International Journal of Mass Spectrometry 222 (2003) 85–99

www.elsevier.com/locate/ijms

Identification of colorants as used in watercolor and oil paintings by UV laser desorption mass spectrometry

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Received 10 April 2002; accepted 21 June 2002

Abstract

Laser desorption mass spectrometry (LDMS), operating in both positive and negative ion modes, is being developed for the non-destructive analysis of artists' colorants. Two commercial pigments, sold as Prussian blue, were examined. One was identified as Prussian blue and the other as copper phthalocyanine, showing the technique's ability to identify pigments. A commercial green pigment was found to be a mixture of a blue pigment (Prussian blue) and a yellow pigment (lead chromate), showing the technique's ability to analyze mixtures of pigments. A lake, carmine alum lake, was shown to contain the dye, carminic acid, and its mordant, alumina, thereby demonstrating the unique ability of the technique to identify both pigments and dyes. (Int J Mass Spectrom 222 (2003) 85–99)

Keywords: Laser desorption; Art; Pigments; Dyes

1. Introduction

During the High Renaissance period (1600s) in Venice, the political climate influenced the way in which Venetian artists portrayed religious figures. Traditionally, artists placed religious subjects such as the Madonna in the center of the painting. During this time period, artists began focusing on landscape details; however, at this time and place, artists were forbidden from choosing landscapes as the primary focus of their paintings. One may wonder why artists from this period consistently selected autumnal colors for landscape features in their paintings. The golden features are considered to be almost exaggerated—what were the artists trying to convey by this consistent choice? The answer to the question is chemical in nature, since the pigment commonly used throughout Italy to paint green trees, copper resinate, darkened and turned golden as time passed [1].

Many questions in the fields of art history and conservation are related to the artist's intentions through the colors selected, how the artist's palette changed as new materials became available, and how colorants may change over time in response to exposure to light, pollutants, and reactions with other colorants. Some of the pigments used by artists today are nearly identical to those used in the ancient world. Lead white, for example, is still popular, and is used side by side with modern synthetics [2]. Presented here are several examples which demonstrate that UV laser desorption mass spectrometry (LDMS) is a viable tool to characterize colorants used in the art world.

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PII S1387-3806(02)00947-8

Artists' paints can be a complex mixture of pigments or dyes and binding media. Dyes are organic molecules that are typically soluble in the medium, while pigments are insoluble inorganic compounds that are frequently suspended in a medium such as linseed oil.

While numerous analytical techniques have been employed by art experts and conservators to characterize pigments, including microchemical spot tests, microscopy, X-ray fluorescence (XRF) and infrared, Raman, and UV spectroscopies [3], each method has its limitations. It is rare that the analytical laboratory in a museum, if present at all, would have an extensive arsenal of tools available for the analysis of colorants. XRF is a popular tool when available and provides useful atomic information. It may be used to determine that a pigment contains metals such as Pb and Cr, however this is insufficient to identify the presence of a specific compound. Also, XRF cannot be used to detect elements lighter than F, an obvious limitation when the colorant is organic [4]. In such cases, the absence of a metal may be the most useful clue. Other methods, such as IR spectroscopy, produce a fingerprint spectrum of the pigment, which can be matched with a standard spectrum. However, the presence of binding media and other pigments can complicate interpretation. Frequently, spot tests are the most direct way to determine the presence of specific chemical species, but such methods are ultimately destructive.

Commercial UV laser time-of-flight (TOF) instruments, developed for matrix-assisted laser desorption/ionization (MALDI) MS, use flat, many-well plates as a sample introduction system. The plate is moved under a focused laser spot to analyze components in a particular well. More generally, it provides a UV LDMS system in which a planar sample can be introduced, and selected locations on the sample can be irradiated. We have found this to be a useful system for analyzing, by direct LDMS, samples ranging from ink on questioned documents [5] to watercolors on paper and oil paints on paper and canvas [6]. In such experiments, no visible damage to the target results from the pulsed laser irradiation. Furthermore, the resulting spectra provide both atomic and molecular information, characteristic of the colorant used. Here, data are presented for very different chemical systems, the blue colorant Prussian blue and the red-violet carmine lake.

Prussian blue is an inorganic pigment, introduced in the early 1700s. It is considered the first of the modern pigments. Prussian blue is a hydrated iron hexacyanoferrate complex, and the generic term "iron blue" refers to both ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3\cdot xH_2O$, and the more soluble $KFe[Fe(CN)_6]\cdot xH_2O$ (alkali ferric ferrocyanide). Ammonium and sodium salts are also used, with $x = 14–16$ [3]. The pigment became instantly popular worldwide for artists' palettes, interior painting, wallpapers, as well as for dying fabrics such as silk [7–9]. Prussian blue was a key material used for making cyanotypes, a primitive photograph and precursor to the blueprint [10,11]. It has also been incorporated into ink, cosmetics, and automotive paint formulations [3]. Artists have used Prussian blue as both a watercolor and an oil paint pigment. When the medium is water-based, alcohol is frequently added, improving the pigment's solubility and preventing flocculation. It was popular, not only as a blue colorant with extremely high "tinting strength" [12], but also as a compatible pigment to be used in mixtures with pigments such as lead chromate, to produce the chrome green pigment [3,13].

Studies of Prussian blue by Mössbauer spectroscopy [14], photoelectron spectroscopy [15], IR [16–18], neutron activation [19], Raman spectroscopy [20], and scanning electron microscopy [3] have been reported. In powder form, Prussian blue is of fine particle size, typically 0.01–0.2 μm in diameter. Dispersed Prussian blue is transparent under optical microscopy, and may appear as a blue streak. Aggregates are opaque, resembling indigo. Complications in identifying Prussian blue using optical microscopy have been discussed [21–23]. As a result of its high tinting strength, Prussian blue is frequently present in only small amounts in oil paints, where impurities, bulking agents and extenders can further confuse identification. Consequently, it is often not detectable using methods such as X-ray powder diffraction analysis [3]. Another problem in identifying Prussian blue involves confirming its presence in a mixture of pigments. For instance, ultramarine blue is an inorganic pigment physically resembling Prussian blue in a painting. Ultramarine blue does not contain Fe; however when the pigment is in a mixture of other pigments that do, a false positive identification for Prussian blue may result [3].

Another class of colorants used in art is the class known as lakes. Such dye-based paints have been used since ancient times. Medieval painters mostly used mineral pigments. Dyes were also available for dyeing fabrics. These dyes were attractive but were chemically inappropriate for paints. The solution was to chemically bind the dyes to mineral substances to make the colors insoluble. The resulting pigment was called a lake. A true lake is defined as a transparent color precipitated on a transparent base [2]. The introduction of lakes also greatly increased the range of pigment colors available. In 1809, some pigments were discovered in a shop in the excavations at Pompeii. Following the analysis of the pigments, Chaptal determined that a particular pink pigment was a madder alumina lake [24]. Madder lakes use coloring substances extracted from madder roots. If a museum laboratory is fortunate to have XFS available as a tool, they may be able to determine that an inorganic material such as alumina (Al_2O_3), tin oxide, or zinc oxide is present as the support, but they could not detect the organic dye.

Carminic acid has been used as a colorant since the 1500s. The natural organic dye is made from the dried bodies of female beetles, *Coccus cacti*, that live on cactus plants in Mexico and in Central and South America. They were brought to Europe soon after the discovery of these countries. Carminic acid and carmine lake are violet-red colorants that continue to be sold as oil paints, even though they are considered to be fugitive, meaning that extended exposure to sunlight can lead to bleaching of the lake. Carmine lakes are known to lose their color when mixed with specific pigments, as well. Consequently, the lake is frequently considered to be unsuitable for most artistic use. Unlike madder lakes, most natural organic lakes will change over time when exposed to light. In many uses, carmine lake is being replaced by the more stable alizarin lake [25].

We present here the results from the LDMS analysis of Prussian blue and carmine lake. Two different pigments, purportedly Prussian blue, were subjected to LDMS analysis and produced very different mass spectra. The colorants were identified from the spectra. Next, an inorganic green pigment was analyzed to determine its composition. Finally, carmine lake was subjected to LDMS analysis to demonstrate that LDMS can be used to characterize both the organic and inorganic structural components of the lake.

2. Experimental

The PE Biosystems Voyager DE time-of-flight mass spectrometer (Framingham, MA) is equipped with a pulsed nitrogen laser (337 nm) and a linear time-of-flight mass spectrometer. For the analysis of positive (negative) ions formed by LD, a sample plate, on which analytes are placed, is held at 20,000 V (−15,000 V), an intermediate acceleration grid in the ion source is held at 94.5% of the plate voltage, and a delay time of 150 ns was used between the laser irradiation pulse and ion acceleration. A typical gold sample plate consisting of 100-wells was used to analyze the green pigment suspended in linseed oil and copper phthalocyanine (Aldrich) dissolved in deionized water directly. PE Biosystems supplies a modified plate that can be used to analyze small polyacrylamide gels from gel electrophoresis experiments. For the analysis of the Prussian blue pigment (Niji Watercolors and Sinopia, San Francisco, CA) and carmine alum lake (Baker Chemical Co., Phillipsburg, NJ), the samples were suspended in either water or linseed oil, and applied to paper (HammerMill Fore MP). The paint-on-paper samples were secured on the modified sample plate, which allowed for a flat target. The instrument was calibrated using dyes applied to paper. Methyl violet (Aldrich) was used to calibrate in positive ion mode, while solvent black 29 (present in an ink supplied by Graphic Controls, Inc., Cherry Hill, NJ) was used in negative ion mode. Positive and negative ion spectra were generated, employing the parameters cited above. Under these conditions, the full resolution of the instrument is realized, even though ions are being formed from a non-conducting surface (paper) in some experiments, instead of a traditional conducting metal surface.

3. Results and discussion

3.1. Prussian blue

Consider the situation in which two watercolor artists have painted with a color in their palette specifically identified as Prussian blue. Fig. 1 shows the positive and negative ion laser desorption mass spectra of Prussian blue (from the supplier Sinopia, San Francisco, CA) of the first artist, directly from paper. The positive ion spectrum, Fig. 1a, is relatively uninformative, with the exception of the interesting peak at *m*/*z* 575, which will be discussed shortly. Some peaks are present, but do not appear to be related to the known structure of Prussian blue. The negative ion spectrum, Fig. 1b, contains a number of peaks that can be rationalized as evolving from an iron cyanate. Assignments were made by considering the masses of Fe (56 amu) and cyanide (CN, 26 amu), and by taking advantage of the characteristic isotopic profile of Fe which, notably, has an (A-2) isotope at *m*/*z* 54 (6.43%). Table 1 lists all of the peaks in the negative ion mass spectrum that have been identified thus far. The most intense peak is identified as $Fe(CN)_3^-$ at *m*/*z* 134.

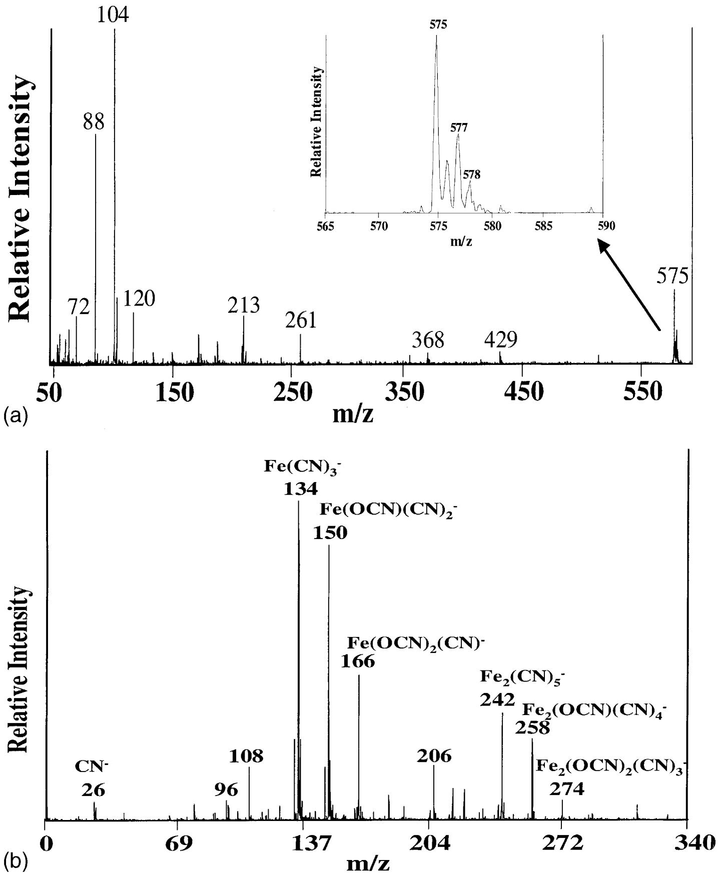

Fig. 1. The LD mass spectra of Prussian blue (Sinopia) from an aqueous solution on paper; (a) the partial positive ion mass spectrum; (b) the negative ion mass spectrum.

Table 1
A list of the identified negative ions formed by laser desorption from Prussian blue (aqueous) on paper, and the corresponding oxidation states of Fe

m/*z*	Assignment	Fe oxidation states
108	$Fe(CN)_2^-$	+1
124	$Fe(OCN)(CN)^-$	+1
134	$Fe(CN)_3^-$	+2
150	$Fe(OCN)(CN)_2^-$	+2
166	$Fe(OCN)_2(CN)^-$	+2
182	$Fe(OCN)_3^-$	+2
190	$Fe_2(CN)_3^-$	(+1, +1) or (0, +2)
206	$Fe_2(OCN)(CN)_2^-$	(+1, +1) or (0, +2)
216	$Fe_2(CN)_4^-$	(+1, +2) or (0, +3)
222	$Fe_2(OCN)_2(CN)^-$	(+1, +1) or (0, +2)
242	$Fe_2(CN)_5^-$	(+2, +2) or (+1, +3)
258	$Fe_2(OCN)(CN)_4^-$	(+2, +2) or (+1, +3)
274	$Fe_2(OCN)_2(CN)_3^-$	(+2, +2) or (+1, +3)

All of the peaks listed in Table 1 had isotopic satellites consistent with the presence of one or more iron atoms. For the majority of the ions listed in Table 1, the metals are in +1 or +2 oxidation states. For example, *m*/*z* 134 has an isotopic signature consistent with the presence of one Fe atom, which would be in a formal oxidation state of +2, complexed with three anionic ligands, to yield a singly charged anion. A number of peaks 16 mass units above $Fe_x(CN)_y^-$ peaks were observed, suggesting the incorporation of oxygen. These could contain Fe–O bonds, or O atoms could be incorporated into the ligands. Consider *m*/*z* 166, corresponding to $[Fe(CN)_3 + 2O]^-$. If both oxygen atoms were directly attached to the metal, it would be in, formally, a +8 oxidation state. Consequently, we tentatively assign it as $[Fe(OCN)_2(CN)]^-$. Also, when oxygen is present in these ions, there are always fewer O atoms present than CN groups, so direct Fe–O bonding need not be invoked.

Evaluation of the ions presented in Table 1 offers insight into the types of ions to expect, and just as importantly, into the ions which would not be found in a LD mass spectrum of similar materials. For example, it appears as though Fe prefers lower oxidation states, despite the fact that there are both Fe^{2+} and Fe^{3+} in the original crystal structure. In the negative ion mass spectrum, there are signals at *m*/*z* 108 and 134, representing the $Fe(CN)_2^-$ and $Fe(CN)_3^-$ ions, requiring Fe to be in the +1 and +2 oxidation states, respectively. However, the absence of a signal at *m*/*z* 160 representing $Fe(CN)_4^-$ is noted, which would require Fe to be in the +3 oxidation state. Furthermore, the most dominant peaks in the mass spectrum, occurring at *m*/*z* 134, 150, and 166, all represent ions in which Fe would have to be in the Fe^{2+} state. Additionally, there are peaks representing $Fe(OCN)_3^-$, but not $Fe(OCN)_4^-$, and peaks representing $Fe_2(CN)_3^-$, $Fe_2(CN)_4^-$, and $Fe_2(CN)_5^-$, but not $Fe_2(CN)_6^-$. For ions such as $Fe(OCN)_4^-$ and $Fe_2(CN)_6^-$, at least one Fe would have to be in the +3 oxidation state. In a case such as $Fe_2(CN)_4^-$, in which mixed oxidation states are possible, the presence of Fe^{3+} need not be invoked.

In these spectra, there are certainly peaks that remain unassigned. However, during the manufacturing of artist's pigments, extenders and bulking agents such as alum, $CaCO_3$, $CaSO_4$, starch, alumina, magnesia, and clay are often added to provide the pigment with specific properties or to reduce the cost of production. As a result, what might be reported to be ferric ferrocyanide may in fact be a complex mixture. In summary, the negative ion spectrum provides ample evidence that the pigment is an iron compound, and that it is specifically an iron cyanide. The molecular information is certainly superior to what would be determined by a method such as XFS, which would only indicate the presence of iron. Clearly, mass spectral peaks containing both Fe and CN are present, which could be used to differentiate Prussian blue from other blue or iron-containing pigments.

Fig. 2 shows the positive and negative ion LD mass spectra of authentic ferric ferrocyanide that was purchased from Aldrich, suspended in water and applied to HammerMill Fore MP paper. Characteristic peaks which may be indicative of the compound in some way, but do not contain iron, are again observed at *m*/*z* 72, 88 and 104 in the positive ion mass spectrum. Again, note the presence of the relatively high mass peak at *m*/*z* 575. Negative ion LDMS is clearly the method for determining the presence of Prussian blue, with the same ions observed as in Fig. 1b.

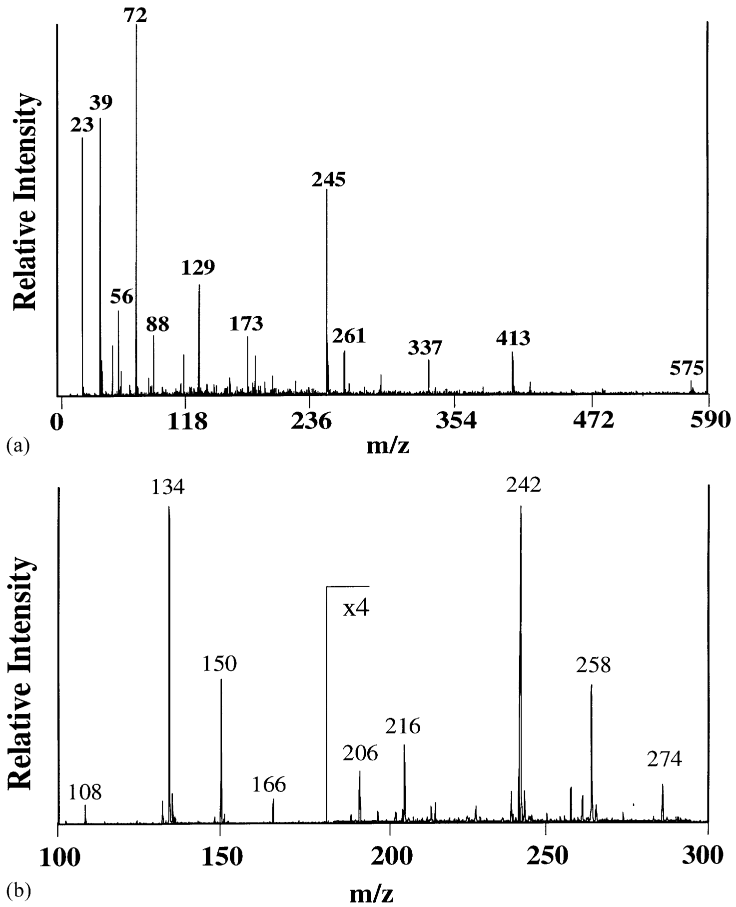

Fig. 2. The LD mass spectra of ferric ferrocyanide (Aldrich) from an aqueous solution on paper; (a) the positive ion mass spectrum; (b) the partial negative ion mass spectrum.

The second artist also employed Prussian blue, but a different brand (Niji Watercolors). The positive and negative ion spectra are shown in Fig. 3. Obviously the spectrum is not of ferric ferrocyanide. While iron blues were used since the early 1700s, until about 1970, phthalocyanine blue is now often used in their place [3]. The peak at *m/z* 575 in the positive ion spectrum represents the molecular ion, M^+, for copper phthalocyanine. Shankai et al. have previously reported the use of MALDI to analyze metal phthalocyanines, and do show that M^+ can be formed [26]. Furthermore, Conneely et al. employed MALDI MS and ESI MS to analyze sulfonated copper phthalocyanine dyes in negative ion mode [27]. The isotope distribution is consistent with the formula $C_{32}N_8H_{16}Cu$, and is dominated by the presence of a copper atom, which has abundant ^{63}Cu (100%) and ^{65}Cu (44.57%) isotopes. In our experience with organic dyes used in ballpoint pen inks, cationic dyes such as methyl violet are detected in positive ion mode and anionic dyes, such as solvent black 29, are detected in negative ion mode [5]. A response in both positive and negative ion modes indicates the presence of a neutral dye, of which copper phthalocyanine is an example. It forms an M^+ peak in positive ion mode, and an $[M–H]^-$ peak in negative ion mode (*m/z* 574).

Fig. 4 shows positive and negative ion spectra of an aqueous solution of copper phthalocyanine (Aldrich)

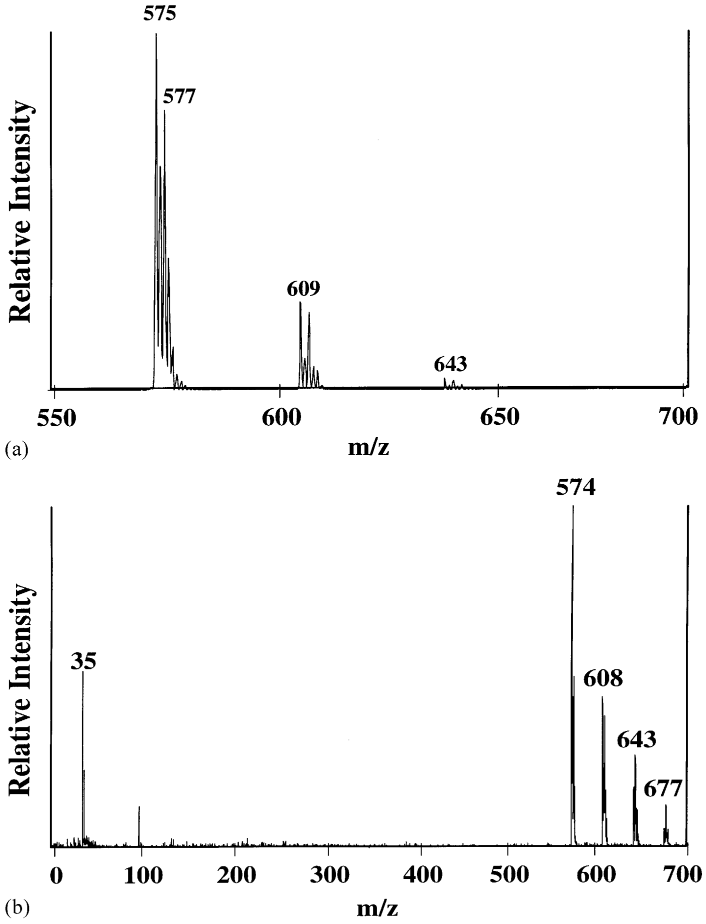

Fig. 3. The LD mass spectra of Prussian blue (Niji) from an aqueous solution on paper; (a) the partial positive ion mass spectrum; (b) the negative ion mass spectrum.

applied to paper. The spectra confirm the assignments in Fig. 3, as well as the identity of the mysterious peaks at *m*/*z* 575 in Figs. 1a and 2a. The additional higher mass peaks in Fig. 3 are noteworthy. In the positive ion spectrum, the peak at *m*/*z* 609 is 34 mass units higher than *m*/*z* 575, suggesting that a H atom has been replaced by a Cl atom. The same conclusion is reached for the next cluster. Negative ion *m*/*z* values and isotopic distributions confirm the presence of a mixture of copper phthalocyanine and copper chlorophthalocyanines. It is known that such compounds can be modified in a number of ways. Sulfate groups can be added to change the color [28]. Additionally, chlorination of the compound will vary the color (produce a greener shade), as well as increase the dye's solubility [28]. Again, if a laboratory was equipped with only the capability of atomic spectroscopy, identification of copper phthalocyanine would have been difficult. The desorption and ionization of the intact dye provides the required molecular information for distinguishing these two watercolors that were both sold under the same name, Prussian blue.

Now that the peak at *m*/*z* 575 in Figs. 1a and 2a has been positively identified as copper phthalocyanine, one must question its presence in the mass spectrum of ferric ferrocyanide. While it is plausible that artist

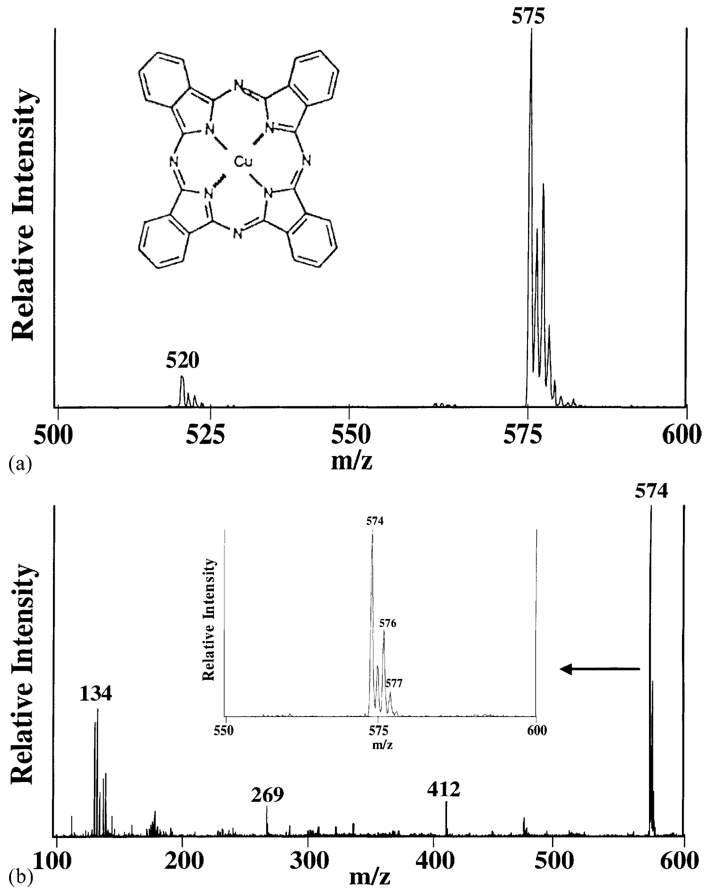

Fig. 4. The LD mass spectra of copper phthalocyanine (Aldrich) from an aqueous solution on paper; (a) the partial positive ion mass spectrum and the structure of copper phthalocyanine; (b) the partial negative ion mass spectrum.

pigment manufacturers might blend some copper phthalocyanine with ferric ferrocyanide to alter the pigment's appearance, one would not expect a chemical company to do so. Positive and negative ion mass spectra of the paper (Fig. 5a and b), reveal that the cationic peak at *m*/*z* 575 and the anion species at *m*/*z* 574 originate from the paper and not from the sample. The paper LD mass spectra were more complex than initially anticipated, however experiments have shown that all of the peaks, excluding the peaks representing copper phthalocyanine, are usually masked by the paint sample covering the paper. The *m*/*z* 574 peak in negative ion mode was masked by the sample in Figs. 1b and 2b, however the peak was observed in other spectra not presented here. The paper industry commonly employs copper phthalocyanine in the paper manufacturing process. The pigment has been used in paper mass coloration, paper surface treatment, and as an additive to paper pulp [28]. Thus, the appearance of the peaks representing copper phthalocyanine in the samples of pigments on paper, is not unexpected.

An extremely dilute aqueous solution of copper phthalocyanine was prepared, so that the solution was visually clear. The spectra (not shown) obtained from 1 μL of this sample, dried on a gold plate, revealed that the pigment was still detectable using LDMS. This is encouraging, since it demonstrates that the sensitivity

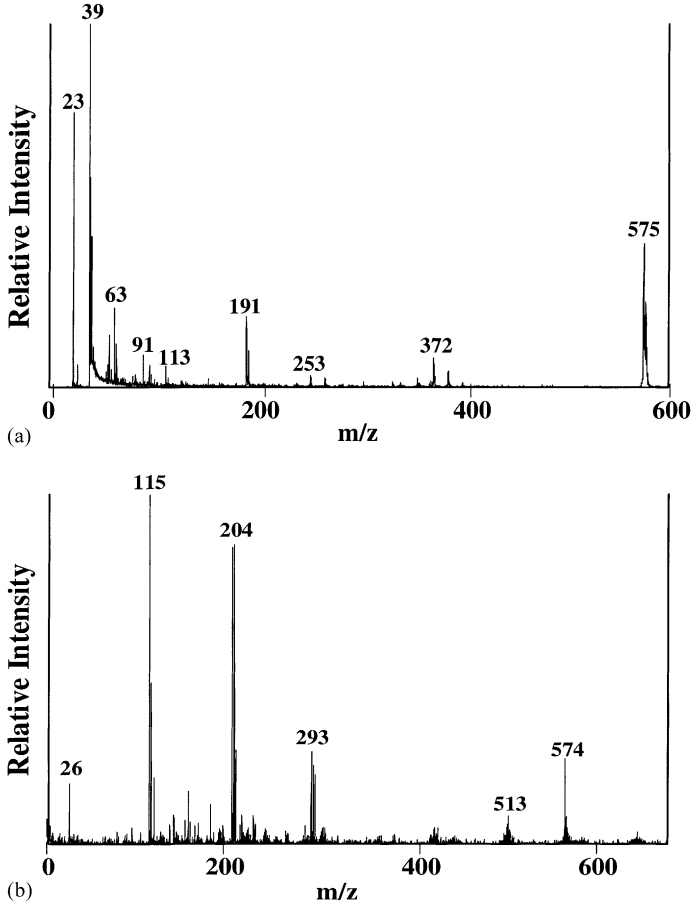

Fig. 5. The LD mass spectra of paper (HammerMill Fore MP); (a) the positive ion mass spectrum; (b) the negative ion mass spectrum.

of LDMS allows for the detection of the pigment, even when its presence is not apparent.

When questions arise concerning colorant composition, the subject is more likely an oil painting than a watercolor painting. In the next example, an oil paint was prepared using an 'old pigment' and linseed oil. The pigment was found in a box of pigments in the Michigan State University Chemistry Department archives. The box consisted of approximately 100 vials of old inorganic pigments, in a dry powder form. The box appears to be a pigment distributor's product case. The age of the pigments remains unknown, however there were clues indicating that the box is from the early 1900s.

3.2. Analysis of a green inorganic pigment, "G13"

A green pigment, designated "G13," was selected for LDMS analyses. The dark green powder was suspended in linseed oil, spotted on a gold sample plate, and allowed to dry. Very informative positive and negative ion spectra of G13 were obtained and these are shown in Fig. 6. Similar spectra were obtained from the pigment suspended in linseed oil and applied to paper. Linseed oil alone, on both paper and metal supports, does not yield ions in the UV LDMS experiment. In the negative ion spectrum (Fig. 6b), a group of familiar peaks are noted at *m*/*z* 134, 150, and 166, containing iron. The isotopic distributions are

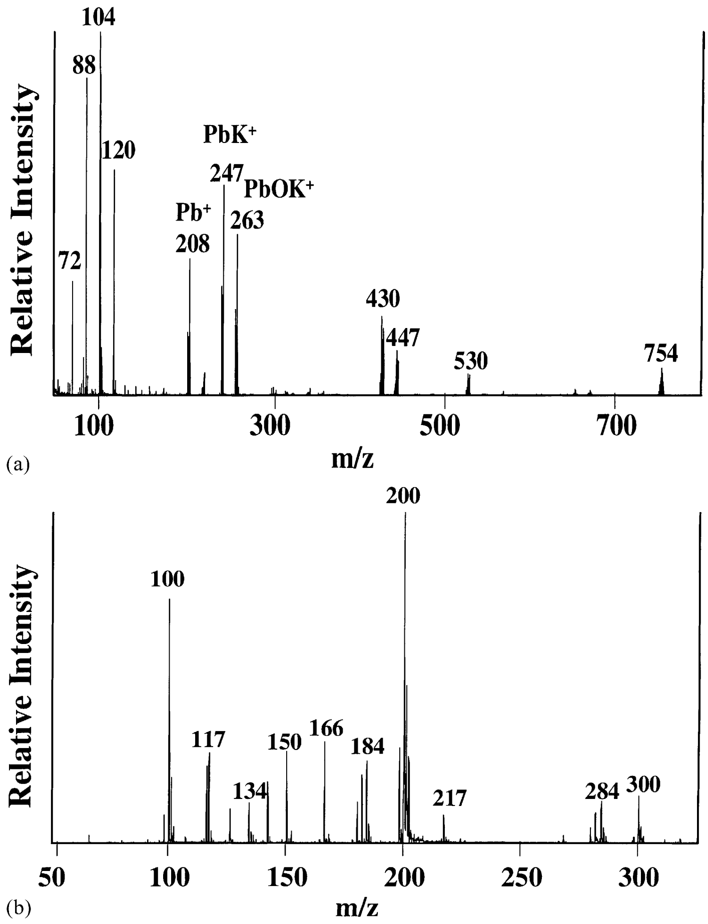

Fig. 6. The LD mass spectra of G13 in linseed oil on a gold sample plate; (a) the partial positive ion mass spectrum; (b) the partial negative ion mass spectrum.

consistent with our previous assignments for ferric ferrocyanide. Considering that ferric ferrocyanide is a blue pigment, one might presume that there is also a yellow pigment present in the mixture. Fortunately, there are numerous other peaks with characteristic isotopic patterns present in the spectra, which are related to a yellow pigment.

In the positive ion spectrum, Fig. 6a, there are numerous isotopic patterns consistent with the presence of lead. An enlarged portion of the spectrum is shown in Fig. 7a. The series begins at *m*/*z* 208, representing Pb^+ ions. The isotopic pattern compares well with the theoretical distribution of Pb isotopes (Fig. 7b). The clusters of peaks 16 and 39 mass units higher are the result of additions of an O atom and a K atom, respectively. The additions do not appreciably alter the isotopic patterns. Lead chromate is a very popular yellow pigment. Analysis of higher mass peaks reveals the presence of ions containing both lead and chromate. The peaks at *m*/*z* 530 represent $Pb_2CrO_4{}^+$ ions (Fig. 7c). The additional Pb atom, as well as the presence of a Cr atom, produces a predictable and characteristic isotopic pattern for this ion (Fig. 7d). The identification of these peaks, along with those at *m*/*z* 754 representing $Pb_3CrO_5{}^+$ ions, were confirmed by comparison with theoretical isotopic patterns.

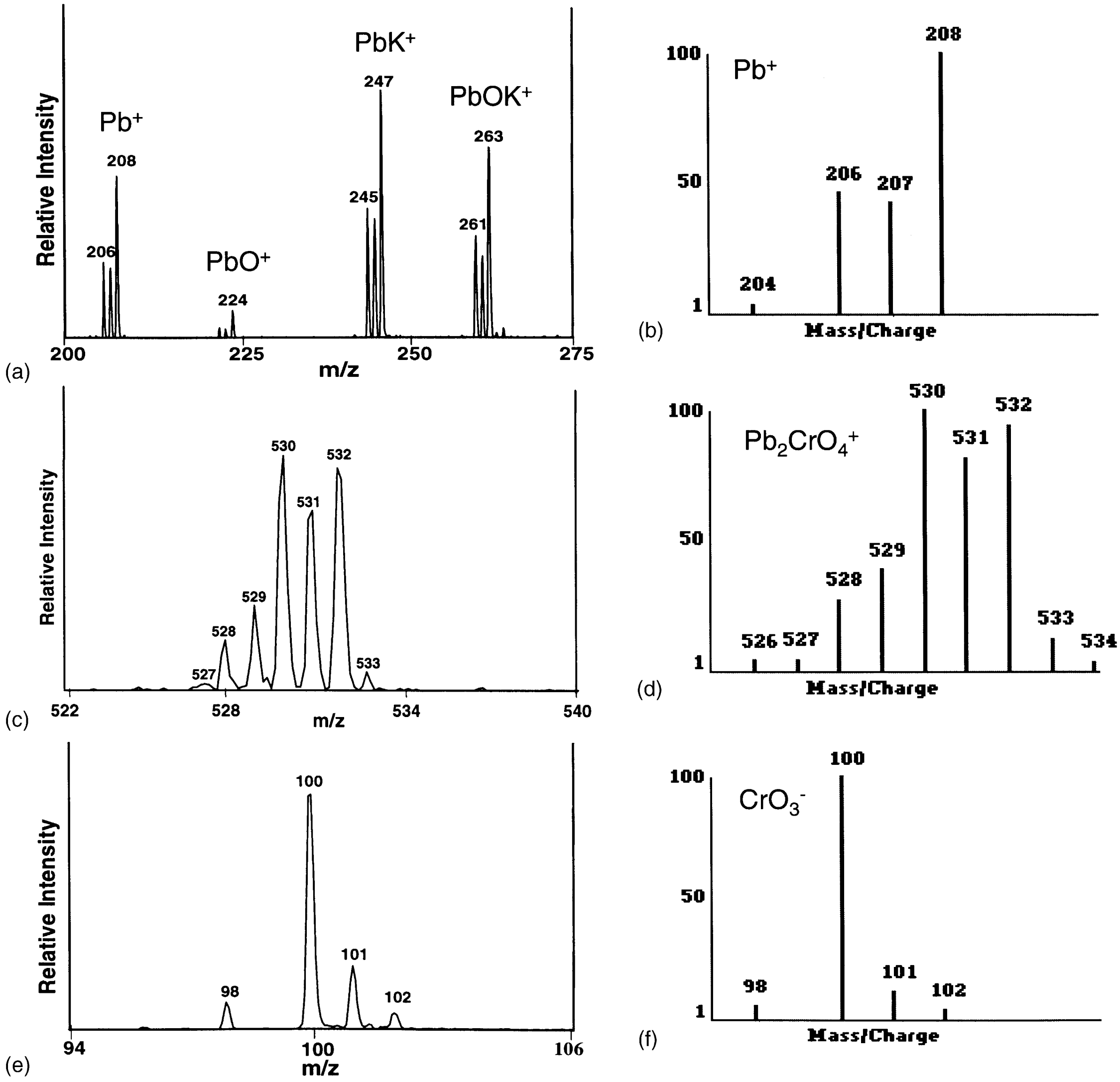

Fig. 7. Enlarged portions of the positive and negative LD mass spectra of G13 in linseed oil on a gold plate; (a, c, e) experimental data; (b, d, f) theoretical mass spectra.

This allows for a confident identification of the ions formed. The remaining peak identifications are listed in Table 2. Additionally, confirmatory ions for the presence of the chromate salt can be found mixed in with the ferric ferrocyanide negative ions (Fig. 6b). In fact, chromium oxide ions appear as the most intense peaks in the mass spectrum, with peaks at *m*/*z* 100, 200, and 300 representing CrO_3^-, $Cr_2O_6^-$, and $Cr_3O_9^-$, respectively. An enlarged portion of the mass spectrum displaying the CrO_3^- isotopic peaks is shown in Fig. 7e. The pattern compares well with the theoretical isotopic pattern in Fig. 7f. A list (author unknown) describing the contents of the vials accompanied the box, in which this pigment was found. The contents of G13 were listed as 66.7% $PbCrO_4$ and 33.3% $Fe_4[Fe_3(CN_6)]$. The mass spectra obtained

Table 2
A list of the identified positive and negative ions for G13 in linseed oil

m/z[a]	Assignment
208	Pb^+
224	PbO^+
247	PbK^+
263	$PbOK^+$
308	$PbCrO_3{}^+$
347	$PbCrO_3K^+$
363	$PbCrO_4K^+$
430	Pb_2O^+
447	$Pb_2O_2H^+$
530	$Pb_2CrO_4{}^+$
754	$Pb_3CrO_5{}^+$
100	$CrO_3{}^-$
134	$Fe(CN)_3{}^-$
150	$Fe(OCN)(CN)_2{}^-$
166	$Fe(OCN)_2(CN)^-$
182	$Fe(OCN)_3{}^-$
184	$Cr_2O_5{}^-$
200	$Cr_2O_6{}^-$
284	$Cr_3O_8{}^-$
300	$Cr_3O_9{}^-$

[a] *m/z* value of most abundant isotopic form.

were consistent with the information provided, that the pigment was a blend of two pigments.

When comparing the negative ion spectra of Prussian blue and G13, differences in a few of the isotopic peak patterns are evident. For instance, the peaks at *m/z* 134 in Fig. 6b resemble that expected for the presence of two Cr atoms. The peaks could actually be an overlap of the isotopic patterns for $Fe(CN)_3{}^-$ and Cr_2NO^-. The peaks at *m/z* 184 are also unique. Again, this may be an overlap of isotopic peaks for two ions: $Fe(OCN)_3{}^-$ (*m/z* 182) and $Cr_2O_5{}^-$ (*m/z* 184). The peak at *m/z* 180 is still unidentified, however it appears to represent another Fe-containing ion.

The analysis of the G13 pigment was very different from the analysis of Prussian blue, in that the pigment was suspended in a transparent medium (dried linseed oil), as opposed to a dry paint sample on paper. This demonstrates the versatility of LDMS to detect different types of paint samples on a variety of surfaces, and in a complex matrix. Additionally, the Prussian blue pigment was a single component, whereas G13 was a mixture of two pigments. Even though the G13 pigment is primarily composed of lead chromate, which would be expected due to the high tinting strength of Prussian blue, both components are still easily detected. This demonstrates that LDMS may be used to detect the presence of multiple pigments in a mixture, which as stated earlier, can be a limitation for other analytical methods in the analysis of a complex paint.

3.3. Carmine lake

Positive and negative ion LD mass spectra (Fig. 8) were obtained for carmine alum lake suspended in linseed oil and applied to paper. As the name implies, the inorganic substrate is alumina (Al_2O_3). In the positive ion LD mass spectrum (Fig. 8a), the major ions are indicative of the aluminum oxide support. These ions are listed in Table 3, and have the general formula $Al_xO_yH_z{}^+$. The negative ion spectrum (Fig. 8b) appears to be dominated by peaks representing an organic compound. A lake is prepared by precipitating an organic dye onto an inorganic substrate. In the case of carmine lake, the organic dye is carminic acid.

To further investigate the ions observed from the lake in linseed oil, positive and negative ion LD mass spectra were obtained of carminic acid suspended in linseed oil and applied to paper. The negative ion spectrum of carminic acid in linseed oil is shown in Fig. 9. Several peaks were identified in the negative ion spectrum derived from the organic dye. Neutral carminic acid weighs 492 Da (M). The peak at *m/z* 491 represents the pseudomolecular $[M–H]^-$ ions. Peaks at *m/z* 473 and 447 represent the neutral losses of H_2O and CO_2 from the deprotonated molecule,

Table 3
A list of the identified positive ions for carmine lake

m/z	Assignment
60	AlO_2H^+
70	Al_2O^+
74	$Ca(OH)_2{}^+$
86	$Al_2O_2{}^+$
104	$Al_2O_3H_2{}^+$
131	$Al_3O_3H_2{}^+$
236	$Al_5O_6H_5{}^+$
365	$Al_8O_9H_5{}^+$

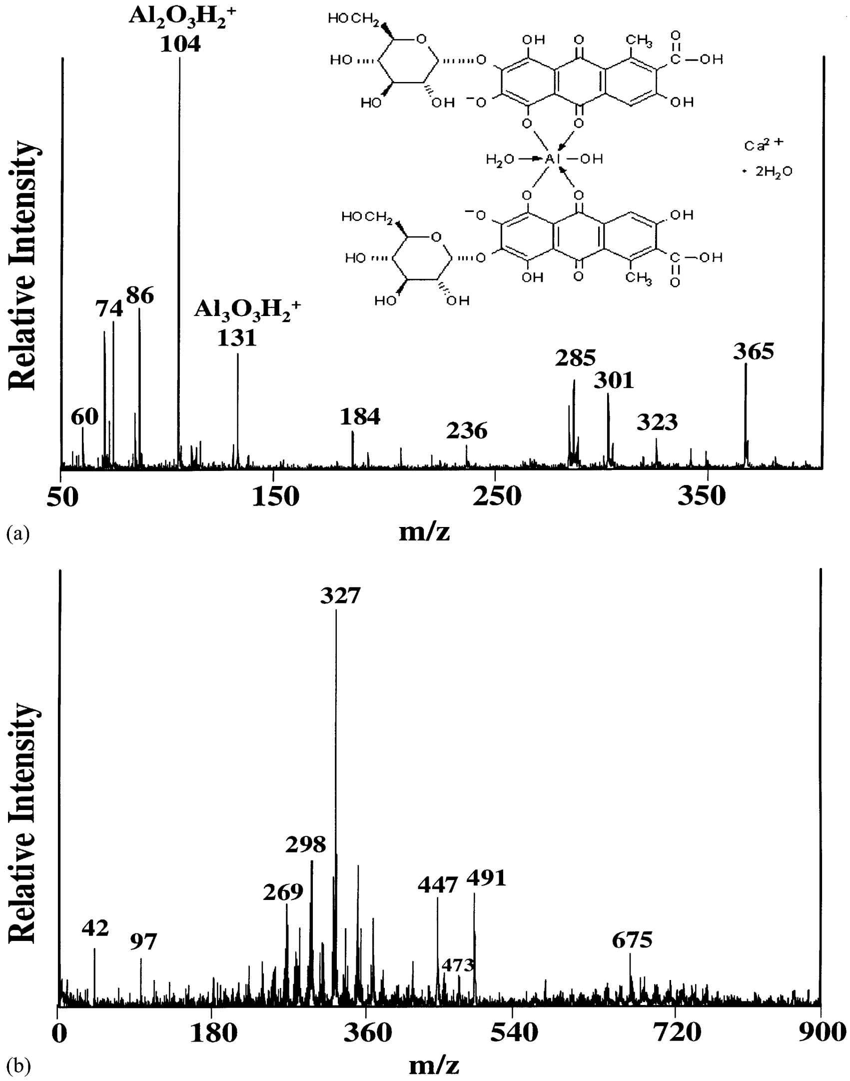

Fig. 8. The LD mass spectra of carmine alum lake in linseed oil on paper; (a) the partial positive ion mass spectrum and structure of carmine alum lake; (b) the negative ion mass spectrum.

respectively. The structure of carminic acid is composed of an anthraquinone base (A), with a glucopyranosyl sugar group (G). Designating the compound as G–A, a reaction occurs in which the sugar group is lost, accompanied by a H shift, reaction (1):

$$\text{G–A} \rightarrow (\text{G}+\text{H}) + (\text{A}-\text{H}) \qquad (1)$$

This leads to the $[(A-H)-H]^-$ ions at *m/z* 327. This could be either a fragment ion peak or the pseudo-molecular ion of an anthraquinone impurity. The same peaks are observed in the negative ion mass spectrum of carmine lake (Fig. 8b), but varying in intensities. This is not unexpected since in the lake, carminic acid is present as a dianion. Additionally, when the alumina support is taken away, all of the peaks listed in Table 3 disappear, which is evident in the positive ion mass spectrum of carminic acid in linseed on paper (not shown). Thus, the presence of both the organic and

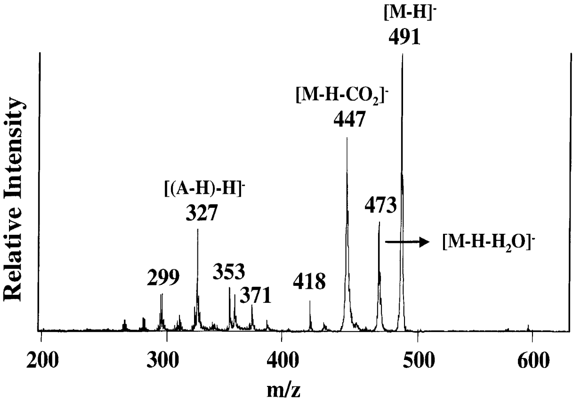

Fig. 9. The partial negative ion LD mass spectrum of carminic acid in linseed oil on paper.

inorganic components of the lake could be detected using both positive and negative ion modes. Currently, other lakes with different inorganic supports such as $CaCO_3$ are being investigated.

As a side note, when carminic acid is applied to paper from an aqueous solution, the sample instantly turns from red to black. Positive and negative ion LD mass spectra (spectra not shown) were obtained of the black sample. Few peaks are observed in the positive ion spectrum and the negative ion spectrum is dominated by C_n^- clusters ($n = 2$–13). Formation of the lake clearly stabilizes the molecule so it can be used as a colorant.

4. Conclusions

While laser desorption mass spectrometry was developed decades ago, currently available TOF instruments for MALDI MS provide an excellent platform for performing UV LDMS experiments. LDMS is a versatile tool for analyzing colorants used in art, including the organic dyes used in watercolor paints, the inorganic pigments used in oil paints, and the organic and inorganic components of lakes. This experiment also has the potential for studying chemical changes that occur when colorants age and undergo color changes, and react with other pigments. With the development of delayed-extraction techniques, such methods become much more amendable to the analysis of ions formed from non-traditional (non-conducting) surfaces. One surprising result is that inorganic pigments could be detected when suspended in a dry, polymerized linseed oil medium. Presumably, a small fraction of the pigments particles are exposed on the surface, where they can absorb the UV light and undergo desorption/ionization. While commercially available laser/TOF instruments do not currently provide the opportunity for introducing “large format samples,” such as an entire document or painting, it is certainly possible from a technical standpoint to construct such an instrument. However, for analyzing paintings, methods for sampling the paint may be preferable to any experiment in which an entire painting would be introduced into a vacuum system.

Acknowledgements

The authors would like to thank Phil Epstein and Applied Biosystems for their continued encouragement and support, and would like to acknowledge Jamie Dunn, Leah Balko, Jason Schumaker, and Dr. Jay Siegel at Michigan State University for helpful discussions concerning the use of mass spectrometry in the analysis of organic dye molecules. We are pleased to participate in the celebration of Jack Beauchamp, an artist in the field of mass spectrometry, on the occasion of his 60th birthday.

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