for the preparation of asphaltum, ranging from 1758 to 1855, noting the original literature source of the recipe, name of the recipe, a list of materials, and a brief excerpt concerning its preparation. From this source, a better understanding of how asphaltum paint was made can be gained, although this insight has serious limitations. First, a source may use antiquated terms to refer to materials that are known today by different names, and between the sources the material may be referred to by different names as well, creating difficulty when trying to interpret a recipe using modern-day terms, or comparing two of the recipes given. For example, several sources refer to “oil of turpentine,” which in itself would seem to distinguish this material from the regular turpentine we know today, but in reality oil of turpentine is regular turpentine, the “oil” referring to the process by which turpentine is distilled.
from the resin of some types of pine trees\textsuperscript{31}. Second, a number of the recipes give no specification as to the amounts of the materials used, the temperatures that they attempt to reach when heating, or the time that any particular step takes, creating ambiguity and uncertainty in recreating the recipes they describe.

Considering the hindrances described above, it is still possible to study the effect that paint preparation has on the marker compounds within asphalt by developing a method of preparing a known sample of asphaltum paint. This method can be developed by considering the general nature of each of the recipes outlined by Carlyle, the pigment properties as described by Kremer Pigments in the Asphaltum MSDS (Material Safety Data Sheet) and Product Data Sheet, and the general steps that are taken in preparing paint from powdered pigments\textsuperscript{32}. For several of the steps outlined below, notes have been made concerning literature recipes that utilize similar methods to provide historical support for the step’s inclusion. Some of the literature references are vague or even contradictory at critical points in their description, so estimations have been made below, and the need for experimentation during the paint making process has been noted. Other adulterations, such as the inclusion of other pigments, resins, or waxes, will not be included, as to allow for a more focused analysis of the affect paint preparation has on the chemical nature of the marker compounds in the pigment.

**b. Procedure**

Approximately 5 grams of the asphaltum pigment (Kremer Asphaltum Pigment) was put into a beaker, and places on a heating plate set at 140\textdegree C. Approximately 5 to 10 grams of turpentine (Sunnyside Pure Gum Spirits of Turpentine) was added incrementally to the pigment as it was heated, with care being taken to ensure that the turpentine did not begin to burn. The melting range of the asphaltum pigment as indicated by the Product Data Sheet was from 143 to
157°C and the boiling point of turpentine was from 150 to 180°C, so the range above provided a
safe temperature to ensure that the pigment melted, but that the turpentine did not begin to boil.

A number of the literature recipes noted that the asphaltum pigment was heated in an oil
until boiling before beginning to work with turpentine or a related solvent. The primary purpose
for this earlier boiling step was to make the original asphalt soluble in turpentine, a property
commonly found in natural asphalt; Field’s Asphaltum recipe and Merimee’s English and Italian
Method concerned asphalts that readily dissolve in turpentine⁴. Since Kremer’s Product Data
Sheet noted that the asphaltum pigment is soluble in aliphatic, aromatic, and chlorinated
hydrocarbons, the known pigment should be soluble in turpentine, so this earlier step was not
needed.

At the same time, drying oil was prepared. This will made the oil significantly more
malleable and easier to mix with the liquid turpentine-asphaltum mixture. Two oils were tested;
gently heated raw linseed oil (Sunnyside Pure Raw Linseed Oil) prepared on February 27 and
February 28, more vigorously heated raw linseed oil prepared on March 12, and room
temperature Linseed Stand Oil (Winsor & Newton Oil Color Linseed Stand Oil) prepared on
March 20. The step of heating the drying oil was advised in Field’s Asphaltum recipe,
Merimee’s Another Preparation, Sully’s Journal Chapman’s Method from Rome recipe,
Osborn’s Asphaltum recipe, and Osborn’s Merimee recipe⁴.

Once the pigment-turpentine mixture had reached a black, tarry consistency, the beaker
was removed from the heating plate and scrapped into a mortar, and the drying oil was
immediately poured in. The mixture was continuously worked together with a pestle until it had
reached a uniform color and consistency, a dark brownish black, that flowed with a thick, syrupy
viscosity. There was some indication that the asphaltum will begin to collect into little grains if
too much or too little drying oil is used, and this problem was noted with the sample that was prepared on March 20 using the linseed stand oil, although this was not noted in the paints prepared with the heated raw linseed oil from February 27, 28 and March 12\(^4\).

Once the mixture had cooled and reached a stable, paint-like consistency, it was applied to a Fredrix painting board that had been divided into five sections. The paints prepared on February 27, 28, and March 12 all had a very thin consistency that could be applied in a very thin coat, as described for asphaltum paint, but the paint prepared on March 20 developed clumps of pigment, characteristic of too much or too little drying oil being added, as noted above. The paints did not dry, which is to be expected considering that even under the best conditions, asphaltum takes months to dry\(^6\).

B. Extraction sample preparation

a. Background

The instrumental analysis of asphalt and other sedimentary organic mixtures can be simplified by separating the constituent compound, based on size, polarity, or another physical property, through a solvent extraction\(^{17}\). During a solvent extraction, a sample of mixed chemical composition is exposed to a solvent; the components of the mixture that are soluble in this solvent dissolve into the solvent, while the components that are insoluble remain in the solid precipitate\(^{33}\). By removing the solvent from the precipitate, by means of a pipette or a separatory funnel, it is possible to separate the components of the original mixture, and these components can be analyzed individually\(^{33}\).

The nature of asphaltene solubility can be better understood when the influence of aromaticity is taken into account. Briefly, an aromatic compound is one that has a number of electrons, negatively charged subatomic particles that move around the nucleus of an atom, that
are not bound to any single atom, but rather travel around a ring of atoms that are bonded together. To illustrate, in the aromatic benzene molecule seen in Figure 7, delocalized electrons would travel along the dotted line.

![Benzene molecule diagram](attachment:image.png)

**Figure 7.** Benzene. Delocalized electrons that travel in circles along the dotted line make this compound aromatic.\(^{34}\)

It has been observed that asphaltenes are insoluble in n-alkane solvents, but are readily soluble in aromatic or polar solvents or a similar nature (for example, asphaltenes would be insoluble in cyclohexane, but would be soluble in benzene)\(^{11,14}\). The solubility of asphaltenes appears to be dependent upon the solvent’s ability to interact with and overcome the π-π interactions between the asphaltene layers\(^{14}\). π-π interactions can occur when two aromatic molecules, such as the one in Figure 7, come face to face; the delocalized electrons spinning along the dotted lines of the two molecules interact with one another in a way that attracts the molecules as a whole together. So, in the solvent extraction outlined above, the asphaltenes are soluble in the chlorinated solvents because the polar nature of these solvents is capable of overcoming the π-π interactions bind the asphaltene layers together, but when a non-polar solvent such as heptanes is introduced, the chlorinated solvent becomes so incredible dilute that the π-π interactions once again bind the asphaltene layers together to form a solid, causing the asphaltene fraction to precipitate out of solution. In an asphalt sample the maltene and
asphaltene fractions exist in a balanced state with one another, and it is only once this balanced state is thrown off, such as by adding a solvent, that separation of the fractions occurs.\textsuperscript{11}

**b. Procedure**

In this experiment, approximately 0.02 grams to 0.03 grams of sample, whether it is the raw pigment, the paint prepared from the raw pigment, or the paint from the Marietta College Portrait (sample from the unvarnished edge was used), was placed in a test tube and diluted with 2.5 mL of a chlorinated solvent, such as dichloromethane or chloroform. Although two different types of chlorinated solvent were used for both the raw pigment and the prepared paint samples, no difference was observed in the degree to which the sample dissolved in the solvents. To ensure the sample completely dissolved, a SP Vortex Mixer was used to mix the sample. At this point, both the raw pigment and prepared paint samples dissolved completely and created a deep black solution, while the paint from the Marietta College Portrait appeared clear, with some chunks of undissolved sample floating in the solvent.

0.5 mL of the sample dissolved in a chlorinated solvent was diluted to 5 mL with hexane. The resulting solutions were clear and amber in color, with a very fine precipitate suspended throughout the solution. The samples were centrifuged for 10 to 15 minutes to separate the solid precipitate, representing the asphaltenes, from the liquid portion, the maltenes. This process was repeated until no solid formed in the solution, indicating that the asphaltenes had completely been removed from the solution.

**A. Gas chromatography-mass spectrometry analysis**

**a. Background**

Given that the asphaltum samples are characterized by organic compounds, gas chromatography-mass spectrometry (GC-MS) is well suited for this analysis.\textsuperscript{8} In the gas
chromatography (GC) step (refer to Figure 8), a liquid sample is introduced to an injector where it is rapidly heated into a vapor. This vapor moves through a column whose interior surface is coated in a medium that resists the movement of the various components of the vapor, and whose temperature is gradually increasing to facilitate continuous volatilization and movement of the compounds. Different components moving through the column at different speeds, resulting in the original mixture of compounds being separated. For example, all of the hopanes of a sample may leave the column at one time, and all of another compound within the sample may leave the column at another time. The compounds are further analyzed in the mass spectrometer (MS) step, wherein the isolated compound from the sample is bombarded with electrons, resulting in the compounds fragmenting into charged ions. These ions hit a detector, which is capable of measuring their mass and charge, and communicates this data to a computer; the identity and quantity of the ions in the sample allows the identity of original compound to be determined.
Of the previously identified types of compounds found in an asphalt sample, the maltenes can be analyzed through gas chromatography-mass spectrometry (GC-MS), and the asphaltenes can be analyzed through pyrolysis chromatography/mass spectrometry (Py-GC/MS), pyrolysis referring to the process of decomposing a compound through heat\textsuperscript{12,37}. Pyrolysis of the asphaltenes results in the thermal decomposition of the cross-linking of the fraction, producing fragments of straight chain alkanes and alkenes, and alkylated mono- and polycyclic aromatic
hydrocarbons\textsuperscript{15}. This differentiation is seen because some bonds, such as sulfur-sulfur and carbon-sulfur, are more easily decomposed, while as carbon-oxygen, are more difficult to decompose; this means that it is possible to select a temperature below which the cross-linking of the fraction can be broken, and above which the polycyclic centers are preserved\textsuperscript{23}.

b. Notes on hopanes and hopanoid analysis

Given the significance of hopanes and hopanoids to this study, specific observations can be made on the instrumental analysis of these compounds. It is possible to identify hopanes and hopanoids by both GC-MS and pyrolysis GC-MS, depending on the structural state of the compound. Hopanes and hopanoids with limited side groups can be analyzed using regular on-column GC-MS, whereas heavier molecular weight structures such as polyfunctionalized hopanoids and hopanoids that are bound to other polycyclic structures within a series of carbon chains, such as what would be observed in the asphaltene layer of an asphalt sample, are too involatile for on-column analysis\textsuperscript{16,30}. Although the compounds in the maltene layer can be analyzed with on-columns GC-MS, they are still relatively large (like most geochemical and petroleum based compounds), and need a longer, slower temperature increase, a higher final temperature, and a less retentive (typically a thinner-filmed) stationary phase\textsuperscript{38}. The problem of volatilization for the asphaltene fraction can be addressed by using pyrolysis GC-MS to thermally decompose the sample into charged fragments that can be analyzed by the GC-MS instrumentation. The use of pyrolysis methods in studying asphaltenes has been well established, being using to analyze both the alkane and alkene side chains and the polycyclic and polyaromatic nuclei\textsuperscript{13}. Common fractions for hopanoid ions are found at m/z 191, 205, 221, 243, 258, and 260\textsuperscript{23,24,30}. 
c. Notes on possible contaminants

Given the prominence of drying oil in asphaltum paint, consideration must be given as to what effect the presence of drying oil may have when testing for asphalt compounds. From a procedural perspective, there are significant differences in sample preparation for the analysis of drying oils than what has been seen in previous research for the analysis of asphalt-based compounds, which is a result of complexity in both the nature of the compounds themselves and in the composition of the drying oil as a mixture. A general method for analyzing drying oil has been developed by Colombini and colleagues, and has been referenced by other researchers, that calls for the microwave assisted acid hydrolysis of the sample, solvent extraction of the hydrolysate, or the compounds produced by the previous hydrolysis step, and additional steps involving saponification and derivatization with silyl reagents before the sample can be analyzed through GC-MS\textsuperscript{10}. The main drying oil compounds that are identified from this method of preparation and analysis are palmitic and stearic acids, and low molecular weight degradation products\textsuperscript{27}. Considering the steps necessary to isolate the components of the drying oil for GC-MS analysis, it is unlikely that the solvent extraction steps to isolate the asphalt-based compounds will have much influence on the drying oil, so the drying oil is unlikely to interfere with the analysis. It can also be noted that the steps outlined above for the analysis of drying oil are applicable to a wide range of drying oils, considering that the major distinguishing characteristic of drying oil is the ratio of palmitic acid to stearic acid, so the above inference about the impact of drying oil on the characterization of asphalt-based compounds can hold for the various kinds of drying oils, as in linseed, walnut, poppyseed, etc\textsuperscript{28}.

Another source of a competing signal could come in the form of beeswax, which was sometimes added to paints to assist in drying, so consideration should be given as to whether the
carbon structures in beeswax may have a detrimental effect on the ability to detect the characteristic compounds of asphalt. In the review written by Vandenabeele and colleagues, wax, much like drying oil, can be thought of as a fatty acid, which would be detected in a gas chromatography study. The main component of beeswax is myricyl palmitate ester (C₁₅H₃₁COOC₃₀H₆₁), along with traces of esters of fatty acids and high molecular weight alcohols, free fatty acids, and hydrocarbons. Although this would cause some difficulty in analyzing and characterizing the drying oils, which would have a similar, fatty acid based structure, the presence of beeswax would likely not be a major interfering factor in identifying the presence of the multi-cyclic compounds that make-up asphalt. This conclusion is supported by previous research, such as the search for asphaltic compounds in mummy pigments performed by Languri and Boon in 2005, which found that pyrolysis GC-MS was able to distinguish carbon chains in the range of C₂₄ to C₃₃, which were characterized as being the profile of the alkanes and alcohol units within beeswax. Due to the specification of the asphaltic compounds being characterized and the evidence of previous exclusion of beeswax compounds, it is apparent that the presence of beeswax will not pose a major hindrance to the search for asphalt.

d. Procedure

Instrumental analysis was performed on Marietta College’s GC-MS, a Hewlett Packard 5890 Series II Gas Chromatograph coupled to a Hewlett Packard 5971 Mass Selective Detector, shown in Figure 9.
Generally, an analysis run was performed with a helium carrier gas flow rate of $1/t = 30$ min$^{-1}$. Scans were performed, as opposed to selective ion monitoring, to ensure that at detectible signal during the entire analysis would be measured, rather than focusing on only a specific number of ionic mass to charge (m/z) ratios. A solvent delay of 2.00 minutes was set (given the large quantity of solvent in any given sample, it is necessary to establish a period of time earlier in the run when the solvent will move through the column in which the mass spectrometer will not collect data, to ensure that the MS is not bombarded with an overwhelming amount of signal from the solvent, which would drown out the signal of the compounds that are actually being searched for). Also, an electron multiplier voltage was set at 200 (relative) and a time window was set at 20 minutes.

The syringe used for injecting the sample was cleaned first with heptane, then the sample being injected. 1 µL was injected into the instrument, and the run was started. The syringe was again rinsed with heptane, and after the pressure gauge recorded a spike in pressure, indicating
that the heptane solvent had come off of the column, the solvent delay was overridden and the instrument began collecting data. The run was extended for 90 minutes.

A general temperature program was developed for this analysis. The initial oven temperature was set at $110^\circ C$; the initial time was set at 2.00 minutes (meaning that once a run was started, the oven was kept at $110^\circ C$); the rate of oven temperature increase was set at $3^\circ C$ per minute (meaning that every minute, the oven was raised $3^\circ C$ in temperature); the final temperature was set at $280^\circ C$ (meaning that the previously mentioned rate increase continues until the oven had reached $280^\circ C$); the final time was set at 20 minutes (meaning that once the oven reached $280^\circ C$, it was held at this temperature for 20 minutes); the injector B temperature was set at $310^\circ C$; and the detector B temperature was set at $325^\circ C$ (the temperatures for injector B and detector B were set this high to ensure that compounds were not left “sitting” at either location after the run had been completed).

Originally, the temperature rate increase was set for a long, slow increase, as described in both the research performed by Languri and other research involving the analysis of raw sedimentary asphalt samples, in order to ensure that the sample had sufficient time along a range of temperatures to achieve volatilization. However, Dr. Egolf observed that this may not be the best temperature rate increase to use for this analysis. If the temperature increase is too slow, then the sample compounds are more likely to stick to the column rather than move through the column collectively at a uniform rate$^{38}$. The resulting peaks from a run experiencing this problem would be incredibly broad. Dr. Egolf noted that if the temperature rate increase is too slow for the sample I am analyzing, the peaks would become so broad that they may overlap and appear as just a collective, noisy baseline. Upon this realization, runs were also performed with
a rate of temperature increase at 20°C per minute, with all of the other above mention instrument parameters and temperature program remaining the same.

**Results**

Table 1 describes the date, preparation notes, and final paint layer observations of the paints prepared from Kremer’s Asphaltum Pigment.

**Table 1.** Date, preparation notes, and paint observations for prepared paints.

<table>
<thead>
<tr>
<th>Date</th>
<th>Preparation Notes</th>
<th>Paint Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-Feb</td>
<td>Gently heated raw linseed oil used</td>
<td>Very thin and fluid paint layer created; color is a medium toned brownish-black</td>
</tr>
<tr>
<td>28-Feb</td>
<td>Gently heated raw linseed oil used</td>
<td>Very thin and fluid paint layer created; color is a medium toned brownish-black</td>
</tr>
<tr>
<td>12-Mar</td>
<td>More vigorously heated raw linseed oil used</td>
<td>Very thin but slightly sticky paint layer created; color is a dark brownish-black</td>
</tr>
<tr>
<td>20-Mar</td>
<td>Room temperature linseed stand oil used</td>
<td>Thick paint layer creaked, with pigment collecting into little grains; color is a dark brownish-black, with some yellowish tinting</td>
</tr>
</tbody>
</table>

Figure 10 shows the four paint prepared paint layers.
Figure 10. Paints prepared with Kremer Asphaltum Pigment. Left to Right: paint from February 27, paint from February 28, paint from March 12, and paint from March 20.

Table 2 reports the various chemical extractions that were performed.
Table 2. Date extractions performed, sample analyzed and chlorinated solvent used, specific extraction step listed.

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample/Solvent</th>
<th>Extraction Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>19-Mar</td>
<td>Raw Pigment/chloroform</td>
<td>Raw pigment initially dissolved in chloroform (319RAWC)</td>
</tr>
<tr>
<td></td>
<td>First heptane dilution</td>
<td>(319RAW3)</td>
</tr>
<tr>
<td></td>
<td>Second heptane dilution</td>
<td>(319RAW2)</td>
</tr>
<tr>
<td></td>
<td>Third heptane dilution</td>
<td>(319RAW1)</td>
</tr>
<tr>
<td></td>
<td>Raw Pigment/dichloromethane</td>
<td>Raw pigment initially dissolved in dichloromethane (328RAWD)</td>
</tr>
<tr>
<td></td>
<td>First heptane dilution</td>
<td>(328RAW3)</td>
</tr>
<tr>
<td></td>
<td>Second heptane dilution</td>
<td>(328RAW2)</td>
</tr>
<tr>
<td></td>
<td>Third heptane dilution</td>
<td>(328RAW1)</td>
</tr>
<tr>
<td>28-Mar</td>
<td>Prepared Paint/dichloromethane</td>
<td>Prepared paint initially dissolved in dichloromethane (328HEPD)</td>
</tr>
<tr>
<td></td>
<td>First heptane dilution</td>
<td>(328HEPD1)</td>
</tr>
<tr>
<td></td>
<td>Prepared Paint/chloroform</td>
<td>Prepared paint initially dissolved in chloroform (328HEPC)</td>
</tr>
<tr>
<td></td>
<td>First heptane dilution</td>
<td>(328HEPC2)</td>
</tr>
<tr>
<td></td>
<td>Second heptane dilution</td>
<td>(328HEPC1)</td>
</tr>
<tr>
<td>15-Apr</td>
<td>MCP Paint/chloroform</td>
<td>Paint sample from Marietta College Portrait initially dissolved in chloroform</td>
</tr>
<tr>
<td></td>
<td>First heptane dilution</td>
<td>(415PNT1)</td>
</tr>
</tbody>
</table>

The label for each extraction refers to the date the extraction was performed (for example, 415 was performed on April 15) and whether the sample was the raw pigment (RAW), the prepared paint (HEP), or MCP (Marietta College Portrait) paint (PNT). For the first step, where the sample is dissolved in the solvent, a D refers to dichloromethane and a C refers to chloroform. If the same kind of sample was dissolved in both dichloromethane and chloroform in the same day, the D or C is carried into the heptane dilution label. The heptane dilutions are numbered in reverse order (first is 3, second is 2, third is 3); this is due to the fact that the most dilute sample was run first on the GC-MS, followed by the next dilute, etc.

Table 3 reports the GC-MS runs performed.
Table 3. Date of run, extraction sample run, and other information about run.

<table>
<thead>
<tr>
<th>Date</th>
<th>Extraction Sample</th>
<th>Notes/Observations/Variations from above described procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-Mar</td>
<td>319RAW1</td>
<td>Extraction sample underwent a x20 dilution; solvent delay of 3 min rather than 2 min used</td>
</tr>
<tr>
<td></td>
<td>319RAW1</td>
<td>Extraction sample underwent a x2 dilution; solvent delay of 3 min rather than 2 min used</td>
</tr>
<tr>
<td>22-Mar</td>
<td>319RAW1</td>
<td>Injector B temp was 300$^\circ$C rather than 310$^\circ$C</td>
</tr>
<tr>
<td></td>
<td>319RAW2</td>
<td></td>
</tr>
<tr>
<td>15-Apr</td>
<td>415PNT1</td>
<td>About 45 minutes into the run, the MS reported a malfunction and aborted the run; the GC run was continued, as to not leave any compounds on the column</td>
</tr>
<tr>
<td>18-Apr</td>
<td>328RAW1</td>
<td>Temperature rate of 20$^\circ$/min used rather than 3$^\circ$/min</td>
</tr>
<tr>
<td></td>
<td>328RAW2</td>
<td>Temperature rate of 20$^\circ$/min used rather than 3$^\circ$/min</td>
</tr>
<tr>
<td></td>
<td>328RAW3</td>
<td>Temperature rate of 20$^\circ$/min used rather than 3$^\circ$/min</td>
</tr>
</tbody>
</table>

For all runs, chromatographic signals appeared as a noisy baseline with no clear, discernible peaks. An example of one of these chromatograms is shown in Figure 11, showing the chromatogram of 319RAW2.
Figure 11. Chromatogram of 319RAW2, demonstrating the noisy baseline and lack of clear peak character needed for characterization.

The only chromatogram that appeared any different was the one of 415PNT1. Since the run was aborted about 45 minutes in, the signal abruptly stops, and the baseline also becomes very erratic before the malfunction.

Discussion

Since the chromatograms had no clear peaks, they were of little use in gather information or drawing conclusions about what the results of this experiment indicated. However, the mass spectra for a variety of retention times were reviewed, and observations could be made from this information, even though library searches for spectra that indicated a number of ion fragments could not relate the signal to any known compound. A majority of the mass spectra peaks were seen with m/z ratios at or around 73, 147, 207, 221, 281, 295, 355, and 429. These peaks correspond the compound dimethylpolysiloxane, which is a contaminant that comes as a result of the septum or methyl silicone column coating breaking down. This is an indication that the
majority of the noisy signal that is observed in spectra such as that in Figure 11 is the result of the detection of normal components found within the GC instrumentation.

However, there still is some notable features within the mass spectra that were observed. Ions with a m/z ratio in the upper 400’s to 500’s were noted, such as that shown in Figure 12, and these larger fragments cannot be attributed to normal sources of contamination. It is possible that these signals are the result of traces of larger compounds within the sample. This would suggest that compounds are indeed present in the sample, but that they are either too heavy or in too low a concentration to adequately be distinguished from the signal from the septum and column coating degradation.

Figure 12. Mass spectrum for 319RAW2 at a retention time of 6.886 minutes, showing an ion with an m/z ratio of 520.

Future Research

In spite of the instrumentally based shortcomings of this study, there are significant opportunities to improve or advance this research in the future, both in how the known asphaltum
paint was prepared, in how the extractions were preformed, and in how the samples were analyzed instrumentally.

The asphaltum paint that was prepared for this study was prepared in a manner that offered the best generalizable results for the widest variety of paints; however, more precise results could be obtained by making a series of paints from a variety of different recipes. The recipes selected would be recipes for which more detailed instructions are provided and which are referenced as being popular during the period of asphaltum’s use, such as the ones reported by Merimee in 1839⁴. This would be an advantageous strategy for developing asphaltum paint samples for a number of reasons, because the prepared paints will be specific for a given recipe, rather than incorporate the general similarities of the various recipes, and it will allow for a consideration of how other additives, such as resins or waxes, may be detected in the sample along with the compounds characteristic of asphalt. However, preparing multiple different kinds of known paint samples will take a significant amount of time, require the purchase of a much larger number of ingredients, and demand a more developed ability of producing paints by hand.

Another way to alter this study in regards to the preparation of known paints is by preparing the asphaltum pigment itself from a raw sample of asphalt. This would not along allow for a study of how the pigment preparation affects the compounds found in the sample, but would also allow for a study of how the origin of the asphalt affects the compounds found in the sample. For instance, previous research by Languri has found that markers characteristic to Dead Sea asphalt can be found in asphaltum paint produced from it²². What would be especially interesting would be to test this with asphalt found in the Mid-Ohio Valley or the surrounding region. If compounds characteristic to local asphalt could be identified in the painting, then this would provide information regarding not only the paint used but also the potential origins of the
painting, and how it came to be in the archives of Marietta College, although this would once again be a very demanding, time and resources consuming extension of this study.

The method of extracting the maltenes from the asphaltenes could also be furthered by exploring different solvents to dissolve the original sample of paint or pigment. The choice of chlorinated solvents was made after reviewing the research performed by Languri, but this does not mean that dichloromethane and chloroform are the only solvents that can be used to dissolve the sample\textsuperscript{12,15,21,22}. Studies of the solubility of asphaltenes have show success in dissolving the sample in polar and aromatic solvents, and perhaps these could be used to achieve more through separation\textsuperscript{13,14}.

Instrumentally, great opportunities exist to further this study by using a GC-MS instrument that is more reliable in collecting data. Changes to the GC-MS analysis could improve the potential of collecting data, such as using a high performance alumina column, which in the past has proved capable of testing for hopanes and hopanoid compounds\textsuperscript{41}. Another way to improve the analysis for marker and biomarker compounds is to obtain stock reference samples from a chemical supplier. This would allow known compounds to be analyzed by the instrumentation that will also analyze the prepared and unknown paint samples, providing a better idea as to the chromatographic and spectral signal that the compounds will produce with that particular instrumentation.

Other instrumentation could be explored to further this study, such as pyrolysis GC-MS. In this instrument, the sample undergoes a pyrolysis step that thermally decomposes larger samples, ones that are not volatile at the temperatures the GC-MS reaches, into smaller fragments that can be analyzed. This would allow for the analysis of the asphaltene precipitates
that were collected during the solvent extraction steps. This is an instrument that Marietta College does not possess, and attempts to contact other institutions were unsuccessful.

Another method to analyze samples of asphalt is through direct temperature-resolved mass spectrometry (DTMS), which was also used in the research performed by Languri\textsuperscript{12}. In DTMS, the temperature of a filament probe, which is in contact with a sample, gradually increases in temperature, which gradually evaporates the components of the sample based on their molecular weight, with lighter molecular weight components evaporating before heavier molecular weight components, before a mass analyzer characterizes the isolated components\textsuperscript{12}. This means that the heptane separation of the maltenes from the asphaltenes may not be necessary, because separation can be performed by the instrument during the analysis.

While specific procedures have not been adequately research, the characteristic nature of asphalt does allow for another potential research route that does not involve GC-MS analysis. It has been noted that asphaltenes have a low hydrogen to carbon ratio, approaching one hydrogen atom for one carbon atom\textsuperscript{13}. Development of a method that determines the approximate ratio of hydrogen to carbon would allow for another means to test the paint; a low hydrogen to carbon ratio suggests asphaltenes, while significantly more hydrogen atoms to carbon atoms suggests a carbon structure besides asphaltenes are present, indicating the presence of a paint that is not asphalt based.
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Appendix A: Solvent Compound Structures

n-Heptane

http://www.chem.purdue.edu/gchelp/molecules/heptane.html

CHCl₃, Chloroform

http://0.tqn.com/d/chemistry/1/0/Q/S/1/Chloroform.jpg

CH₂Cl₂, Dichloromethane

http://www.euromarineconsortium.eu/wiki/File:Dichloromethane.PNG
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