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Applications of laser desorption mass spectrometry for the study of synthetic organic pigments in works of art

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ABSTRACT

This paper describes the application of laser desorption mass spectrometry (LDMS) to the identification of synthetic organic pigments in microscopic samples from works of art. This work demonstrates the value of LDMS as a complementary analytical tool for use in the conservation laboratory alongside techniques such as Fourier transform infrared (FTIR) spectroscopy and energy dispersive spectroscopy (EDS). In many cases LDMS, used in both positive and negative ion modes, provides sensitive and specific identification of pigments based on exact mass, fragment ions, and isotopic patterns. The analyses are rapid, require minimal sample preparation, and are often free from significant interferences from background or additional components such as paint binding media. High-confidence identifications are achieved even for samples containing mixtures of colorants, including inorganic pigments in some cases. Examples are presented in which LDMS provided data that was valuable in addressing questions regarding materials used in paintings attributed to Jackson Pollock and in the investigation of the materials and techniques of the self-taught American artist James Castle.

1. Introduction

1.1. Modern organic pigments

In the past 50 years, the use of synthetic organic pigments in works of art has grown rapidly, supplementing traditional inorganic pigments and biologically derived organic colorants. Synthetic organic pigments of multiple, distinct chemical classes (phthalocyanines, naphthols, azos, etc.) have gained popularity in the marketplace for a variety of reasons including decreased toxicity and cost, improved light fastness and durability, and wide availability. In a recent publication, Lomax and Learner gave a historical overview of the development of modern organic pigments including dates of introduction and first availability [1]. The identification of materials in works of art, including pigments, is important for addressing issues such as proper display environment, effective, safe cleaning procedures, and questions of provenance, attribution, and artists' techniques. Thus, techniques for the analysis of modern organic pigments have continued to evolve within the museum and academic communities. To aid in their studies, conservation scientists and conservators employ a range of modern analytical tools such as micro-FTIR and Raman spectroscopy, different forms of chromatography and mass spectrometry, alone and in combination, as well as optical microscopy and wet chemical techniques. Detailed discussions of analytical techniques currently used in art conservation can be found in recent publications [1–3].

1.2. Laser desorption mass spectrometry

Laser desorption ionization mass spectrometry (LDMS, *without matrix*; matrix assisted laser desorption ionization (MALDI)-MS, *with matrix*) has been a standard analytical technique in the biosciences for many years [4]. MALDI is most commonly used for analysis of high-molecular weight (MW) compounds, such as peptides, proteins and oligonucleotides. Both MALDI and LDMS are also used effectively for the analysis of low-MW compounds [5], and several studies relating to analysis of pigments and dyes have been published illustrating the value of LDMS in the study of art materials. The doctoral thesis by Wyplosz [6] is the most complete and comprehensive reference available, covering principles and instrumentation of LDMS, analytical results for many pigment classes in a variety of media, illustrative examples and applications, and an extensive bibliography. Grim and Allison used LDMS to identify pigments of types used in watercolor and oil paintings [7] and for the study of illuminated manuscripts [8]. Soltzberg et al. [9] recently examined a series of dyes and pigments and compared two different sample preparation techniques. Looking beyond art applications to

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the forensic sciences, LDMS has been used for the identification of organic pigments in automotive coatings [10] and the analysis of various types of inks and dyes [11–16].

1.3. LDMS in conservation science

The present work investigates the application of LDMS to the analysis of artists' materials, particularly modern organic pigments, and was undertaken because of a perceived need for additional techniques to complement current analytical capabilities. Techniques commonly used for organic pigment analysis, such as FTIR and Raman spectroscopy, can be limited by matrix and other background effects and often do not address mixtures effectively. Pyrolysis gas chromatography/mass spectrometry (PyGC/MS) and direct temperature-resolved mass spectrometry (DTMS) have been used for more than a decade with some success, but do not work well with all common classes of pigments [1]. LDMS was therefore investigated as a complementary means for characterizing modern pigments with the aim of circumventing weaknesses associated with background, mixtures and poor specificity.

This paper describes LDMS used for the analysis of artists' materials in conjunction with other complementary techniques in a conservation science laboratory. Applications are presented in which LDMS provided data that was valuable in addressing questions regarding materials used in paintings attributed to Jackson Pollock, and for the investigation of the materials and techniques of the self-taught American artist James Castle.

2. Experimental

2.1. Sample preparation

Various stainless steel or gold-plated sample plates were used, but the most convenient were the Applied Biosystems (Framingham, MA) Opti-TOF® MALDI Plate System using 192-well stainless steel inserts. New inserts were cleaned ultrasonically in ethanol and blown dry with air prior to use. The inserts are relatively inexpensive, accommodate a large number of samples, and can be used to archive samples for future use with LDMS and other techniques such as FTIR and Raman spectroscopy.

Paint samples were generally analyzed directly without preparation except for being cut to size, when necessary, prior to placement onto the sample plate. Sample selection and handling were done under a 30× stereo viewer with a sharp needle or a very fine, moistened artist's brush. In most cases, as small a sample as could be seen and handled under these conditions was sufficient to produce LDMS data. None of the samples we have analyzed has been weighed, but we estimate that the smaller samples – a few tens of microns in dimension – weighed no more than a few tens of micrograms.

Pigment standards and particulate paint samples were applied directly to the plate and immediately coated and adhered to the plate using a dilute solution of Magna (Golden Artist Colors, New Berlin, NY, polybutyl methacrylate) in xylene (1:10, v/v, Magna:xylene) to minimize the possibility of sample loss or cross-contamination of adjacent samples. This procedure produced little or no background in LDMS spectra and effectively secured and isolated the samples. The Magna solution was applied from a hand held Eppendorf Gel Loading Tip (TGL-103R Ultra Micro Gel Loader) that had been filled *via* capillary action.

Soft acrylic paint samples and waxy samples were pressed in place on the sample plate and spread as thinly as possible with no overcoating. In addition, depending on the nature of the material and the goal of the analysis, solvents were applied directly onto or near the sample and allowed to flow into the sample to extract components from the bulk (on-plate extraction) for analysis. Liquids were applied from a hand held gel loading tip.

2.2. Mass spectrometry

Two instruments were used interchangeably:

- PerSeptive Biosystems Voyager-RP BioSpectrometry Workstation (laser desorption with time of flight (TOF) detection) using Grams/32 software for data analysis (Applied Biosystems). Spectra were collected in positive and/or negative ion linear mode with continuous extraction. The system used a pulsed UV laser (337 nm, 2 ns pulses) and a 1 m flight tube. Source parameters were optimized for best resolution ($m/\Delta m$), approximately 900 at 390 amu, which was sufficient for isotopic resolution of most samples.
- PerSeptive Biosystems Voyager-DE Pro BioSpectrometry Workstation (laser desorption with TOF detection) with Data Explorer™ software (Applied Biosystems) for acquisition and data processing. The system was equipped with a pulsed UV laser (337 nm, 2 ns pulses) and a 1 m flight tube with reflectron. Source parameters were optimized for best resolution, approximately 1600 at 390 amu (linear mode) and 3500 at 390 amu (reflector mode.) Delayed extraction was set at 100 ns.

With both instruments, spectra were typically obtained from 100 co-added laser shots, although if necessary this number could be increased to improve signal/noise (s/n). Positive and negative mass scales were calibrated externally using CsI ions above and below masses of analyte ions.

Data reported here were obtained by LDMS; i.e., without matrix. Many samples were heterogeneous, and ion intensities varied from location to location on the sample. Thus, when a particular ion or group of ions was observed, sampling was repeated several times at different locations to assure that the data were repeatable and consistent. Spectra were routinely collected in both positive and negative ion modes.

2.3. Data interpretation

No commercial databases are currently available for searching or comparing LDMS pigment spectra. However, the Society of Dyers and Colourists' *Color Index International* (www.colour-index.org/) contains structures and other information for a very large number of pigments and related materials. From the published structures, we tabulated exact masses and isotopic intensities of several hundred relevant pigments, and that information was used as the first step toward the identification of unknowns. Most modern organic pigments form ions in LDMS *via* gain or loss of a single proton, so identification by exact mass and isotopic intensity is usually straightforward. Some cases discussed in the applications below also rely on radical and fragments ions to validate identification. Spectra were interpreted in comparison with data from pigment standards where possible.

Since exact masses and isotopic patterns form the basis for pigment identification, the goal of LDMS measurements is to obtain near-baseline isotopic resolution, adequate s/n to assure accurate isotopic intensity ratios, and accurate mass assignments (±0.2–0.3 amu). In practice, a mass range of 25 to ~1500 amu and unit resolution to approximately 800 amu has been sufficient to analyze successfully the majority of samples encountered in our studies.

3. Results and discussion

3.1. Analysis of materials from paintings attributed to Jackson Pollock

In 2002 a group of 32 paintings was discovered in a Long Island storage facility wrapped in brown paper with an inscription suggesting that they were experimental works painted by Jackson Pollock (1912–1956). An analytical examination of three of the paintings was conducted to gain an understanding of the artist's materials choices with the unforeseen result that multiple anachronous materials were found raising doubts about the provenance and attribution of the works. A full discussion of the analysis of these paintings can be found in [17].

The application of LDMS and FTIR to material from the found paintings illustrates the importance of using complementary techniques to increase confidence in materials analysis, especially in the publicly scrutinized, high-profile project that this became. A total of seven different organic pigments were identified by LDMS, some in more than one painting. One of the most significant findings was pigment PR254 (CI 56110) (nomenclature as per the Society of Dyers and Colourists), which was found on a badly damaged painting executed on light, blue-coated cardboard (Fig. 1). PR254 is a diketopyrrolo-pyrrole (DPP) pigment (Fig. 2b) that was not commercially available until the late 1980s [18], and its presence on the painting clearly challenges the attribution to Pollock, who died in 1956.

Fig. 2 shows the positive ion LDMS spectrum (a) from a dark red/brown paint sample from the damaged painting along with the spectrum (b) from a PR254 reference standard. The sampling location of the painting is shown in Fig. 1. Each spectrum contains Na and 2Na adducts in addition to $[M+H]^+$. The inset, Fig. 2a, compares masses and isotopic patterns of the $[M+H]^+$ of paint (a) and reference standard (b) that are a very good match. In addition, the inset shows a radical cation, $[M^{\bullet+}]$, formed by a second ionization process, loss of an electron. In our experience, and consistent with previous work [6], radical ions are characteristic of several classes of pigments including anthraquinones and quinacridones in addition to DPP compounds. Its observation here further supports the identification. Analysis of a chloroform extract from the paint by

Fig. 1. Damaged painting attributed to Jackson Pollock showing the sampling location of a dark red/brown paint.

FTIR also gave a good match for PR254 (Fig. 3), corroborating the LDMS data and allowing identification of the pigment with very high confidence. The origin of the broad absorption between 1000 and 1200 cm^{-1} is unknown, but is likely due to co-extracted paint matrix components.

No other colorants were detected in the red/brown paint sample by LDMS or FTIR, and the dark shade of the paint could be due to the presence of a carbon black, which would not have been detected by either technique. We are aware of only one pigment isobaric with PR254, PY11 (CI 10325), a nitro compound, which would not be expected to form a radical cation and which would easily have been distinguished from PR254 by FTIR.

Separate from the 32 works discovered in 2002, samples were analyzed from a painting described by its owner as "in the style of Jackson Pollock" and said to have been acquired in 1949 (James Martin, Orion Analytical, personal communication). For purposes of attribution, the work had been examined by FTIR (Orion Analytical, Williamstown, MA), and spectra from a sample of red paint showed features consistent with an acrylic binder in addition to

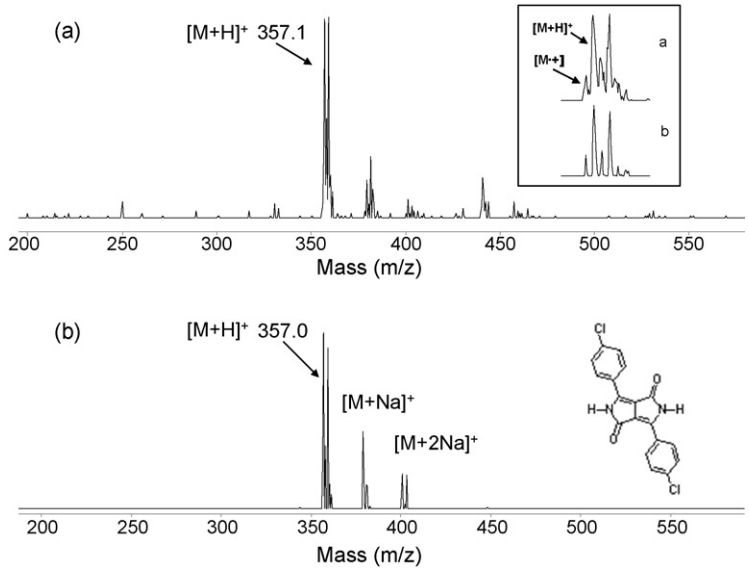

Fig. 2. (a) Positive ion LDMS spectrum from dark red/brown paint. (b) Spectrum and structure of PR254 reference standard. The inset compares the $[M+H]^+$ isotopic patterns for (a) dark red/brown paint and (b) PR254 reference standard and indicates the radical cations, $[M^{\bullet+}]$.

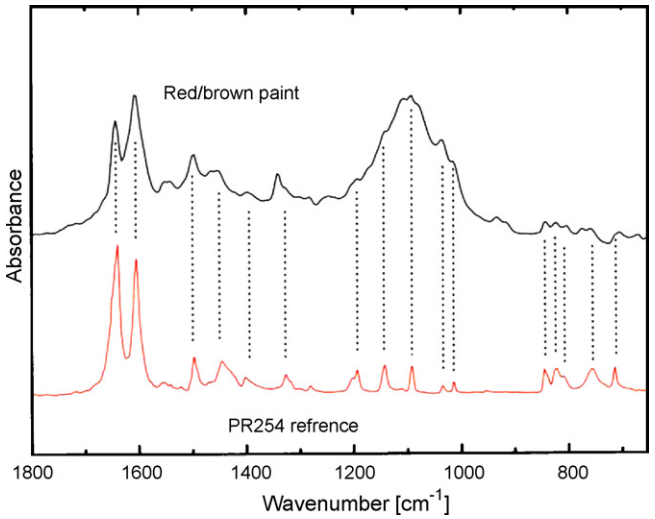

Fig. 3. FTIR spectra from a chloroform extract of the red/brown paint and PR254 reference. See text for details about broad absorption centered at 1100 cm^{-1}.

features related to organic pigments, partially obscured by the binder absorptions. FTIR analysis of solvent extracts from the paint revealed at least two colorants, one of which showed features consistent with PY74 plus additional bands that could not be attributed with confidence to any single pigment (Fig. 4).

PY74 was under development by E.I. du Pont de Nemours and Company in 1957 and commercial production began as early as 1961 [19]. Its presence, therefore, raises questions about the provenance and attribution of the work to Jackson Pollock. LDMS analysis was undertaken to supplement the FTIR data and clarify the pigment identification.

Fig. 5 shows the negative ion LDMS spectrum from the red paint and clearly indicates the presence of three pigments: PY74 (CI 11741) or PY65 (CI 11740) (*vide infra*), PY3 (CI 11710), and PR188 (CI 12467). The monoazo pigment PY3, identified by exact mass and isotopic pattern, had previously been observed by FTIR in other samples from this painting, so its observation here corroborated that identification. The inset in Fig. 5 shows the isotopic patterns of the $[M-H]^-$ for PR188 reference standard (a) and the red paint (b) that compare very well. PR188, a naphthol AS pigment, was identified confidently from the LDMS data by the molecular mass and isotopic pattern. To our knowledge, the molecular mass is unique among pigments. PR188 had not previously been identified by FTIR, but after the LDMS results were known, comparison of an FTIR reference spectrum with that of the extract showed good correlation with PR188.

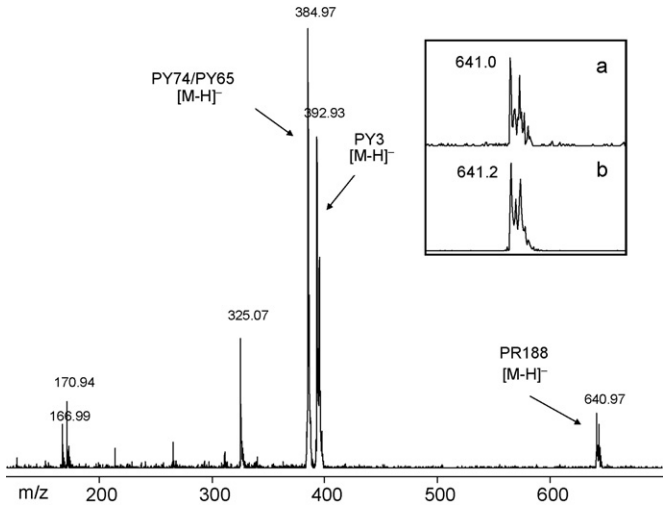

Fig. 5. Negative ion LDMS spectrum from the red paint sample. PY74 and PY65 cannot be distinguished from this data alone (*vide infra*). PY3 was identified based on exact mass and isotopic data in addition to FTIR data. PR188 was identified based on exact mass and isotopic data in addition to characteristic fragments (see Fig. 6) and FTIR data. The inset shows the $[M-H]^-$ for (a) PR188 reference standard and (b) the red paint.

Fig. 6 shows the positive ion LDMS spectrum of a chloroform extract from the red paint, in which the $[M+H]^+$ of PR188 is observed in addition to intense ions at m/z 522^+ and 123^+ derived from PR188 and less intense ions related to the other two pigments. This spectrum illustrates the complementary nature of positive and negative ion data, which often provide additional information about the sample. Here, the intense ions at m/z 522^+ and 123^+ are assigned to fragments from PR188 as indicated in the inset in Fig. 6, further corroborating the identification of this pigment. Mass and isotopic data for the two major fragments match theoretical values as well as actual values produced from a reference standard (data not shown).

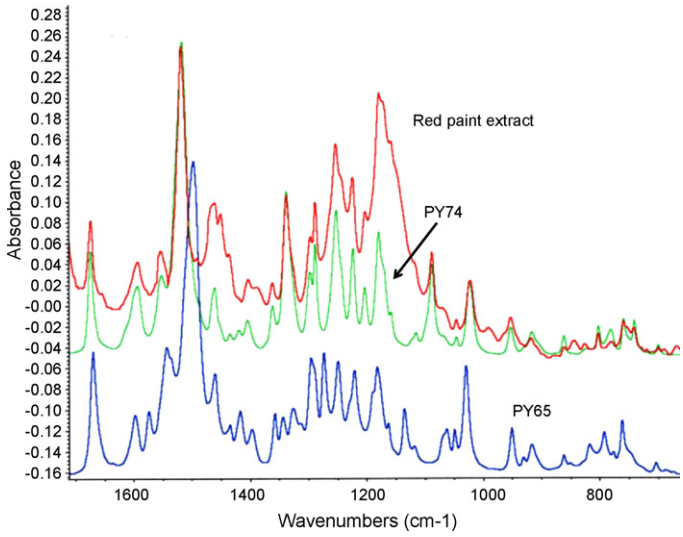

Fig. 4. FTIR spectra from the red paint extract and reference standards PY65 and PY74.

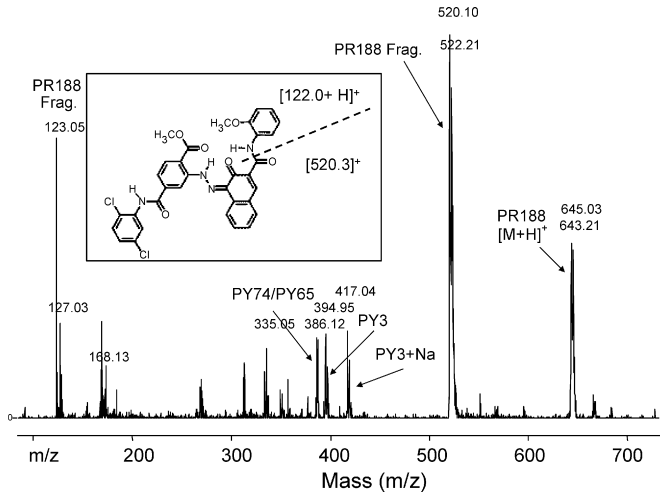

Fig. 6. Positive ion LDMS spectrum from the chloroform extract of the red paint showing fragments assigned to PR188, m/z 520.10^- and 123.05^-. Identities of fragment ions are indicated in the inset. Most of the remaining ions are accounted for by the two other pigments present.

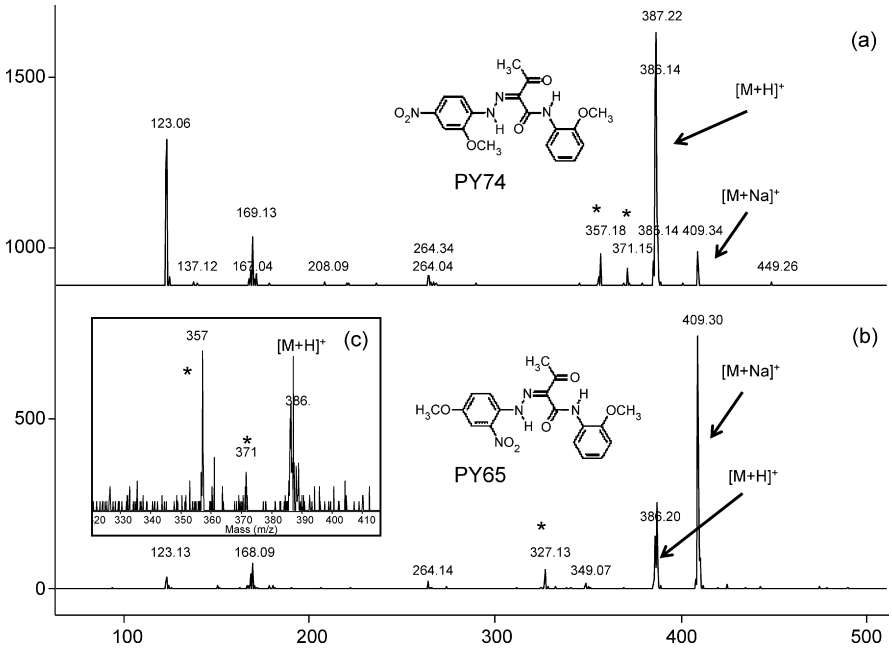

Fig. 7. Positive ion LDMS spectra from (a) reference standard PY74 and (b) reference standard PY65. Ions unique to each compound are indicated (*). The inset (c) shows a portion of the positive ion spectrum from the red paint indicating (*) ions that confirm the identification as PY74.

PR188 first appeared in the Color Index Additions & Amendments Number 23 (New Series) in April 1969, but dates pertaining to discovery, development and patent of the pigment remain the subject of study (James Martin, Orion Analytical, personal communication).

The monoazo pigments PY74 and PY65 are positional isomers, so exact mass and isotopic data alone are insufficient to provide identification. However, the positive ion spectra from standards of PY74 and PY65 (Fig. 7) show fragment ions that are characteristic of each isomer. The origin of the characteristic fragment ions in PY74 (m/z 357$^-$ and 371$^-$) can readily be assigned (data not shown), but the origin of the fragment ion in PY65 (m/z 327$^-$) is not obvious, and it may originate from a complex rearrangement. However, analyses of two different sets of standards showed the same fragments indicating that they are reliable markers for the two compounds. Inset (c) in Fig. 7 shows a portion of the positive ion LDMS spectrum from the red paint, in which the two ions characteristic of PY74 are observed, but the ion characteristic of PY65 is not. Based on this evidence, together with the FTIR data, the yellow pigment was confidently identified as PY74.

In all, three pigments were identified in these paint samples based on LDMS analysis and corroborated by FTIR data. LDMS was particularly valuable for the identification of PR188, which was not readily discernible in the FTIR spectra because of interference from absorption bands relating to the paint matrix. The LDMS and FTIR data provided a solid basis for addressing questions about the provenance of the painting, which was not likely painted before the 1960s.

3.2. The drawing materials of James Castle

James Castle (1899–1977), a self-taught artist who was deaf and did not speak, read or write, produced unique and innovative works of art throughout his life in and around Boise, Idaho. He is best known for drawings made with a medium of stove soot mixed with his own saliva, but he also made colored works using a variety of colorant sources applied to found paper or card supports such as envelopes or food packages. According to oral accounts from family members and acquaintances, his colors included dyes extracted from colored papers and more conventional artists' materials such as water-based paints and wax crayons. A scientific study of his materials was carried out in preparation for the retrospective exhibition *James Castle: Portrait of an Artist* at the Philadelphia Museum of Art (Fall, 2008) [20]. LDMS was used in the study in conjunction with other analytical techniques, including FTIR and energy dispersive spectroscopy (EDS) to gain a better understanding of Castle's diverse sources of color.

A yellow paper fiber from an untitled colored drawing by Castle, one of a series known as his "Dream house" pictures (Fig. 8) gave the LDMS spectra in Fig. 9. Castle made the drawing on the reverse of a panel from a Home Dairies Ice Cream carton, roughening the waxed card surface before applying his colorants. As with other samples described in this paper, the yellow fiber was analyzed directly with no preparation except to fix the single fiber to the sample plate with dilute Magna.

Fig. 8. James Castle untitled (Dream house) not dated. Found paper, color of unknown origin, soot. 5 1/2 × 7 3/4 in. *Courtesy*: J. Crist Gallery, Boise, Idaho, #0438.20.

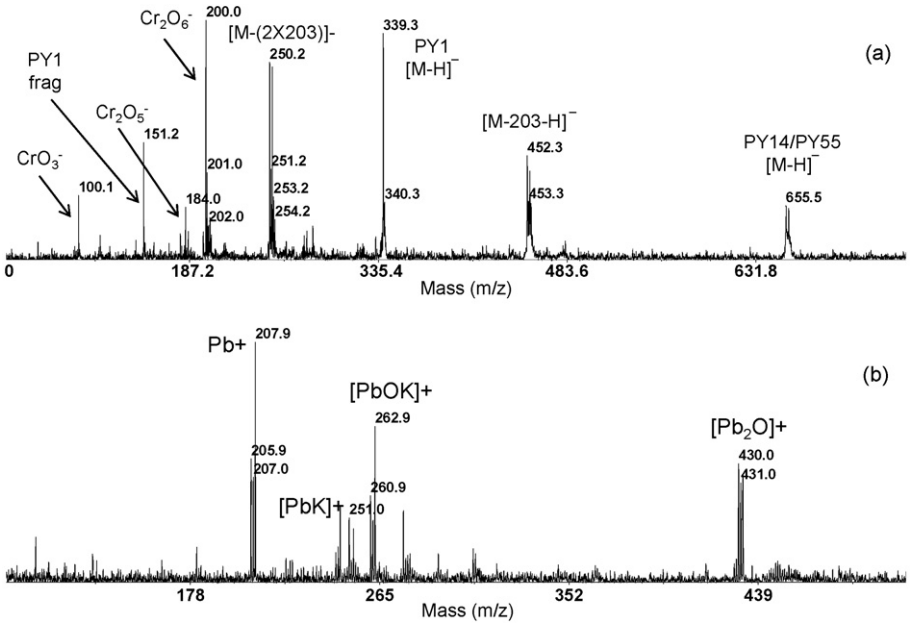

Fig. 9. (a) Negative ion LDMS spectrum from single yellow fiber from the J. Crist "Dream house" drawing by James Castle. Ions assigned to PY14 or PY55: m/z 655.5$^-$, 452.3$^-$ and 250.2$^-$; PY1: m/z 339.3$^-$ and 151.2$^-$; chromate species: m/z 100.1$^-$, 184.0$^-$ and 200.0$^-$. (b) Positive ion spectrum from single yellow fiber. Major ions are assigned to Pb-containing species as indicated.

The negative ion spectrum in Fig. 9a, in contrast to the simple spectra frequently observed with organic pigments, shows a complex pattern of peaks that can be attributed to the presence of multiple colorants. The series of negative ions, m/z 250.2$^-$, 452.3$^-$ and 655.5$^-$, identify one component as a diazo pigment, either PY14 (CI 21095) or PY55 (CI 21096). These pigments are positional isomers differing in the locations of only the methyl groups on the two terminal rings (Fig. 10), but their negative ion spectra are identical and cannot be used to distinguish between them. Reference spectra from PY14 and PY55, which are notable for both the number and intensity of fragment ions, matched the ions assigned in Fig. 9a. Examination of the structure in Fig. 10 allows assignment of the observed fragment ions: the ion at m/z 452.3$^-$ originates from scission of one azo bond producing [M−203−H]$^-$ and scission of both azo bonds produces the ion at m/z 250.2$^-$. The presence of two chlorines in the fragments, indicated by the M+2 isotopes, is consistent with these assignments.

Additional ions in Fig. 9a could be assigned to the monoazo pigment PY1 (CI 11680) (m/z 339$^-$ and the fragment at m/z 151$^-$) based on exact mass and isotopic pattern as well as comparison with the spectrum from a reference standard.

The series of anions at m/z 100$^-$, 184$^-$ and 200$^-$ in Fig. 9a is diagnostic of chromate species as has been shown by Grim and Allison [7]. This finding, in combination with the clusters of lead species observed in the positive ion LDMS spectrum in Fig. 9b (recognized as such by the characteristic lead isotopic pattern) indicates a yellow lead chromate pigment (PY34, CI 77600). The presence of lead and chromium was confirmed by EDS analysis of a separate yellow fiber from the same location. Lead species assigned in the LDMS positive ion spectrum, Fig. 9b, are consistent with those discussed by Grim and Allison [7]. Lead species dominate the spectrum, obscuring ions from the pigments observed in negative ion mode but known from reference spectra to form cations, again emphasizing the benefit of examining all samples in both positive and negative ion modes.

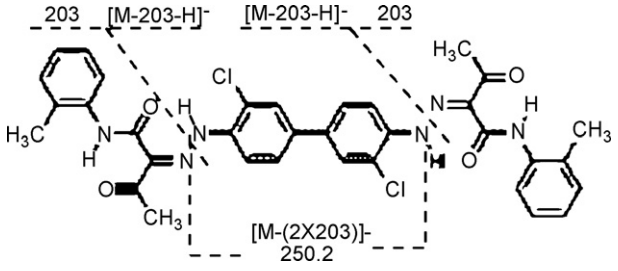

Fig. 10. Structure of PY14 indicating the origin of major fragments observed in the negative ion spectrum (Fig. 9a) from the yellow fiber. Isobaric PY55 differs only in the positions of methyl groups on the outer aromatic rings and produces identical fragment ions.

The identification in the yellow fiber of a mixture of pigments – a diazo yellow (PY14 or PY55), a monoazo yellow (PY1), and lead chromate – demonstrates the potential for LDMS to characterize complex samples containing both organic and inorganic pigments. None of the pigments was detected by FTIR analysis of samples from the same color area in the drawing, suggesting a greater sensitivity in the LDMS analysis of these colorants on fibers. However, heterogeneity in Castle's coloring material may also be a factor.

The same pigments identified in the yellow fiber were also found in materials obtained from Castle's studio (provided by the J. Crist Gallery, Boise, Idaho). Diazo yellow (PY14 or PY55) was identified in a green tempera paint and a yellow wax crayon and was detected in combination with chrome yellow on a yellow-green colored fabric wad believed to have been used by Castle to apply and manipulate color on his drawings [20]. These findings provide an intriguing insight into possible color sources and techniques used in this drawing.

The "Dream house" picture was one of six of Castle's colored works examined in the study using LDMS, and the analyses allowed identification of 15 colorants, including azo (PR4, PR6, PR49:1, PY6, PY14 or 55), quinacridone (PO48 or 49, PV19), triarylcarbonium (PB1, PV39) and phthalocyanine (PB15) types. Castle's colorants and media are discussed in detail in a separate publication [20].

In some cases the pigments identified proved valuable as dating markers for Castle's drawings, for which no reliable chronology exists. Analysis of an orange paper fiber from another of the "Dream

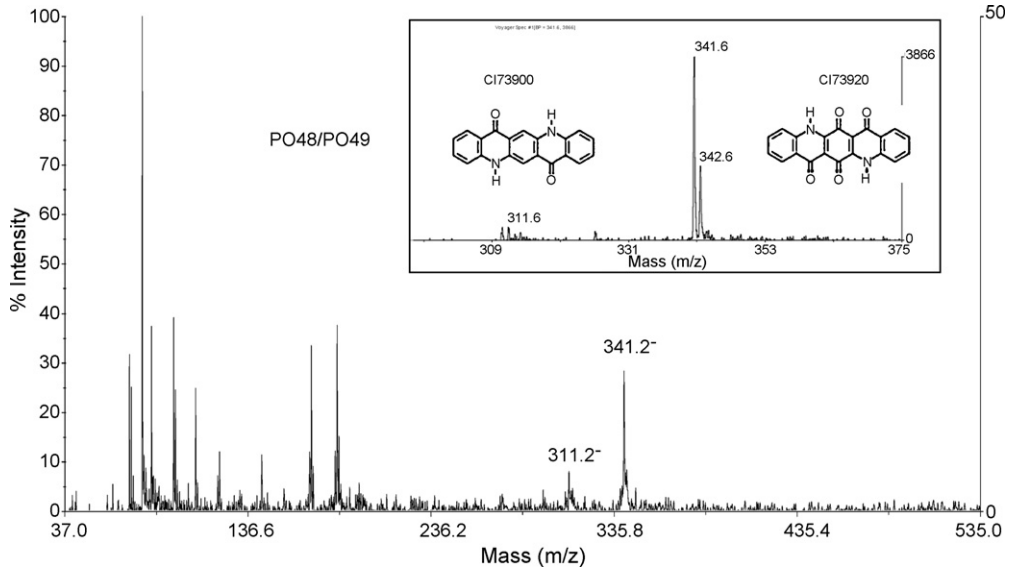

Fig. 11. Negative ion LDMS spectrum from a single orange fiber from the PMA "Dream house" drawing by James Castle. Molecular anions from CI 73900 (311.2^-) and CI 73920 (341.2^-), the components of both PO48 and PO49, are indicated. Component structures and spectrum from reference standard is shown in the insert.

house" pictures from the collection of the Philadelphia Museum of Art (PMA #337-2007-23) revealed the presence of a quinacridone pigment, either PO48 or PO49. These pigments are both mixed crystal phases of PV19 (quinacridone, CI 73900) and a quinacridone quinone (CI 73920). The negative ion LDMS spectrum obtained from the orange fiber is shown in Fig. 11 and exhibits molecular ions for both components of the pigment. Reference standards for both PO48 and PO49 produced similar LDMS spectra and could not be differentiated. The orange fiber sample, like many others from Castle's works, was very heterogeneous, and the spectra were position sensitive but repeatable. The identification of PO48 or PO49 indicates that the drawing could not have been executed before 1958, the year in which the first quinacridone pigments were marketed by E.I. du Pont Nemours and Company [21].

4. Conclusions

We have described the use of LDMS in conjunction with complementary analytical tools in a conservation science laboratory and have shown by way of applications the significant information and results that can be obtained with it. The applications described show that LDMS has the requisite sensitivity and specificity to analyze modern organic pigments encountered in microscopic samples from works of art. In addition, LDMS requires minimal sample preparation, is very effective for the analysis of pigment mixtures, and is not limited by background and matrix effects. In many cases, identifications can be made with high confidence based on exact mass and isotopic patterns alone. However, the synergistic use of complementary techniques, such as FTIR and EDS, is valuable in many cases to enhance the confidence of pigment identification. Ions related to admixed inorganic pigments can be observed, adding to the understanding of the total material composition.

Despite the positive results with LDMS analysis of materials from a variety of sources, pigments in certain samples could not be detected or identified confidently for reasons as yet unknown. Such samples will be the subject of ongoing study with this developing technique. Also, in our experience as well as that of others [6], certain pigment classes, pigment lakes, for example, have proven difficult to analyze, and will require further development. Finally, in the examples presented, LDMS was used for qualitative determination of pigments; further study is needed to explore the potential of the technique for quantitative analysis.

The benefits of pigment analysis have been well recorded in the conservation literature over the last 80 years. Frequently, modern organic pigments have eluded consistent identification in the museum laboratory. This may explain in part why contemporary artists' materials and techniques have not received the same scrutiny as more traditional materials. The use of LDMS as described in this article provides an additional tool to understand the materials of modern works of art, and will continue to find applications relating to authenticity, conservation treatments, and the study of artists' materials and techniques.

Acknowledgements

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