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The use of direct temperature-resolved mass spectrometry (DTMS) in the detection of organic pigments found in acrylic paints used by Sam Francis

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ABSTRACT

When analyzed in the dry, powdered form, most of the hundreds of modern synthetic organic pigments that have been introduced throughout the 20th century can be effectively characterized by direct temperature-resolved mass spectrometry (DTMS) [S.Q. Lomax, M. Schilling, T. Learner, in: T. Learner, P. Smithen, J.W. Krueger, M. Schilling (Eds.), Modern Paints Uncovered, Getty Conservation Institute, Tate Modern, London, 2007, p. 105]. However, their detection in paint formulations is often far more difficult, as these pigments are usually present in only very low concentrations, due to their relatively high tinting strengths. The situation is also more complex when one attempts to identify these pigments from microscopic samples of paint taken from actual works of art, due to the frequent manipulation, mixing, or adulteration of paints by artists during their application. A project aiming to characterize the wide range of pigments found in the paints of Sam Francis (American, 1923–1994) prompted work to investigate more fully the sensitivity of a DTMS system by comparing various ionization conditions, including electron impact (EI) at 70 and 16 eV, and chemical ionization (CI) with iso-butane in both positive- and negative-ion modes. Overall, it was found that negative-ion CI conditions showed the best results for detecting the majority of synthetic organic pigments tested: the very limited fragmentation it produced in most of the pigments resulted in a much stronger and more readily detectable molecular ion that could be more easily distinguished from the lower *m*/*z*-value ions typically coming from other components in the paints.

1. Introduction

For the art conservation profession, the ability to establish the type of paint on a work of art is an essential component of investigating how that paint might alter with age, in response to environmental conditions, or after conservation treatments. It is also a fundamental requirement in studying the materials and techniques of an artist and probing issues of authenticity. In recent years, great advances have been made in developing and testing suitable analytical techniques for determining the main classes of binders, pigments and other components in modern (i.e., post 1940s) paints [2].

Two of the most successful techniques for this involve mass spectrometry: pyrolysis-gas chromatography-mass spectrometry (PyGCMS) and direct temperature-resolved mass spectrometry (DTMS), and most classes of synthetic binders (e.g., acrylic, alkyd, epoxy, polyurethane, polyvinyl acetate) can be readily differentiated with either technique [2–4]. Identifying modern, inorganic pigments is relatively straightforward using established X-ray techniques, such as energy dispersive X-ray (EDX) analysis, or X-ray diffraction (XRD). However, three issues make identifying synthetic organic pigments far more problematic. First, the particle size of these pigments is rarely sufficiently large to enable their identification by optical microscopy. Second, most of these pigments possess extremely high tinting strengths, resulting in low concentrations in paint formulations. And third, the existence of hundreds of such pigments, compared to a handful of traditional ones, requires testing an extremely large selection of reference samples for any potential analytical technique used to distinguish them.

Recent work on assessing how to best detect these organic pigments has concentrated on understanding the chemistry, properties, and uses of the various pigment classes likely found in paints [5], and on a number of analytical techniques including DTMS, which has shown considerable potential for organic pigment identification [1,2,4,6]. Lomax et al. [1] found that DTMS using electron impact (EI) at 70 eV typically produced a combination of molecular ion and fragmentation in most of the pigments tested, which could be problematic in paint formulations where the fragment ions were masked by those from the binding medium. However, low voltage ionization at 16 eV has been successfully used to produce DTMS spectra with minimal ion fragmentation [7–9], and Boon and Learner [6] showed that 16 eV could be

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Fig. 1. Paints found in Sam Francis' Santa Monica studio. Photo: Aneta Zebala, Conservator, Sam Francis Foundation, 1997.

advantageous for identifying acrylic emulsion binding media and a small number of organic pigments with the technique. That same study also found that chemical ionization (CI) with ammonia facilitated the interpretation of the mass spectra from acrylic copolymer binders, although no pigment spectra under CI were presented.

Other analytical techniques have also been investigated for their applicability to the full range of organic pigments, in particular FTIR and Raman spectroscopy. FTIR gave excellent spectra for all classes of organic pigments and could readily differentiate them in their dry, powdered form [1,2], but other components in a paint film – the binding medium and fillers in particular – frequently mask the pigment's diagnostic peaks, and consequently the technique often fails to detect the pigment when analyzing paint films. More recently, Raman spectroscopy has been shown to be highly effective at detecting a wide range of synthetic organic pigments in paint formulations [10–12]. Other potentially useful techniques include laser desorption ionization mass spectrometry (LDI-MS) in positive and negative modes [6,13–15], and secondary ion mass spectrometry (SIMS) [4]. Although PyGCMS can also successfully detect azo pigments, the largest class of organic pigments used in modern paints, it was far less successful in identifying phthalocyanines, quinacridones, benzimidazolones, dioxazines, or any other class of organic pigment [2,16].

An ongoing study of paints used by Sam Francis (American: 1923–1994), one of the most influential painters in the 20th century and often associated with the Abstract Expressionists, has highlighted the need for further improvement of some of these analytical techniques. The study included a collection of sixty-four pots of pre-mixed paint (Fig. 1) that were found in his studio in Santa Monica, California after his death in 1994, as well as paintbrushes, working tools, study fragments, and completed works of art. Francis is known to have used a number of different paint types in his work, but much of his post-1970 work is thought to have been created with acrylic emulsion paints, the most commonly used synthetic polymer in artist's quality paints. These are thought to have been supplemented by custom-made formulations created by his studio assistant Dan Cytron, who would often include pigments and binders less common to artist's paints [Cytron, personal communication, 2007]. As a result, a very broad range of synthetic organic pigments is likely in his paints, including pigments from the monoazo, anthraquinone, dioxazine, disazo, indanthrone, monoazo, phthalocyanine and quinacridone classes. This makes a study of Sam Francis' painting materials an excellent case study for testing and improving analytical techniques for the identification of organic pigments. This paper reports on recent work developing DTMS techniques for this purpose.

2. Experimental

2.1. Samples

Table 1 lists all the acrylic and pigment samples used for this research. The main source for the paints of Sam Francis was the

Table 1
Reference samples of binding media and pigments used in this study.

Sample	Name	Pigment class	Company
p(*n*BA-MMA)	Acrylic Gloss Medium, 1994	n/a	Winsor & Newton
p(EA-MMA)	Acrylic Medium and Varnish, 1994	n/a	Liquitex
PR7	Monolite Red 4RH	Monoazo	ICI
PR9	PR9	Monoazo	Rowney
PR112	Permanent Red FGR	Monoazo	Clariant
PR122	Sunfast Magenta 122	Quinacridone	Sun Chemical
PR170	Sunbrite Red 170	Monoazo	Sun Chemical
PR188	Novoperm Red HF3S	Monoazo	Clariant
PR202	Cinquasia Magenta RT-343-D	Quinacridone	Ciba
PR206	Cinquasia Maroon RT-792-D	Quinacridone	Ciba
PR207	PR207	Quinacridone	Royal Talens
PR209	Hostaperm Red EG trans.	Quinacridone	Clariant
PO5	Monolite Red 2G	Monoazo	Avecia
PO43	Hostaperm Orange RG	Perinone	Clariant
PO48	Cinquasia Gold YT-923-D	Quinacridone	Ciba
PO49	Cinquasia Orange	Quinacridone	Kremer Pigments
PO72	PV Fast Orange H4GL 01	Disazo	Clariant
PY3	Heuco Gelb 100300	Monoazo	Heubach
PY12	Sunbrite Yellow 12	Disazo	Sun Chemical
PY16	Permanent Yellow NCG	Disazo	Clariant
PY83	Sunbrite Yellow 83	Disazo	Sun Chemical
PY97	Novoperm Yellow FGL	Monoazo	Clariant
PY126	Permanent Yellow DGR	Disazo	Clariant
PY127	2127 Diarylide Yellow	Disazo	Lansco
PY151	Hostaperm Yellow 4HG	Monoazo	Clariant
PG7	Monastral Green GNX-C	Cu phthalocyanine	Avecia
PG36	Monastral Green 6Y-C	Cu phthalocyanine	Avecia
PB15	5561 Cu Phthalocyanine Blue	Cu phthalocyanine	Lansco
PB15:1	Monastral Blue LBX	Cu phthalocyanine	Avecia
PB15:2	Monastral Blue FBN	Cu phthalocyanine	Avecia
PB15:3	Monastral Blue BG	Cu phthalocyanine	Avecia
PB15:4	Monastral Blue FGX	Cu phthalocyanine	Avecia
PV19	Monolite Violet 4R	Quinacridone	Avecia
PV23	Monolite Violet RN	Dioxazine	Avecia
PV37	Cromophtal Violet B	Dioxazine	Ciba

collection of sixty four pots of pre-mixed paint left in his studio, which were stored in non-commercial containers and consecutively numbered (Fig. 1); samples presented in this paper (e.g., SF14) reflect the numbers written on the pots. It is unknown whether the paints were mixed within the studio or custom-ordered or both. Dan Cytron formulated custom acrylic paints for Sam Francis for many years [Cytron, personal communication, 2007], and Golden Artist Color provided a number of custom acrylic dispersions to the Francis studio in the early 1990s [17]. Samples from the paint pots were collected in 1997 and applied to standard microscope slides in 2004 for easy storage, sampling, and analysis. A range of pure binding media was also painted out on microscope slides for testing, including the two main types of copolymer used in acrylic emulsion paints: poly-*n*-butyl acrylate-methyl methacrylate, p(*n*BA-MMA), or poly-ethyl acrylate-methyl methacrylate, p(EA-MMA).

It was also possible to sample paints from the archives of his working materials – paintbrushes, poles, study fragments on paper and canvas, as well as personal papers – that had been donated by the Sam Francis Foundation (SFF) to the Getty Research Institute's (GRI) Special Collections [18]. Twenty-five paint samples were selected based on information from the SFF and Dan Cytron to include a broad timeline and custom-mixed paints. GRI-1 is a study fragment on canvas—large areas of yellow with a few red and blue splatters. GRI-3, a study fragment on paper, has a large circle of a light blue wash and areas of bright raspberry and red drips. GRI-4 is a smaller study fragment on paper with rich apple-green, violet, black, and red paints; it is from the early 1970s when Sam Francis' painted a series referred to as Fresh Air. GRI-6 is a colorful and thickly painted study fragment on paper. GRI-8 is another study fragment on paper with red, purple, and blue paint. GRI-9 refers to a long-handled aluminum paintbrush pole, covered with splatters of paint. Unlike the paint pots, the study fragments and paintbrush handles were not individually numbered; the codes (e.g., GRI-8) are used solely to keep track of the samples.

Samples were also collected from Sam Francis' painting *Untitled* (SFP78-18), see Fig. 2; SFP78-18 is representative of the series of grid paintings Francis created during the late 1970s. Sample selections were based on color variety and appearances similar to those found on tools and study fragments in the GRI's collection. All samples were collected with a clean, sharp surgical scalpel, and were typically less than 50 μg in weight.

2.2. DTMS

DTMS analyses were performed using the JEOL MStation (JMS-700), a double-focusing magnetic sector mass spectrometer. Temperature resolution was achieved by ramping a current at 0.5 A/min over 2 min through the direct probe's 100-μm diameter platinum filament, resulting in a final temperature of approximately 800–1000 °C. Via the resulting temperature rise, increasingly less volatile components were released and ionized. Positive ions were formed by electron impact (EI) at 70 or 16 eV, or with chemical ionization (CI) with isobutane; negative ions were created only by CI. The magnetic field was scanned linearly over the peak range $m/z = 10–2000$ with 3000 resolution, and the calibration was performed in FAB (fast atom bombardment) mode using Ultramark 1621 in a glycerol matrix.

For pigments, a 1–2 μL drop of chloroform ($CHCl_3$) was applied to the tip of the filament. A dissecting needle dipped in the pigment was then touched to the $CHCl_3$ drop, resulting in pigment particles becoming suspended in the solvent. As the solvent evaporated, the pigment evenly coated the tip of the filament. The acrylic paints were treated similarly. To ease handling, a fraction of the paint fragment swelled in approximately 20 μL of $CHCl_3$ before a small piece was added to the filament in a drop of solvent. As the solvent evaporated, the sample attached itself to the filament.

3. Results and discussion

3.1. Pigments

All pigments gave clear spectra in each of the four ionization modes tested, namely: EI at 16 eV; EI at 70 eV; CI positive ion; and CI negative ion. In general, the spectra obtained with EI at 16 eV and CI negative ion contained much stronger molecular ions, as might be expected from these softer forms of ionization. CI with ammonia was not tested, but all pigments in this very broad selection gave strong molecular ions with isobutane, although in most cases CI in positive ion mode resulted in a high level of fragmentation and was therefore not deemed successful.

Each of the major classes of pigments is discussed in turn below.

3.1.1. Azo pigments

Azo pigments comprise the largest class of synthetic organic pigments, and are typically various shades of red, orange and yellow. Monoazo pigments (e.g., PR7, PR9, PR112, PR170, PR188, PO5, PY3, and PY97) each contain one azo (–N=N–) group, whereas disazo pigments (e.g., PY12, PY83, PY126, and PY127) contain two [5,19]. Chemical structures for the monoazo pigments, seen in Fig. 3, show various coupling components, which can lead to many fragmentation possibilities.

A good example of how the various ionization modes of DTMS affected the mass spectra of all organic pigments is seen in Fig. 4, which compares mass spectra from PY83 (a disazo pigment) and PY97 (a monoazo pigment) analyzed by EI+ 70 eV, EI+ 16 eV, CI+ and CI−. The molecular ions for PY83 and PY97 are $m/z = 818$ and 590, respectively, and if produced in sufficient intensity could be

Fig. 2. Sam Francis *Untitled* (SFP78-18), 1978, acrylic on canvas, 90 "x 60". Photograph courtesy of Jonathan Novak Contemporary Art, Los Angeles.

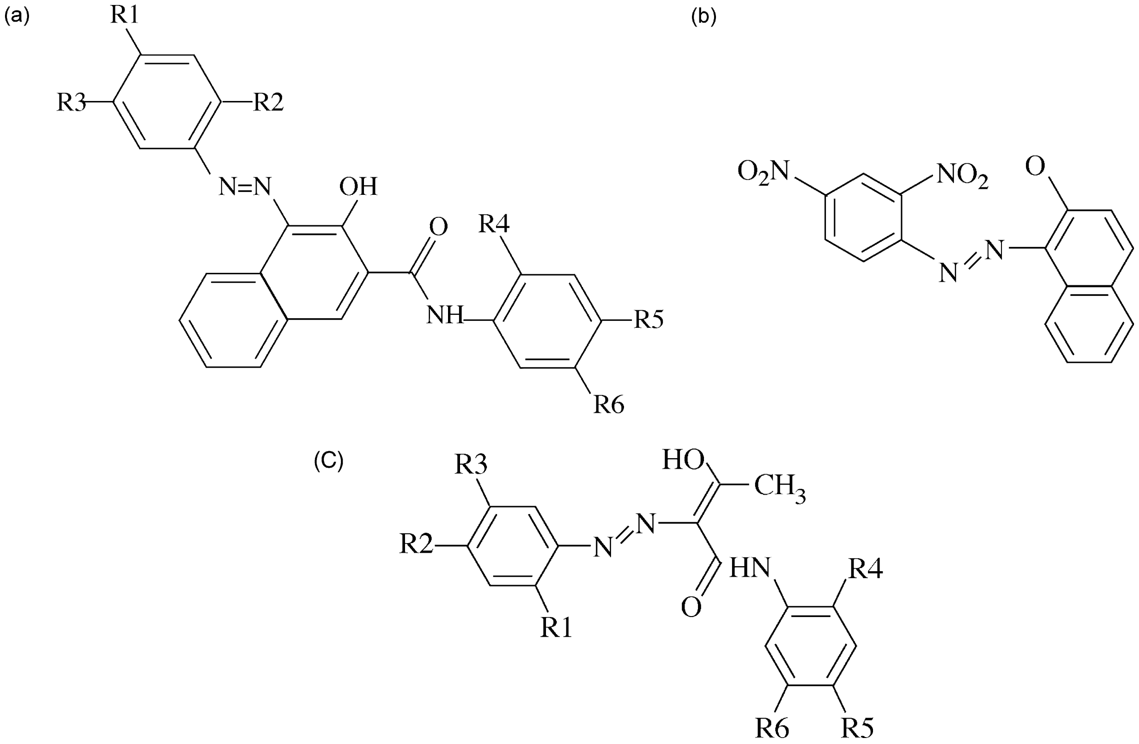

Fig. 3. General chemical structures for the (a) red and (b) yellow monoazo pigments analyzed by DTMS. (c) shows the structure of PO5, a common orange azo pigment.

used as characteristic peaks for each pigment (see Table 2). When ionized at 70 eV, the most intense ions detected were *m*/*z* = 187 and 172 for both pigments: the molecular ions have much lower intensities, and would be difficult to detect if the sample size was diminished (as would be the case in a paint formulation). However, reducing the electron energy to 16 eV significantly reduced fragmentation with EI, especially for the monoazo PY97. The positive CI spectrum was somewhat comparable to electron impact at 70 eV, in that it showed a very weak molecular ion. However, the spectra produced using the negative ion mode CI displayed dramatically reduced molecular fragmentation and very intense molecular ions that were characteristic to each pigment.

When analyzing these pigments in paint formulations, DTMS spectra will obviously also contain ions from other components in

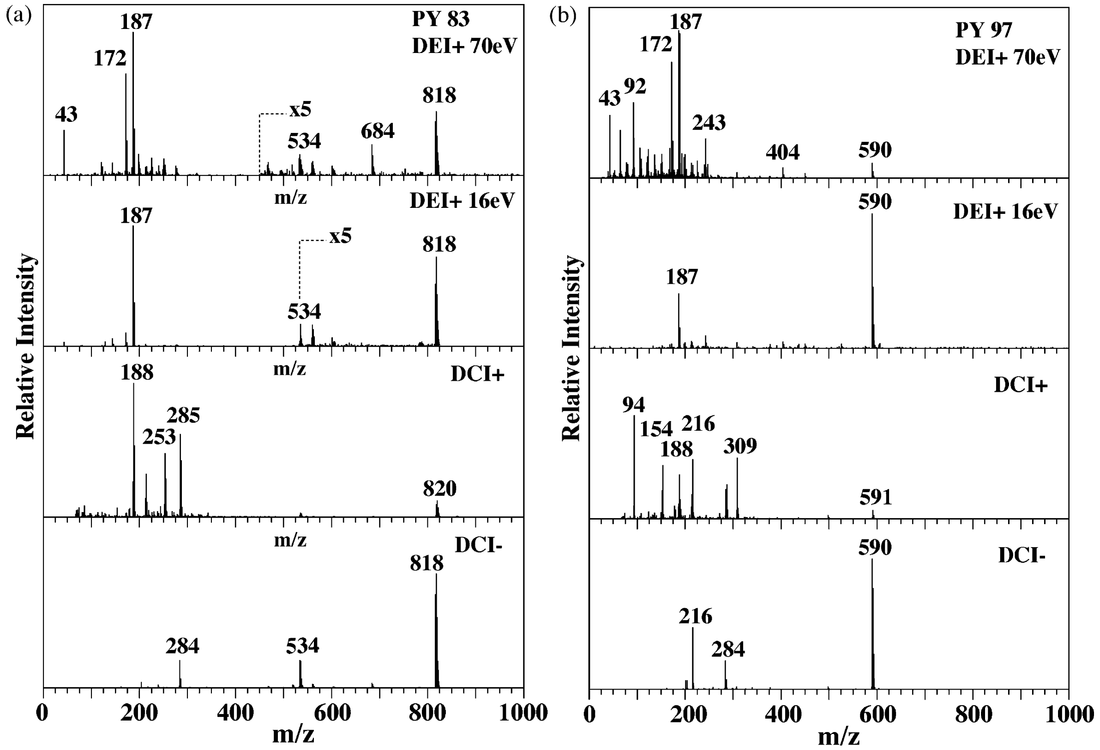

Fig. 4. Comparison of ionization methods for two azo pigments: (a) disazo PY83 and (b) monoazo PY97.

Table 2
Azo pigments. Comparison of EI+ 70 eV and CI− ionization effects on monoazo and disazo pigments.

Pigment	EI+	CI−	MW	Samples
PR7	323, 294, 463	463	463	SF05, GRI-9a
PR9	161, 343[a]	465	465	GRI-4d, SFP78-18-4
PR112	377, 483, 289	482, 483	483	SF53
PR170	318, 454, 169	454	454	SF04, GRI-3b, GRI-8b
PR188	169, 178	641, 302	642	SF12
PO5	143, 115, 338	338	338	SF29
PY3	127, 394	394, 364	394	SF06, SF52, GRI-4c, GRI-9e, SFP78-18-3
PY97	187, 172 (404, 590)	590, 216, 284	590	–
PO72	149, 278, 522	533, 304, 740	670	–
PY12	93, 275, 438, 628	628, 440, 190	566	–
PY83	187, 172, 818, 534	818, 534, 284	818	SF03, SF17, SF24

[a] Data from Lomax et al. [5].

the paint film, in particular the binding medium. DTMS was found to distinguish the two main acrylic copolymers used in acrylic paint formulations – p(EA-MMA) and p(*n*BA-MMA) – in all modes of ionization tested, although there was significant variation in the relative degree of this differentiation. For example, Fig. 5 shows the mass spectra for both copolymers obtained with CI negative, compared to those from 70 eV EI. The most intense fragments created with EI+ 70 eV are common to both types of emulsions: $m/z = 41$, 69, 100 are fragments of MMA, and $m/z = 55$ can be due to either the EA or *n*BA monomers [2]. Identifying the specific copolymer depends upon less intense fragments, such as the EA or *n*BA-*n*BA-MMA trimers, $m/z = 255$ or 283, respectively. Negative CI, on the other hand, produced distinct high-intensity peaks with much reduced fragmentation: $m/z = 240$, 254 from p(EA-MMA) and $m/z = 282$ from p(*n*BA-MMA).

For the complete analysis of a paint film, it is clearly advantageous if the pigment peak positions do *not* coincide with those of the binding medium, and the average mass spectrum of the total ion count (TIC) should clearly display both components. Sometimes, 70 eV EI was perfectly adequate for this, as seen in Fig. 6(a), which gives an example of an azo pigment-containing p(EA/MMA) acrylic paint film. This figure shows the average mass spectrum of SF05, a red paint sample from the Sam Francis studio, in which peaks

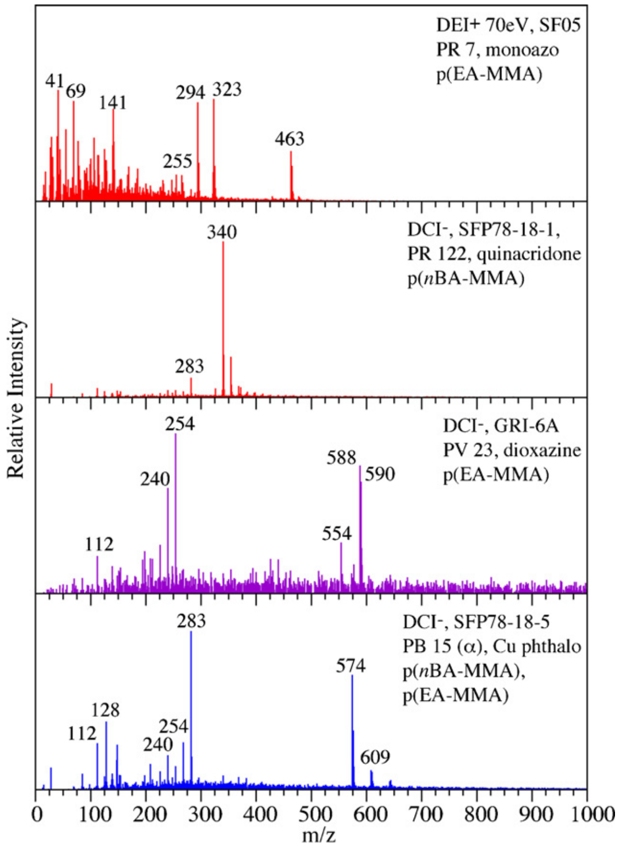

Fig. 6. DTMS analyses of Sam Francis paint samples; the pigments and binding media are identified by the average mass spectra of the TIC. (a) Red studio paint, SF05, ionized by EI+ 70 eV. Monoazo pigment, PR7, identified by $m/z = 294$, 323, 463 and the p(EA-MMA) binding medium is identified by $m/z = 255$. (b) Red paint sample from *Untitled*, SFP78-18-1, ionized by CI−. The quinacridone PR122, is given by the characteristic molecular ion, $m/z = 340$, and the binding medium is p(*n*BA-MMA). (c) Purple paint sample from study fragment, GRI-6A. The pigment is dioxazine PV23; the acrylic is p(EA-MMA). (d) Blue sample, SFP78-18-5, from *Untitled*; the pigment is PB15. The most intense acrylic peak is p(*n*BA-MMA), with some p(EA-MMA), which could be a minor component of the paint or from any ground layer in the sample.

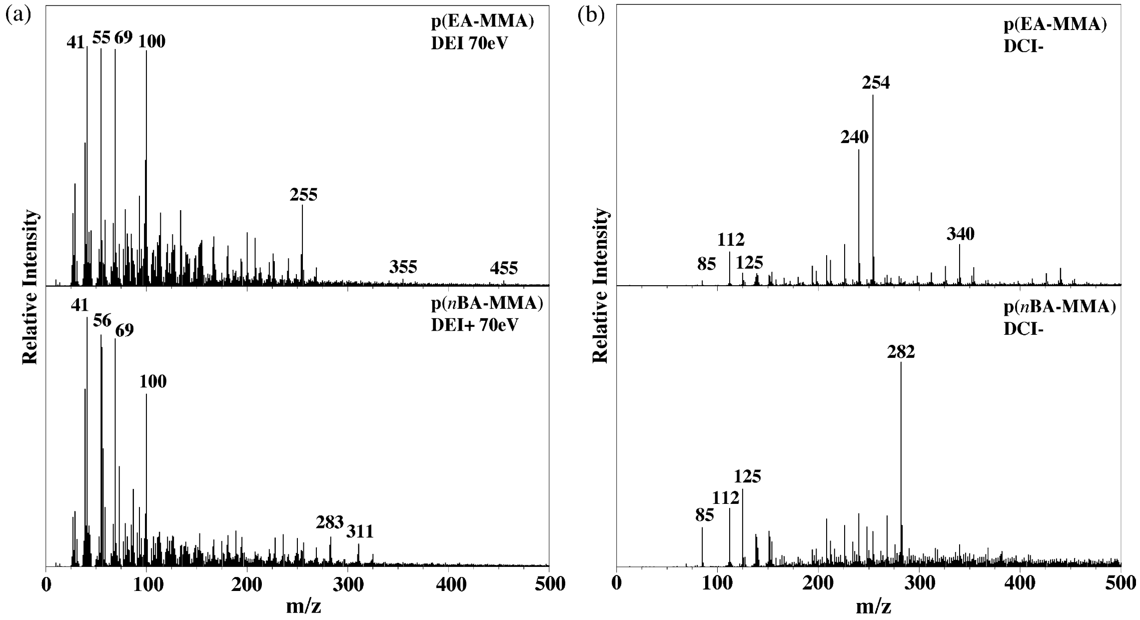

Fig. 5. Averaged mass spectra for DTMS analyses of acrylic binding media, p(EA-MMA) and p(*n*BA-MMA), ionized by (a) EI+ 70 eV and (b) CI−.

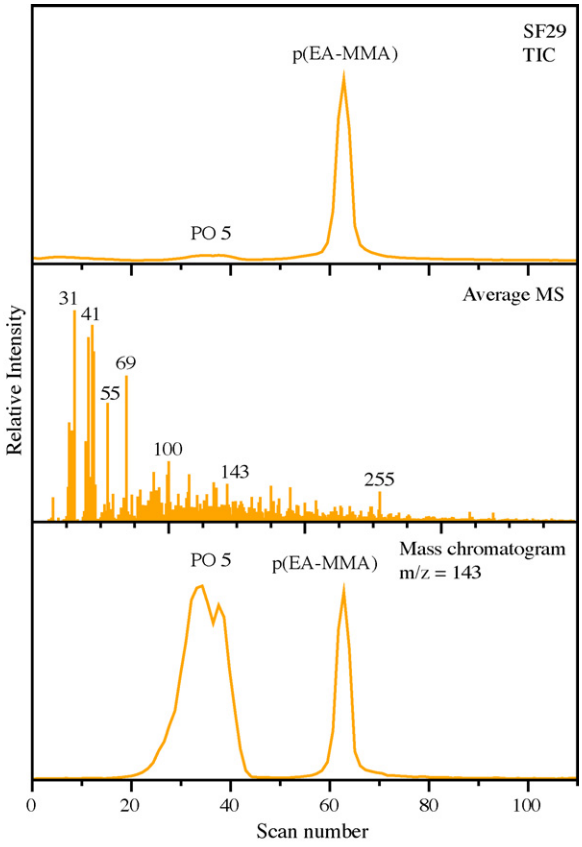

Fig. 7. DTMS analysis of studio paint sample SF29, ionized by EI+ 70 eV. Pigment identification relied on the low pyrolysis temperature compared to that of the binding medium, since the characteristic fragment ion of the pigment, PO5 at $m/z = 143$, coincides with the EA sesquimer of the binding medium.

from both the desorped pigment PR7 (characteristic fragments at $m/z = 323, 294$ and 463) and the pyrolyzed acrylic binder (characteristic fragments at $m/z = 41$, 69 and 255) were clearly distinguished when ionized by EI+ 70 eV.

However, this separation of components was not always possible. The main peak for the monoazo orange pigment PO5, for example, using EI+ 70 eV was $m/z = 143$, which was also the peak for the EA sesquimer. In sample SF29, this pigment was identified using another feature of the DTMS technique—the ability to resolve components via the temperature ramp. Here the pigment undergoes desorption at a lower temperature than the pyrolysis of the acrylic copolymer—the total ion chromatogram (TIC) in Fig. 7 shows the pigment and acrylic medium completely resolved using DTMS. The TIC identifies the presence of an azo pigment; an average mass spectrum of the pigment peak (not shown) was used to identify the pigment; and the selective ion current mass chromatogram at $m/z = 143$ gave the contributions from both PO5 and p(EA-MMA).

With most of the azo-containing paint samples from the Sam Francis painting materials, the situation was similar to the example given for PY83 and PY97: that EI caused too much fragmentation to conclusively identify the pigments when present in paint and for all of those labeled GRI and SFP78-18, CI in negative mode was successfully employed.

3.1.2. Quinacridone pigments

Quinacridone pigments (e.g., PR122, PR202, PR206, PR207, PR209, PO48, PO49, PV19) are all based on the structure of PV19 (see Fig. 8), and PR206, PR207, PO48, and PO49 are mixed crystal phases containing PV19 [19]. Fewer substitution sites and mixed crystal phases gave limited numbers of characteristic ions (see Table 3), which has the advantage of more quickly identifying a quinacridone pigment in a paint sample. On the other hand, fragmentation from EI+ 70 eV can greatly complicate a specific pigment assignment when present in a paint film. The spectra of PO48, PO49, and PR206 contain a strong molecular ion at 344 when obtained in CI− mode (see Fig. 9). Peak $m/z = 312$ is detectable in PO48 and almost as intense as $m/z = 344$ in PR206. The relative intensities of these peaks with EI+ 70 eV were not as distinct. This, combined with the additional peaks from an acrylic binding medium (and other paint components), necessitated using chemical ionization to confirm the pigment. For example, Fig. 9 also shows the mass spectra for sample SF19: in the 70 eV EI mass spectrum, the ion at $m/z = 344$ was very weak. However, using CI−, the pigment could be assigned as PO48. Another example is shown in Fig. 6(b), where the quinacridone PR122 was readily identified from its strong molecular ion at $m/z = 340$ in the mass spectrum achieved with negative ion CI from the red paint sample from Francis' painting *Untitled* (SFP78-18).

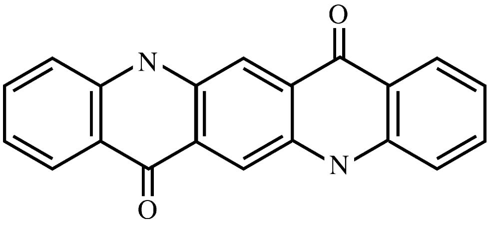

Fig. 8. Chemical structure of quinacridone pigment PV19.

Table 3
Quinacridone pigments. Comparison of EI+ 70 eV and CI− ionization effects on quinacridone pigments.

Pigment	EI+ 70 eV	CI−	MW	Samples
PR122	340, 170	340	340	GRI-4b, SFP78-18-1
PR202[a]	380, 312	380, 312	380	–
PR206[a]	312, 344, 255	344, 312	312, 344	–
PR207[a]	312, 380	312, 380	312, 380	–
PR209	380, 289	380 (344)	380	–
PO48[a]	312, 344, 286	344 (312)	312, 344	SF19
PO49[a]	342, 286, 76	344 (342)	312, 344	–
PV19	312, 255, 76	312 (622)	312	SF32

[a] These pigments are mixed crystal phases containing two separate molecules.

3.1.3. Dioxazine pigments

Dioxazines are particularly strongly tinting pigments, often resulting in very small concentrations within paint formulations. For PV23, two characteristic ions ($m/z = 588$, 590) appeared with both EI+ 70 eV and CI− (see Table 4) and did not overlap with the acrylic peaks. However, the pigment's peaks intensities with EI+ 70 eV were sometimes quite low. Since there are fewer violet synthetic organic pigments than other colors, using mass chromatograms to verify pigment peaks was often very helpful. Table 4 also lists results for PV37, an uncommon pigment in artist's quality paints, but shown here in order to compare dioxazines. Fig. 6(c) shows the unmistakable signature for PV23 in sample GRI-6A using CI− ionization, with the pigment's molecular ions highly visible.

Table 4
Dioxazine pigments. A comparison of EI+ 70 eV and CI− ionization effects on dioxazine pigments.

Pigment	EI+ 70 eV	CI−	MW	Samples
PV23	588, 590	588, 590, 554	588	SF08, SF09, SF22, F34, SF63, SF64, GRI-4e, GRI-6a
PV37	105, 640, 631	726, 1452	726	–

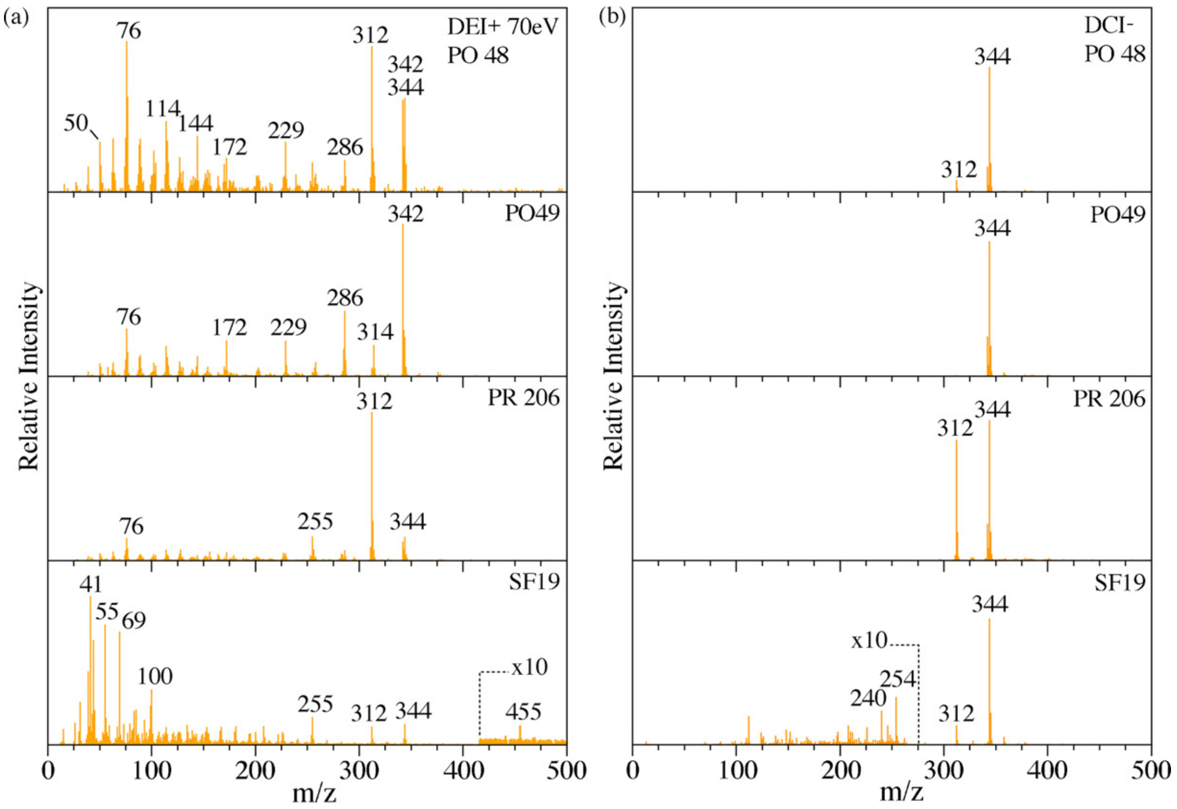

Fig. 9. Comparison of (a) EI+ 70 eV and (b) CI− ionization effects on quinacridone pigments PO48, PO49, PR206, and studio paint sample SF19. These pigments are all crystal mixtures of two structures, one of which is that of PV19 (Figure 8). Excessive fragmentation from EI produces inconclusive spectra when identifying the pigment in a paint film.

3.1.4. Phthalocyanine pigments

Ionization effects on phthalocyanine blue (PB15:1, PB15:2, PB15:3, PB15:4, PB15:6) and green (PG7, PG36) were also studied. For all the blue pigments, regardless of the ionization method employed, the molecular ion $m/z = 575$ was the most significant ion observed (see Table 5). It was also possible to differentiate the α forms (PB15:1 and PB15:2) from the others, which lack mono-, di- and tri-chlorinated species that produce at $m/z = 609$, 643, and 677, respectively [14]. In contrast, the β (PB15:3 and PB15:4) and ε (PB15:6) forms only displayed the non-chlorinated molecular ion at $m/z = 575$.

Table 5

Phthalocyanine pigments. A comparison of EI+ 70 eV and CI− ionization effects on blue and green Cu phthalocyanine pigments.

Pigment	EI+ 70 eV	CI−	MW	Samples
PB15	575	575	575	SF11[c], SF58[c], SF60[c], GRI-1c[c]
PB15:1-α	575, 609, 643, 677	575, 609, 643, 677	677	SF18[c], GRI-9d[c], SFP78-18-5[c]
PB15:2-α	575, 609, 643, 677	575, 609, 643, 677	677	SF18[c], GRI-9d[c], SFP78-18-5[c]
PB15:3-β	575	575	575	–
PB15:4-β	575	575	575	–
PB15:6-ε	575	575	575	–
PG7	1127[a], 266	266, 230, 1127[a]	1127	SF13, SF14, SFP78-18-6
PG36	1795[a,b]	363, 319, 1748[a]	Variable	–

[a] Isotopic peaks pattern centered at this position.

[b] Data from Lomax et al. [5].

[c] Exact form of PB15 could not be determined.

Although there was little difference between EI+ 70 eV and CI− in spectra of PB15 pigments, the binding medium can greatly affect the pigment signal. Fig. 10 shows a comparative analysis using blue paint from a study fragment on canvas, GRI-1C. The electron impact mass spectra appeared consistent with that of the pure medium and implied the pigment was inorganic, but comparing mass chromatograms of $m/z = 575$ with neighboring ions suggested PB15. The chemical ionization spectrum confirmed the pigment is PB15, although the exact form (being either β or ε) of the pigment could not be ascertained.

The green phthalocyanines were more problematic. Fig. 6d is a mass spectrum of sample SFP78-18-5, a blue paint in *Untitled*. The peaks at $m/z = 609, 643, 677$ clearly designate this pigment as the α-form of PB15. Note that both p(*n*BA-MMA) and p(EA-MMA) acrylic media are present, with the former being most intense; p(EA-MMA) could be a minor component to the paint or the presence of an additional material inadvertently collected when sampling the painting.

For PG7 pigment, EI at both 16 and 70 eV, as well as negative ion CI, all produced mass spectra with the signature isotopic peaks pattern at $m/z = 1127$ for the fully (i.e., hexadeca-) chlorinated Cu phthalocyanine (see Fig. 11), as reported by Wyplosz [14]. However, CI negative was found to be far more efficient in detecting this pigment than EI, mostly thanks to selective ionization, and successfully detected PG7 in studio paint samples SF13 and SF14, as well as the green paint from *Untitled* SFP78-18-6. Note also that both p(EA-MMA) and p(*n*BA-MMA) are present. In this entire study, this was the only case where a mass chromatogram was necessary to identify the pigment when the paint film was analyzed in CI negative mode. Analyses of PG36, however, were less successful. In this study, high m/z series of peaks were visible, but with very low intensities. Neither EI nor CI produced spectra that could lead to identification of

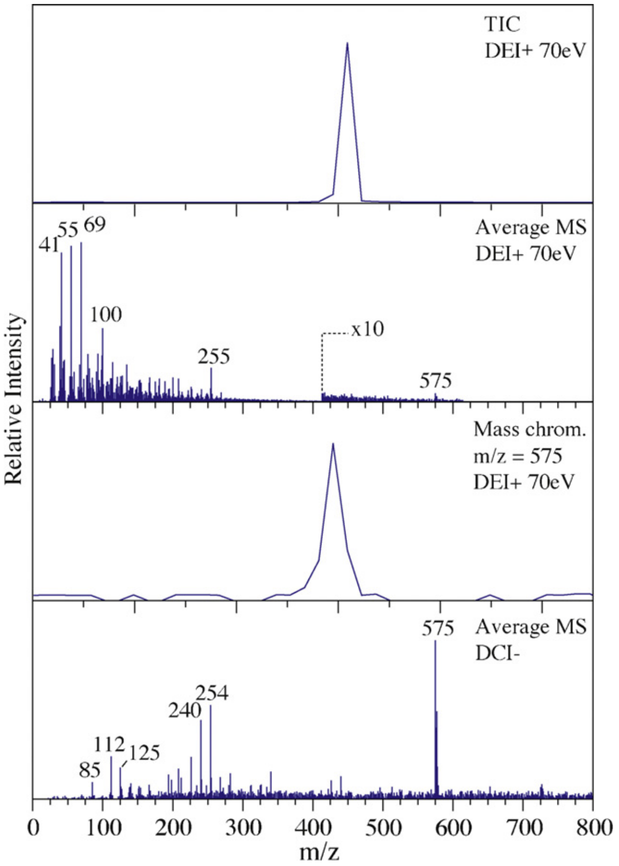

Fig. 10. Comparative analysis of ionization methods using blue paint from study fragment sample GRI-1C. With EI−, the binding medium signal overwhelms the pigment, but the mass chromatogram at $m/z = 575$ suggests pigment PB15. However, both the binding medium, p(EA-MMA), and pigment, PB15, are identifiable in the average mass spectrum using CI−.

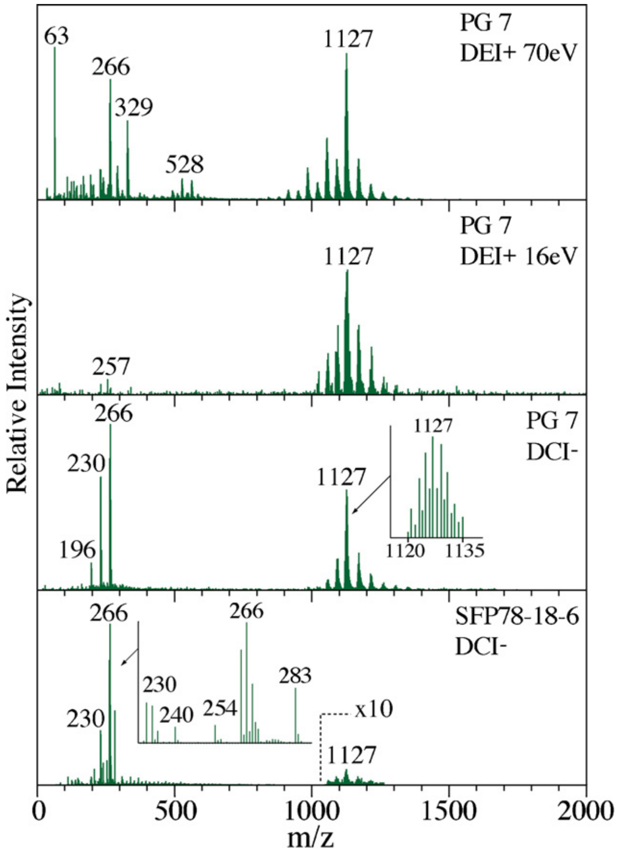

Fig. 11. EI+ 70 eV, EI+ 16 eV, and CI− applied to phthalocyanine pigment PG7. Green sample SFP78-18-6, contains PG7, p(*n*BA-MMA), and p(EA-MMA).

PG36 in a paint film, even though it was identified in some of the studio paint samples using Raman spectroscopy analysis [12].

3.2. *Sam Francis case study*

Table 6 lists the synthetic organic pigments detected in the Sam Francis paint samples from his Santa Monica studio, study fragments on canvas and paper, one of his long-handled paintbrush poles, and his grid painting *Untitled* (SFP78-18). All sixty-four studio paint samples were tested using EI+ 70 eV. Of those, organic pigments were conclusively identified in only nineteen of the samples; another seven were either tentatively assigned or set aside for further study. They were as follows: PY83 or PY97 for SF03 (see Section 3.1.1); further testing for green samples SF13 and SF14 (see Section 3.1.4); PO48, PO49, or PR206 for SF19 (see Section 3.1.2); quinacridone class for SF32; PY3 for SF52; and further testing for SF53. With all these samples, CI− was the best – and often the only successful – ionization method applied. The samples in question included monoazo, disaso, quinacridone, and phthalocyanine pigments.

The studio paints had been previously analyzed by FTIR and EDX, but FTIR was unable to identify the organic pigment in seven of the samples that were analyzed successfully by DTMS: PY83 (SF03); PO48 (SF19); PV23 (SF09, SF34, and SF64); PY3 (SF52); and PR112 (SF53).

Many of the objects sampled in the GRI collections were dated to the early 1970s, and *Untitled* (SFP78-18) was painted in 1978. During that period in Francis' career, he used intense colors, many custom-mixed paints, and a very broad range of pigments [Cytron, personal communication, 2007]. Towards the end of his life, illness and concerns about the toxicity of many pigments led Francis to utilize more commercially available paints, including acrylic dispersions from Golden Artist Colors, Inc. (GAC) [17]. The sales orders from GAC suggest that some of the studio paints could have been made with their acrylic dispersions. Sample SF53 contains PR112, the pigment in GAC dispersion Naphthol Red Light. PY3, the pigment found in SF05 and SF52, is also present in Hansa Yellow Light and Permanent Green Light, which also contains PG7. PY83, the pigment in GAC Diarylide Yellow, was also found in SF17 and SF24. Quinacridone Red and Quinacridone Violet (PV19) are potential matches for SF32. And at least 3 gallons of Dioxazine Purple (PV23) were ordered by Francis in the early 1990s; PV23 was found in SF08, SF09, SF22, SF34, SF63, and SF64.

Of the twenty-four samples collected from the study fragments and paintbrush pole, pigments were positively identified for sixteen (see Table 6). Mass spectra for six of the samples showed no indication of any pigment peaks, and further tests are required to determine if these contain inorganic pigments. Although the mass spectra indicated the presence of organic pigments for the remaining two samples, they did not match any of the pigments tested; these might be more unusual pigments, an area where further work is needed.

Eight samples were collected from *Untitled* (SFP78-18), most of which were chosen because of similarities to samples from the GRI special collections. DTMS analyses using CI negative ionization identified pigments in seven (see Table 6). The mass spectrum for the unidentified pigment, from a violet paint sample, showed no indication of any pigment peaks, and further testing is needed to verify if it has an inorganic pigment. PR9, PY3, PR122, and PB15 were

Table 6
Summary of results from Sam Francis paints case study. Paint samples from Sam Francis' Santa Monica, CA studio are noted by "SF" before the sample number written on the paint pot; those collected from the GRI Special Collections are noted by "GRI"; and all samples from the painting *Untitled* (SFP78-18) are denoted by the painting code. Only those samples containing identifiable organic pigments are listed.

ID	Color	Pigment	Pigment class
SF01	Orange	PO43	Anthraquinone
SF02	Yellow	PY127[d]	Disazo
SF03	Orange-yellow	PY83	Monoazo
SF04	Red	PR170	Monoazo
SF05	Deep red	PR7	Monoazo
SF06[a]	Bright yellow	PY3	Monoazo
SF08	Purple	PV23	Dioxazine
SF09	Purple	PV23	Dioxazine
SF11	Bright blue	PB15	Cu phthalocyanine
SF12	Red	PR188	Monoazo
SF13	Dark green	PG7	Cu phthalocyanine
SF14	Dark green	PG7	Cu phthalocyanine
SF17	Orange-yellow	PY83	Disazo
SF18	Dark blue	PB15	Cu phthalocyanine
SF19	Brown	PO48	Quinacridone
SF20	Bright orange	PO43	Anthraquinone
SF22	Purple	PV23	Dioxazine
SF23	Red	PO43	Anthraquinone
SF24	Orange-yellow	PY83	Disazo
SF29	Deep orange	PO5	Monoazo
SF31	Translucent green	PG36[b]	Cu phthalocyanine
SF32[c]	Deep red	PV19	Quinacridone
SF34	Lilac	PV23	Dioxazine
SF35	Green	PG36[b]	Cu phthalocyanine
SF48	Dark green	PG36[b]	Cu phthalocyanine
SF51	Dark blue	PB60	Indanthrone
SF52	Olive green	PY3	Monoazo
SF53	Pink	PR112	Monoazo
SF58	Blue-green	PB15	Cu phthalocyanine
SF60	Dark green	PB15	Cu phthalocyanine
SF62	Bright green	PG36[b]	Cu phthalocyanine
SF63	Dark brown-violet	PV23	Dioxazine
SF64	Purple-blue	PV23	Dioxazine
GRI-1a	Yellow	PY16	Bisacetoacetaryilde yellow
GRI-1c	Blue	PB15	Cu phthalocyanine
GRI-2a	Yellow	PY16	Bisacetoacetaryilde yellow
GRI-3b	Red	PR170	Monoazo
GRI-4b	Magenta	PR122[d]	Quinacridone
GRI-4c	Apple	PY3[d]	Monoazo
GRI-4d	Red	PR9	Monoazo
GRI-4e	Purple	PV23	Dioxazine
GRI-6a	Purple	PV23	Dioxazine
GRI-8a	Purple	PR181[e]	Thioindigoid
GRI-8b	Red	PR170	Monoazo
GRI-9a	Red	PR7	Monoazo
GRI-9d	Blue	PB15	Cu phthalocyanine
GRI-9e	Yellow	PY3[d]	Monoazo
SFP78-18-1[c]	Red	PR122	Quinacridone
SFP78-18-3[g]	Apple	PY3	Monoazo
SFP78-18-4[f]	Red	PR9	Monoazo
SFP78-18-5[c]	Blue	PB15	Cu phthalocyanine
SFP78-18-6	Green	PG7	Cu phthalocyanine
SFP78-18-7[a]	Orange	PO43	Anthraquinone
SFP78-18-8[c]	Yellow	PY3	Monoazo

[a] Both p(*n*BA-MMA) and p(EA-MMA) were detected.
[b] Identified by Raman spectroscopy.
[c] The binding medium is p(*n*BA-MMA).
[d] The pigment listed is the closest match.
[e] This sample may contain pigments other than that listed.
[f] The binding medium was not detected.

detected in samples from the painting *and* the study fragments and long paintbrush handle.

4. Conclusion

Although mass spectrometry with EI at 70 eV has shown some measure of success for analyses of synthetic organic pigments [1], the extent of fragmentation can obscure the very material of interest. This is especially true with modern paints, where the signal from the binding medium can dominate or otherwise obscure ions from high-tinting, low-concentration pigments. DTMS testing on the Sam Francis studio paint samples highlighted this disadvantage of electron impact ionization, where almost half of the samples that contained organic pigments could not be conclusively identified. The use of lower energy (16 eV) improved the potential for identification of pigments detection by decreasing fragmentation, but ultimately negative ionization CI was found to be the method yielding the best results for most pigment classes tested, including the monoazo, disazo, quinacridone, dioxazine, and phthalocyanine families.

DTMS takes advantage of azo pigments having desorption temperatures different from acrylic emulsions in cases where the medium dominates the pigment signal. When the pigment and medium were thermally resolved, most of the analyses using EI+ 70 eV clearly showed characteristic fragment ions that were easy to interpret. However, when the issue is pigment fragmentation, such that spectra from two pigments cannot be easily distinguished, then other ionization techniques must be employed. It was only when negative CI was applied to SF03 that PY83, rather than PY97, could be identified, for example (see Section 3.1.1). The situation was further exemplified by the quinacridones, where various pigments are crystal mixtures of the PV19 structure with one quite similar (see Figs. 8 and 9). Dioxazine pigment PV23 was detectable using EI at 70 eV in all studio samples, except for the lightest lilac (SF46) sample. The phthalocyanine pigments were the most challenging class of pigments to study. Even so, negative CI was still an improvement over EI at 70 eV.

The overall improvement observed in detecting the organic pigments in the acrylic paints of Sam Francis using negative CI demonstrated it as very useful method for studying modern paint samples from works of art, where samples are necessarily few and sizes are typically microscopic.

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