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Identification of Organic Pigments in Automotive Coatings Using Laser Desorption Mass Spectrometry*

ABSTRACT: When one looks at an automotive coating, one sees color due to pigments. Modern organic pigments, with high molar absorptivities, may be only minor components of the mixture. Laser desorption mass spectrometry (LDMS) has been shown to be a useful tool for the analysis of colorants such as pen ink dyes. Here, LDMS is used to determine its utility for the identification of pigments, in simple media and in more complex paints. Small paint chips can be introduced into the LDMS instrument, and when an ultraviolet laser is focused on a portion of a chip, ions representative of the pigment(s) are selectively formed. Some pigments such as quinacridones and copper phthalocyanine are very stable and are desorbed and ionized intact. In contrast, benzimidazolones, which contain some single-skeletal bonds, form fragment ions. This method proves to be sensitive and convenient, as no sample preparation is required. The presence of inorganic pigments in addition to modern organic pigments can be determined, and pigments can be directly identified in actual automotive paint chip samples.

KEYWORDS: forensic science, laser desorption, mass spectrometry, pigments, paint, coatings

Organic coatings are routinely encountered as trace evidence. Commonly encountered coatings include architectural paints, automotive coatings, nonautomotive vehicular coatings, industrial coatings, artist's paints, fingernail polishes, beverage- and food-container coatings, marine coatings, and aircraft coatings. Typical cases where paints are encountered include breaking and entering, or burglaries where a tool may have been used to gain access to a home or safe; violent interactions where a coating from a weapon may be transferred to a victim or surface in the local environment; and vehicular incidents where one vehicle hits an inanimate object, another vehicle, or a person.

In the forensic laboratory, a multitude of techniques have been used to characterize and compare various forms of paint that are received as evidence. Some of the more common techniques include stereomicroscopy, polarized light microscopy (PLM), chemical and solubility tests, Fourier transform infrared spectroscopy (FTIR), pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS), Raman spectroscopy, ultraviolet visible microspectrophotometry (UV-vis MSP), and X-ray diffraction (XRD) (1).

Pigments are an essential component of any coating that is intended to hide the color of a surface by providing a more desirable appearance. With the exception of clear coats, such as clear lacquers and varnishes, pigments are found in all paints. The best pigments will provide the most hiding power with the least amount of pigment incorporated into the film. Often, several different pigments are used to achieve a desired color or effect (2).

Several variables must be taken into consideration when attempting to determine what pigments are appropriate for a specific product. Economic factors tend to carry the most weight. Environmental considerations also play an important role in the selection of pigments. With shifts away from pigments containing heavy metals such as lead and cadmium, the use of organic pigments has increased (3,4). Other factors include the resistance of the pigments to light, heat, and solvents. Inorganic pigments tend to have excellent resistance to all of these factors. Organic pigments, however, are typically susceptible to some form of degradation that would limit their range of applications. For example, if a particular pigment were susceptible to degradation via UV radiation, it would not be suitable for exterior applications. Advancements in the pigments and coatings industries have made the use of several organic pigments possible for automotive applications. One such advancement in automotive coatings was the development of UV-resistant clear coat systems. By placing a clear UV-resistant layer over the color coat, organic pigments that are otherwise susceptible to photolytic degradation can be used. Several classes of pigments have become available with resistive characteristics that are suitable for automotive use. Some of these classes include, but are not limited to: benzimidazolones, quinacridones, and phthalocyanines. In-depth discussions of the history, specific uses, and chemistries of common organic pigments have been provided by Lewis (4,5) and Wicks et al. (3).

Various methods have been utilized to identify and analyze pigments. Some of these methods include PLM, chemical tests, XRD, FTIR, X-ray fluorescence (XRF), UV-vis MSP, and Raman spectroscopy. Crown (6) provides an in-depth discussion of many of the techniques that have been used for the analysis of paints and pigments. As previously mentioned, PLM is a very powerful and inexpensive technique that can be utilized by the forensic scientists to characterize and identify various microscopic particles including pigments. McCrone et al. (7) provide a good description of the capabilities of PLM for this type of analysis. XRD is an excellent instrumental technique for the identification of pigments in paints; however, as discussed by Curry et al. (8), it is much

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better suited for the characterization of inorganic pigments. More recently, Voskertchian (9) investigated the use of visible light spectroscopy for the quantitative analysis of organic pigments in paints. Desiderio (10) recently utilized Py-GC/MS to identify benzimidazolone-class organic pigments in automotive coatings. It should be noted that Py-GC/MS, although capable of providing valuable information, is a labor intensive and time-consuming technique. Chromatography is difficult to use due to the chemical nature of most pigments. Pigments are colorants that are insoluble in most common solvents (11) and are difficult to vaporize at temperatures suitable for GC. Although uncommon in many laboratories, MS has also been used for pigment identification. Acampora et al. (12) utilized MS to identify pigments present in counterfeit bank notes. Unfortunately, as previously stated, automotive coatings are complex mixtures, therefore this type of *in situ* mass spectrometric examination would be difficult in this context. Suzuki and colleagues (13–18) have published a series of papers using FTIR to successfully identify various classes of both inorganic and organic pigments in automotive paints, and have recently begun to investigate the use of Raman spectroscopy (19) in conjunction with FTIR. This combination would provide complementary information that would lead to more definitive conclusions. In related work, micro-Raman spectroscopy and micro-Fourier transform-Raman spectroscopy have shown promise in analyzing pigments of interest in art (20,21). Both FTIR and Raman spectroscopy are relatively simple to use and capable of handling small amounts of material in a nondestructive fashion. However, both the techniques do have some drawbacks. As paints are mixtures, their IR spectra will contain information on all components. The resulting spectral overlaps and generally low concentrations of organic pigments can make it difficult, if not impossible, to identify pigments that are masked by significant binder absorptions. Raman techniques are susceptible to interference due to fluorescence.

Although laser desorption mass spectrometry (LDMS) is not widely available, it is a viable option for the analysis of pigments. It is a fast, relatively nondestructive technique, which can handle very small samples. The generally low detection limits of this technique, accompanied by its selective ability to detect pigments in the presence of binders, make it ideal for analyzing low concentrations of organic pigments that might go unnoticed when using FTIR and Raman spectroscopies. The majority of the research in the forensic literature that utilizes LDMS concentrates on its use for the identification of pigments, colorants, and dyes in questioned documents. Grim et al. (22,23) have evaluated the use of LDMS for the analysis of various inks. Dunn et al. (24) investigated the use of LDMS in conjunction with intentional photodegradation for the identification of dyes that are commonly found in red inks. Balko and Allison (25) utilized LDMS to detect and identify security ink dyes in the presence of other colorants on currency and fabrics. During the course of their work, they were able to detect and identify Pigment Blue 15, a phthalocyanine-class blue organic pigment that is commonly utilized in paints. Siegel et al. (26) have outlined the applications and types of possible examinations that can be performed on inks using LDMS during the questioned document examinations. Repp and Allison (27) used a combination of thin-layer chromatography, UV-visible spectroscopy, and LDMS to analyze and characterize dyes and pigments in inks used to label iron pipe that could be used to manufacture pipe bombs. LDMS has been used to examine pigments, colorants, and dyes in artistic/historical media. Grim and Allison (28) were able to identify various colorants in both water

color and oil-based paintings. This same group also identified several inorganic pigments used in historical manuscripts (29). The work by Wyplosz (30) provides an in-depth look at the power and utility of LDMS for the identification of organic pigments. Many of the pigments identified by Wyplosz, specifically quinacridones and phthalocyanines, find application in automotive coatings.

The purpose of this work is to explore the value of LDMS for the identification of organic pigments in automotive coatings.

Methods and Materials

Instrumentation

The LDMS system used was a PerSeptive Biosystems Voyager-DE Biospectrometry Workstation equipped with a pulsed UV laser (337 nm, 2 nsec pulses) and a 1 m flight tube. Data acquisition was carried out using both positive- and negative-ion spectrometry. The accelerating voltages utilized were 20 kV for positive mode and –18 kV for negative mode. The delay time, between the laser pulse and application of the ion-source accelerating voltage, was typically set at 100 nsec. Data from 50 laser shots were averaged to produce the reported spectra. Although most of the mass spectra shown here are in the m/z range of 10–1000, the range of time-of-flight MS is very large. For this particular instrument, ions have been detected above m/z 100,000 in MALDI-MS experiments.

Pigments

The following pigments were utilized for this study: Quinacridone Red Y- γ crystals (pigment violet 19-*Sun Chemical Sunfast Violet 19*), Quinacridone Magenta (pigment red 122-*Sun Chemical Sunfast Magenta 122*), Benzimidazolone Orange (pigment orange 36-*Sun Chemical Sunfast Orange 36*), and Copper phthalocyanine (phthalocyanine blue 15-*Sun Chemical Sunfast Blue 15*).

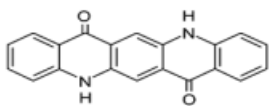
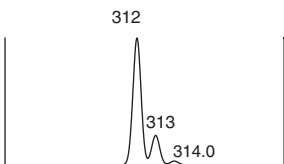
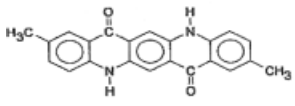
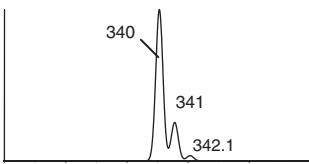
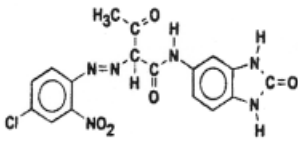
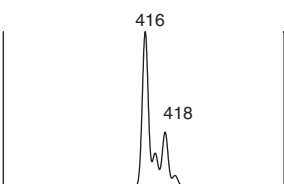
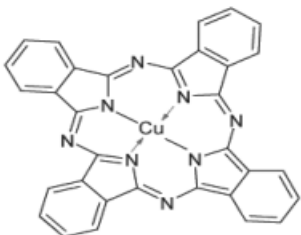
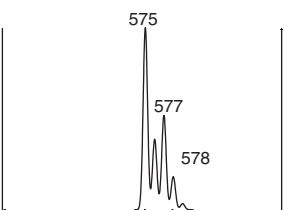
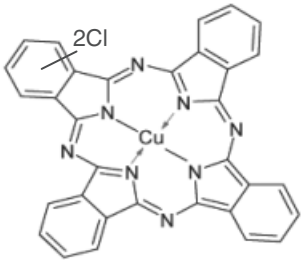
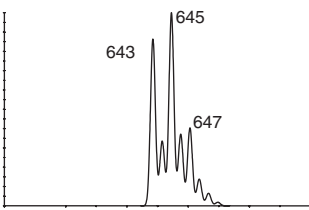
Automotive Paints

The automotive paints used for this project were drawn from in-house automotive paint collections at the New Jersey State Police (Office of Forensic Sciences, Hamilton, NJ) as well as sample panels from the Reference Collection of Automotive Paints (Collaborative Testing Services Inc. [CTS], Herndon, Virginia). For an in-depth discussion of the reference collection, the reader is referred to the work by Suzuki (17), which provides an excellent discussion of these samples. It should be noted that some of the panels that were utilized for this research are the same selections as those used by Suzuki and Marshall (13,14).

Sampling

Small paint chips can be introduced into this mass spectrometer, by using double-stick tape, to adhere them to a modified sample-introduction plate that has been used previously (22–27). Pigments, available in powdered form, would become dispersed throughout the instrument if introduced directly. To study laser desorption of simple pigments, they were mixed with a UV-curing polyester resin and a thin sample was made (Sun Cure Instant Resin, D. Sea International, Atlantic Beach, FL). Portions of hardened pigmented resins were then introduced into the instrument, handled as a paint chip.

TABLE 1—Pigment information.

Name	Structure	Theoretical Isotope Pattern
Name: Red Y Family: Quinacridone Formula: $C_{20}H_{12}N_2O_2$ MW: 312 g/mol		
Name: Magenta Family: Quinacridone Formula: $C_{22}H_{16}N_2O_2$ MW: 340 g/mol		
Name: Orange 36 Family: Benzimidazolone Formula: $C_{17}H_{13}ClN_6O_5$ MW: 416 g/mol		
Name: Blue 15 Family: Phthalocyanine Formula: $C_{32}H_{16}CuN_8$ MW: 575 g/mol		
Name: Dichlorinated Phthalocyanine Blue15 Family: Phthalocyanine Formula: $C_{32}H_{14}Cl_2CuN_8$ MW: 643 g/mol		

In the case of the reference collection samples, as the topcoat was also the color coat, the entire panel could be secured onto the sample plate and analyzed. In-house automotive samples were prepared by removing a shaving of the coating that penetrated through the clear coat to expose the underlying color coat, then securing the material on the modified sample-introduction plate using double-stick tape.

Instrument Calibration

In a time-of-flight MS experiment, ion velocities are measured indirectly by determining ion flight times. The distance traveled influences the time. When working with samples of various thicknesses, calibration of the m/z axis becomes important. To achieve this, a dot of ink from a pen that has been previously studied is applied onto the surface of each sample. Commonly applied is a dot of ink from a blue ballpoint pen that contains the dye crystal violet. When the laser impinges on this dot, known cations from the dye are generated and can be used for calibration.

Results and Discussion

The goals of this preliminary survey are to determine if pigments will yield ions in the LDMS experiment, if the ions formed are representative of the pigments, and if pigments can be detected in the complex matrix of actual automotive coatings. LDMS spectra will be shown for a variety of pigments, representing some important classes, either in simple matrices or in real automotive samples.

Quinacridone Red Y (Pigment Violet 19— γ Crystals)

The formula and structure for this red pigment is shown in Table 1. To determine if pigments do yield a useful mass spectrum in the LDMS experiment, a simple “paint” was made by adding this pigment to a simple polyester resin, and performing LDMS on the resulting dried matrix. Figures 1A and B show the positive- and negative-ion spectra that result when Quinacridone Red Y in polyester is irradiated with 337 nm light. Not only are ions readily formed, but also are related to the compound. In both the spectra,

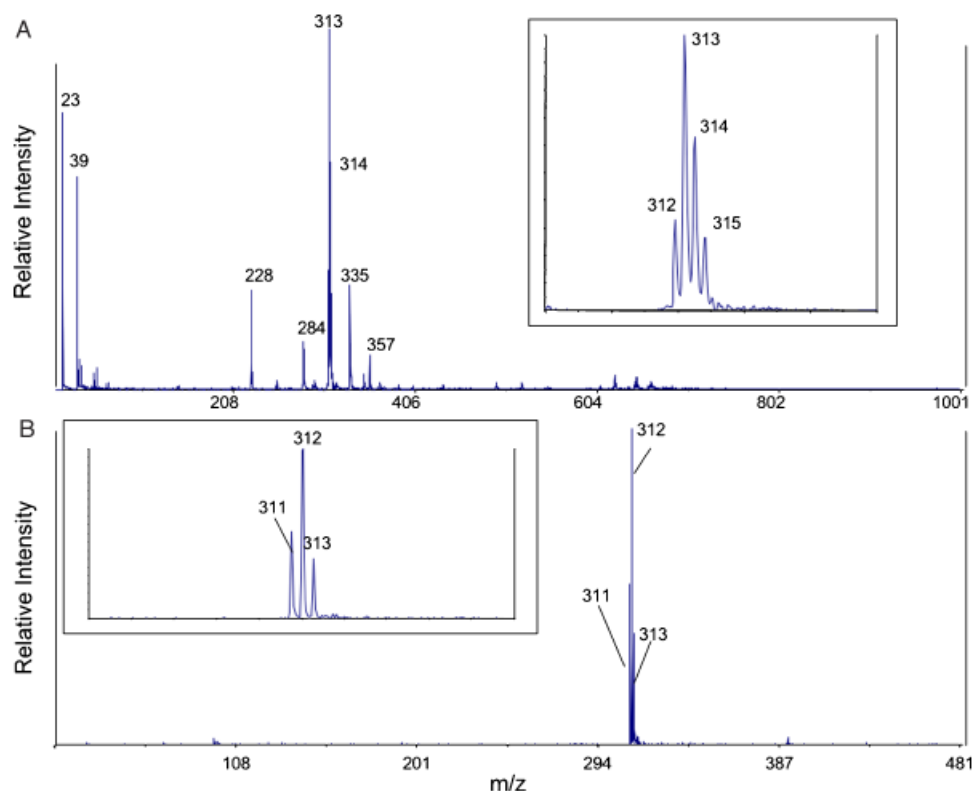


FIG. 1—(A) Positive- and (B) negative-ion laser desorption mass spectrometry spectra of Quinacridone Red Y in a polyester resin.

the largest peak represents the intact pigment molecules. The positive-ion spectrum contains low mass peaks at m/z 23 (Na^+) and m/z 39 (K^+). The negative-ion spectrum is exceedingly simple, containing peaks only representing the pigment.

For a neutral analyte, M, there are a number of ways that the molecule may be ionized in the LDMS experiment.



In the positive-ion mode, the molecule may be represented as an odd-electron molecular ion (reaction [1]), a protonated molecule (reaction [2]), or an adduct ion of an abundant cation in the sample such as an alkali metal ion (reaction [3]). In the negative-ion mode, molecules may be ionized as molecular anions (reaction [4]) or as deprotonated molecules (reaction [5]). There is insufficient information in the literature at this time to predict *a priori* as to which path a given molecule may take. The insets in Figs. 1A and B show the molecular ion regions of the positive- and negative-ion spectra, respectively. Table 1 shows the isotope pattern that is expected for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$. This is not what is observed. Consider the inset in Fig. 1A. The largest of the peaks is m/z 313, and thus represents the MH^+ form of the molecule. However, there is also a peak at m/z 312, which must represent the M^+ form. Thus, the peaks observed in the molecular weight region of the

spectrum represent two distinct chemical forms, the ionized molecule and the protonated molecule, with the MH^+ ions being formed with a higher probability than the M^+ ions. Similarly in the inset in Fig. 1B, there is a peak at m/z 312, which represents the molecular anion. The set of peaks seen must represent overlapping isotopic patterns for both M^- and $[\text{M} - \text{H}]^-$ ions, with the molecular anion formed with higher probability than the deprotonated form. Thus, the patterns observed are not as simple as the pattern shown for this analyte in Table 1, because the observed data represent the sum of two overlapping patterns, each offset by 1 Da.

A comparison of the positive- and negative-ion spectra can provide additional information. There are several peaks in the positive-ion spectrum. In most of the LDMS, performed on colorants such as organic dyes to date, molecules are usually desorbed intact with little fragmentation. If there are several peaks, do they represent several components? The simplicity of the negative-ion spectrum suggests that there is, likely, only one pigment present, so the positive ions formed with m/z values less than 312 may be fragment ions. The “fragment ion” at m/z 284 could be due to loss of CO from the intact molecular ion, M^+ :



While the fragment ion also could evolve from the protonated molecule, we suggest that it does so from the radical cation, as loss of carbon monoxide from ionized cyclic ketones is well known in electron impact ionization (31), where fragment ions evolve from radical molecular cations. Another peak of note in Fig. 1A is seen at m/z 335. The simple isotopic pattern matches that shown in Table 1 for the analyte. This peak represents the sodium ion adduct MNa^+ , which is a useful peak for confirming MW and elemental composition. If this sample represented an

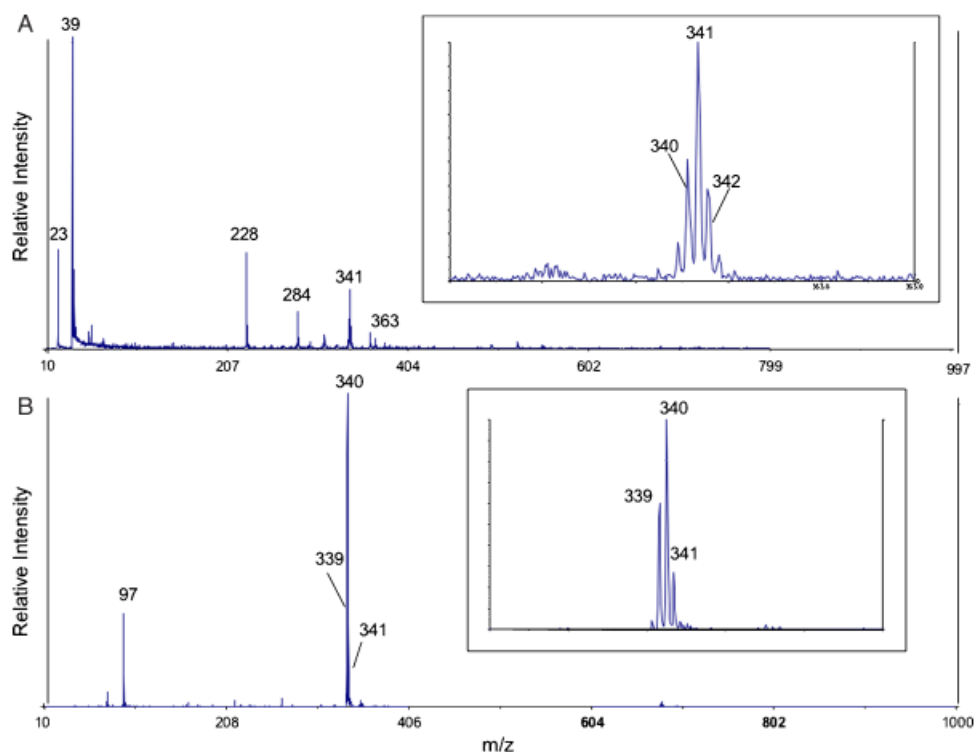


FIG. 2—(A) Positive- and (B) negative-ion laser desorption mass spectrometry spectra of QM in polyester.

unknown, one could interpret the information provided in many ways. As the isotopic patterns for M^+ and MH^+ overlap, it may be unclear if the compound has an MW of 312 or 313; however, a peak that is 22 Da higher than 313 suggests that m/z 313 represents a protonated molecule and 335 a sodium ion adduct. Thus, the isotopic distribution at m/z 335 becomes that which could be compared with that expected for a given analyte.

Quinacridone Magenta (Pigment Red 122)

Figure 2 shows the positive- and negative-ion LDMS spectra of Quinacridone Magenta, again in a simple polyester matrix. The insets show the molecular ion regions. If the spectra shown in Figs. 1 and 2 are compared, several observations can be made. In both, the negative-ion spectra are simpler. Both quinacridones generate MH^+ and M^+ ions, with the former being more abundant. Both generate M^- and $(M-H)^-$ ions, with the former being the dominant. Both form sodium adducts 22 Da above the MH^+ peak. From this simple comparison, these may be the trends for quinacridones; however, additional compounds should be studied before making any definitive conclusions. There are two peaks of interest in Fig. 2A (the positive-ion spectrum) at m/z 228 and 284. These peaks were also observed in Spectrum 1A. We have had experience with LDMS of many pigments using the same polyester matrix, and these peaks are observed in several spectra (not shown). We tentatively suggest that they must be, at least in part, due to the matrix.

Benzimidazolone (Pigment Orange 36)

In this instance, a very different pigment is studied, again in a simple polyester resin. For the reader to appreciate the simplicity of the spectra, all data have been shown for the first two pigments.

As the trends shown in Figs. 1 and 2 continue, with the negative-ion spectra providing the simplest and most informative data, from this point on, only the spectra which we believe to be most useful will be shown. In the case of Pigment Orange 36, the negative-ion spectrum is the most informative, and is shown in Fig. 3. The structure shown in Table 1 illustrates that benzimidazolone-class pigments significantly differ from quinacridones, in that they contain some single backbone bonds, rather than exclusively fused ring systems. Another characteristic worth noting is that this analyte pigment contains a chlorine atom. The two isotopes of chlorine, ^{35}Cl and ^{37}Cl , which exist in a 3:1 ratio, are clearly detected as shown in the isotope pattern for this pigment in Table 1. The negative-ion spectrum in Fig. 3 shows that the benzimidazolone molecules are ionized (see inset) as intact anions, M^- , consistent with the theoretical isotope distribution. The negative-ion spectrum also contains a dominant peak at m/z 171. Because of the relatively low mass of this peak, it is unlikely that this represents a second pigment. Instead, it is our belief that this is a fragment ion of the parent molecule. The proposed structure of this fragment ion is shown below the peak in Fig. 3. The radical molecular anion undergoes a low-energy N–N bond cleavage with an accompanying H shift from the departing radical. These are often described as a 1, 2-elimination. The ratio of the peaks at m/z 171 and 173 are consistent with this being a fragment ion that contains a chlorine atom. The peak at m/z 174 is apparently unrelated, and its identity is not yet known. It is interesting to note that a major pyrolysis product of benzimidazolone, determined by pyrolysis GC/MS, is 4-chloro-2-nitroaniline, $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)\text{NH}_2$, which corresponds to the cleavage of the same bond (10).

This example shows that benzimidazolone-class pigments can be detected by LDMS, they form M^- ions in the negative-ion experiment, the presence of halogens is apparent from the isotopic

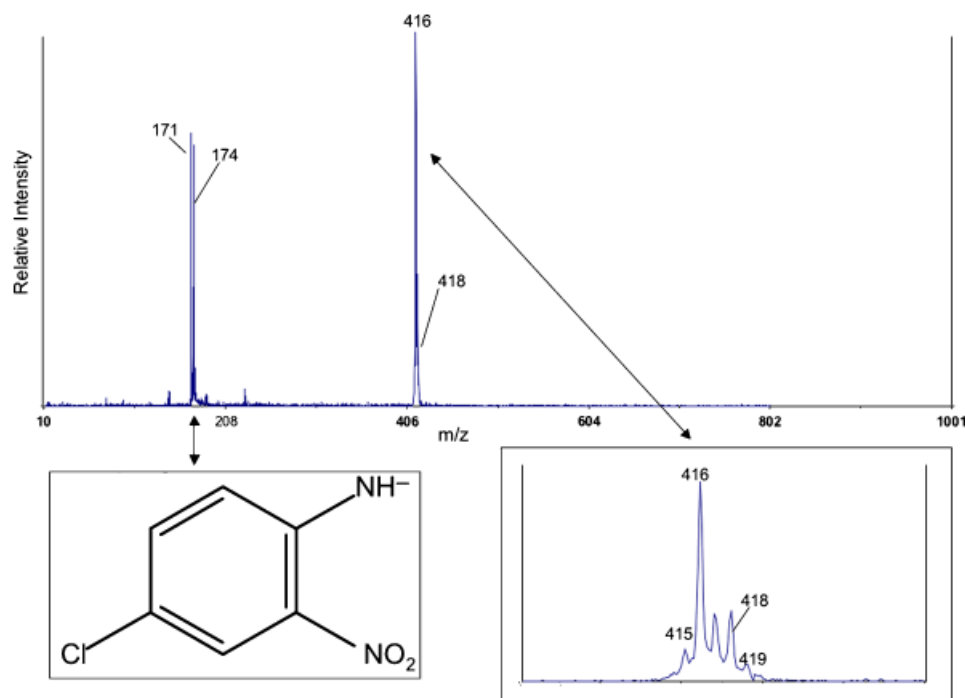


FIG. 3—Negative-ion laser desorption mass spectrometry spectrum of Pigment Orange 36.

pattern, and the ionized molecule can fragment to yield an abundant fragment ion.

Copper Phthalocyanine (Phthalocyanine Blue 15)

In comparison with the previously discussed pigments, phthalocyanine-class pigments represent a difference in not only pigment type but also size and complexity as well. The sample used was sample panel number DN87 0475 from the CTS reference collection of automotive paints. It is an actual automotive coating that has been used in production. As such, in addition to pigments, it also contains a binder, fillers, and other components that an actual paint would be expected to contain. The concentrations of the

pigments are therefore at the levels that one would find in real automotive paint samples. Although Suzuki has studied many of these CTS reference panels and identified several organic pigments by FTIR, as of yet, there is no published information on the identification of copper phthalocyanines in automotive coatings in this manner.

It should be noted that this pigment has a high molar absorptivity, and thus can yield intense colors at low concentrations when incorporated in an organic binder. In the context of automotive coatings, the presence of this pigment at such low concentrations would limit its detectability using a method such as FTIR, where the primary absorption would be coming from the more abundant binder and extender components. In contrast, when LDMS is used, the

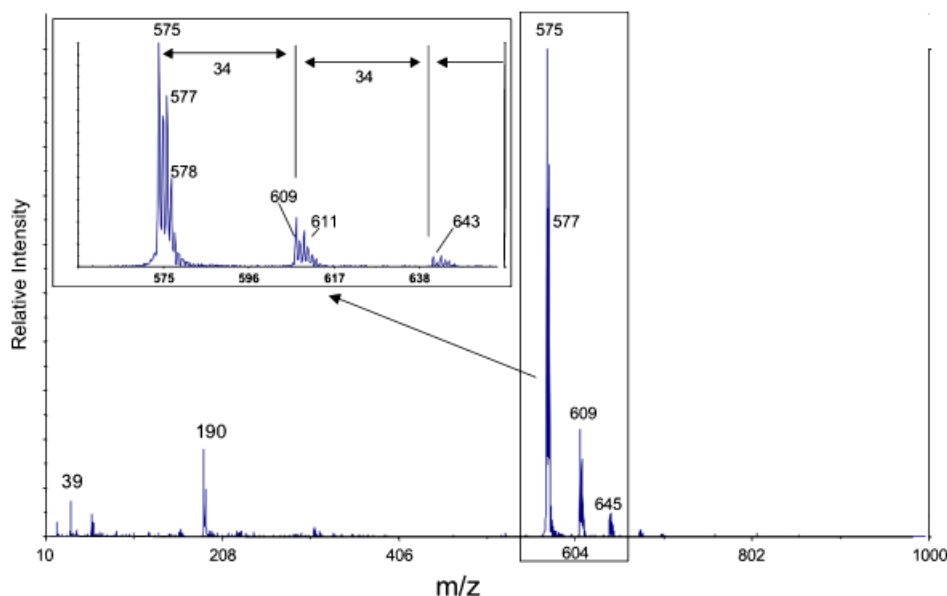


FIG. 4—Positive-ion laser desorption mass spectrometry spectrum of copper phthalocyanine.

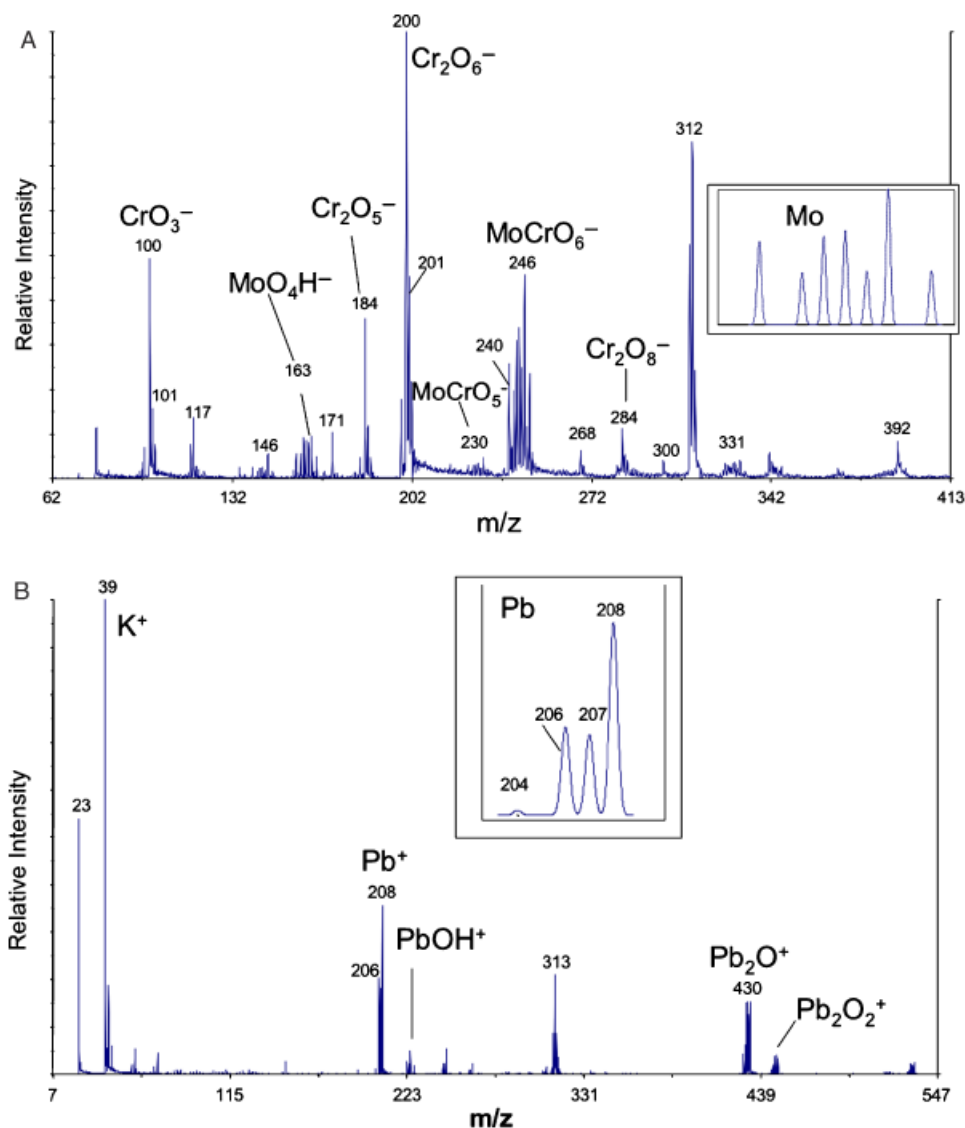


FIG. 5—Positive- and negative-ion laser desorption mass spectrometry spectra of PA76E007, a red CTS panel.

pigments will absorb the UV laser light with little to no interaction with the binder; thus, it is a selective method for detecting many colorants. (It has been suggested that, for some analytes, sample amounts as low as 10^{-20} g can be detected (32).)

Table 1 shows the structure and MW of copper phthalocyanine. Figure 4 shows the positive-ion mass spectrum of a CTS paint panel that was found to contain this pigment. The pigment yields a molecular cation, M^+ , with an excellent signal-to-noise ratio. The negative-ion spectrum (not shown) is similar, with the M^- ion as the only peak(s) in the spectrum.

Copper phthalocyanine can be chlorinated to shift the color. As more hydrogens are replaced with chlorines, the color of the pigment will shift from blue to green. As such, the perchloro-(fully chlorinated) copper phthalocyanine, $\text{C}_{32}\text{Cl}_{16}\text{CuN}_8$, is green. The spectrum in Fig. 4 shows the presence of minor amounts of the mono-, di-, and tri-chloro copper phthalocyanines. When an H atom is replaced by a Cl atom, each set of peaks is separated by 34 mass units. Note, as shown in Table 1, the isotopic patterns change as well with the addition of each chlorine. The theoretical isotope patterns match well with the actual data for each. Apparently, small amounts of the chlorinated pigments may be added for in-

creased stability of the blue base compound. Thus, we cannot only detect the pigment at the low levels used in automobile coatings but also detect the partially chlorinated forms that are present in even lower amounts. In other samples containing copper phthalocyanine, the chlorinated forms are detected as well, suggesting that the pigment is often distributed as a mixture.

CTS Reference Sample PA76E007

This sample is a red paint panel from the CTS collection. Analysis of this sample yielded both positive and negative ions, shown in Fig. 5, consistent with the presence of a pigment with an MW of 312. Suzuki previously determined the presence of Pigment Violet 19, a phase isomer of Quinacridone Red Y, in this sample. Therefore, the detection of this pigment in this study was expected. It should be noted however that the distinction between these two forms of the quinacridone can be accomplished using FTIR, whereas LDMS, providing only molecular weight and isotope data, would not be suitable for such a purpose.

The spectra in Fig. 5 are more complex than anticipated. The complexity of the spectra is suggestive of the possible presence of additional colorants. First, consider Fig. 5A, the negative-ion spectrum. There are two peaks at m/z , 100 and 200. These have been seen previously (28) in LDMS studies of PbCrO_4 , and have been identified as CrO_3^- and Cr_2O_6^- . The identification comes from m/z values and the unique isotopic pattern indicative of the presence of Cr. While ^{52}Cr is the major isotope, there is also a less abundant "A-2" isotope, ^{50}Cr . The peak 2 Da, lower than the major peak for each, is consistent with the presence of Cr in these ions; theoretical isotope distributions match the data obtained. There is a set of peaks in the range m/z 240–248, which could be due to a combination of species and overlapping isotopic patterns. It also happens to match the isotope pattern for the element molybdenum, which is shown as an inset in Fig. 5A. However, the most abundant isotope of Mo is ^{98}Mo , which does not account for the masses of the ions that contain molybdenum. As the presence of Cr and O has been determined, there are combinations of these atoms that would be consistent with this cluster of isotopic peaks, notably MoCrO_6^- . This could be considered as a complex such as $(\text{MoO}_3)(\text{CrO}_3)^-$, to link it to the simpler fragments such as m/z 100, CrO_3^- .

The positive-ion LDMS spectrum shown in Fig. 5B contains a cluster of peaks around m/z 208 which is consistent with the isotopes for the element Pb, and represents the Pb^+ species. Higher m/z peaks such as m/z 430 and 448 have masses and isotope distributions consistent with the assignments Pb_2O^+ and Pb_2O_2^+ . There are many peaks in the spectrum indicating the presence of lead.

Thus, the combination of positive- and negative-ion data indicate the presence of a metal oxide, containing lead, molybdenum, and chromium. Molybdate orange, $\text{PbSO}_4 \cdot \text{PbCrO}_4 \cdot \text{PbMoO}_4$, was

a pigment used in automotive coatings until 1986. XRD spectra match library data for molybdate orange as well.

The example demonstrates that, in the context of an actual automotive paint sample, both organic and inorganic pigments can be simultaneously detected. We note that Suzuki (18) confirms the presence of this inorganic pigment in this sample as well. Organic pigments exist as distinct molecules, and molecular ions are generated in this experiment. In contrast, inorganic pigments do not contain distinct molecules; therefore, the crystal lattice fragments in unexpected ways upon laser irradiation to yield an interesting set of anions and cations. As of yet, sufficient work has not been carried out in the area of LDMS of inorganic compounds to develop predictive capabilities in terms of what may be expected. In this case, the presence of chromium was apparent from the negative ions and lead from the positive ions.

Contemporary Automotive Coating

A portion of a fender from a Red 1999 Pontiac Grand Am was obtained. The clear coat was shaved off to expose the color coat. The positive-ion LDMS spectrum is shown in Fig. 6A. Figure 6B shows an expansion of the m/z 280–430 region. The peaks at m/z 312/313 again suggest the presence of Quinacridone Red Y (with accompanying fragment ion at m/z 284, and Na^+ adduct at m/z 335) designated as M in the figure. There is also a set of peaks in the m/z 350 region of the spectrum. A second compound (M') could have an MW of 356, so the peaks could represent M'^+ at m/z 356 and $\text{M}'\text{H}^+$ at m/z 357. The number of higher mass isotopes suggests the presence of chlorine atoms. Rather than attempt to sort out the overlapping peaks in this region, the isotopic pattern is clearly revealed in the $[\text{M}' + \text{Na}]^+$ peaks at m/z 379, 381, etc. The

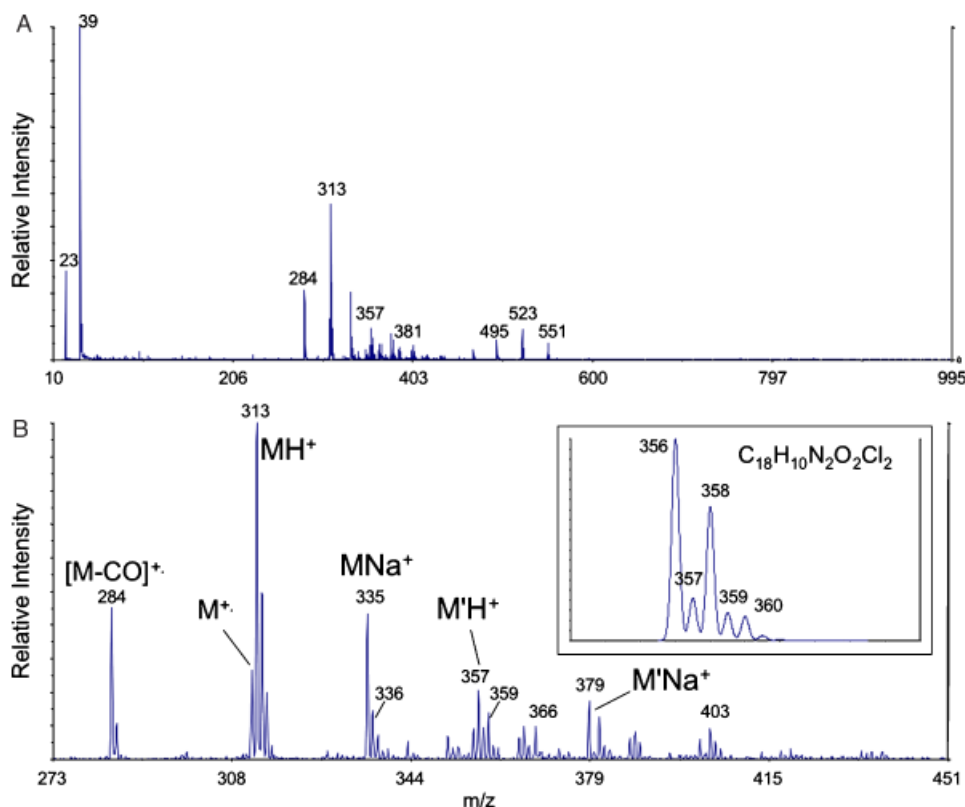


FIG. 6—(A) Positive-ion laser desorption mass spectrometry spectrum of a fender panel from a 1997 Pontiac Grand Am and (B) expanded view of a portion of the spectrum shown in (A).

isotopes are not consistent with the 3:1 pattern indicative of a Cl, but rather with the 9:6:1 pattern indicative of the presence of two chlorine atoms. The presence of two Cl atoms, the MW of 356, and the fact that the color is red, is consistent with the assignment of DPP red Bo as the pigment responsible for these mass spectral peaks. The compound $C_{18}H_{10}N_2O_2Cl_2$ has the theoretical isotope pattern as shown in the inset of Fig. 6B.

Conclusions

When pigments, either in a simple or complex mixture, are irradiated with pulsed UV radiation, the pigments selectively absorb the energy, and are desorbed and ionized. With no sample preparation, positive- and negative-ion mass spectra of the ions formed can be collected. At the pigment levels used in actual car paint, signals can be generated with high signal-to-noise ratios. Inorganic pigments in the presence of organic pigments can be detected. While one could easily generate an LDMS library of automotive coating samples, it is important to note that these mass spectra can be interpreted. Collected data (pigment color, MW, isotopic information, tendency to form fragment ions) were used with information on available and commonly used organic pigments to make molecular identifications.

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