Beyond the Surface of Architectural Paint: A Comparative Analysis Using DART-MS and Spectroscopic Techniques

Geraldine Monjardez[a]*, PhD, John Laetsch III[a], MS, Morgan Carpenter[a], MS, Alleigh N. Couch[a], MS Patrick Buzzini[a], PhD and J. Tyler Davidson[a], PhD

[a] *Department of Forensic Science, College of Criminal Justice, Sam Houston State University, Huntsville, TX, U.S.*

Sam Houston State University

INTRODUCTION

Architectural paint is a form of transferred trace evidence encountered in forensic investigations, particularly in cases involving forced entry. Although no standardized analytical protocol exists, examinations typically progress from non-destructive to increasingly invasive techniques.

DART-MS is a direct mass spectrometry approach that has gained popularity for the analysis of trace materials in recent years, and although its use for paint analysis has been explored, these studies focused on automotive paint rather than architectural paint [1,2]. Despite shared characteristics, architectural and automotive paints differ in key chemical and physical properties. Architectural paints are typically single-layered paint systems and generally do not contain cross-linking compounds (i.e., melanine, epoxy), whereas automotive paints are multilayer systems with complex resin formulations, additives, and pigments.

In light of increasing interest in the forensic application of direct analysis in real time-mass spectrometry (DART-MS) for trace evidence examination, this study assesses the capabilities of DART-MS relative to Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) for the analysis of architectural base paints and their mixtures. This study also investigates the potential integration of DART-MS into a paint analysis workflow as a complementary technique.

MATERIALS & METHODS

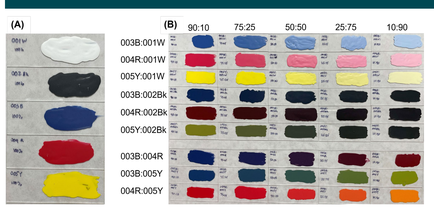

Figure 1: Five base colors (white, black, blue, red and yellow) **(A)** and mixed paint samples smeared onto labeled glass microscope slides **(B)**.

Paint Mixtures Preparation: Forty-five binary mixtures were created in ratios of 90:10, 75:25, 50:50, 25:75, and 10:90 (**Figure 1B**) from five base color paints (**Figure 1A**) in known proportions. The base colors and mixtures were applied to individual glass microscope slides and allowed to air dry (**Figure 1**).

Sample Preparation and Instrumental Set-Up for DART-MS: Thin paint shavings were placed on QuickStrip™ mesh (**Figure 2**) and analyzed using a DART JumpShot® ion source connected to an Agilent 6530 Q-TOF mass spectrometer equipped with a Vapur® API interface. Analyses were conducted in both positive and negative ionization modes with a gas heater temperature of 350 °C and 500 °C for a total of four spectra per replicate.

Figure 2: Samples prepared on QuickStrip™ mesh showing the placement of paint chips within position **(A)** and overall **(B)**.

Sample Preparation and Instrumental Set-Up for micro-FTIR: Paint shavings were rolled flat using a roller knife before being transferred onto a polished sodium chloride pellet. Seven spectra were collected for each paint using a micro-FTIR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. Each spectrum was collected in transmission mode using 128 scans, a spectral range of 4000-650 cm^{-1}, and a resolution of 4 cm^{-1}.

Sample Preparation and Instrumental Set-Up for SEM-EDS: Paint shavings were placed onto SEM stubs covered with carbon tape. Elemental composition maps were collected at three locations for each sample under high vacuum using a magnification of 1000x, an accelerating voltage of 15 kV, a spot intensity of 70, and a working distance of 10 mm.

RESULTS & DISCUSSION

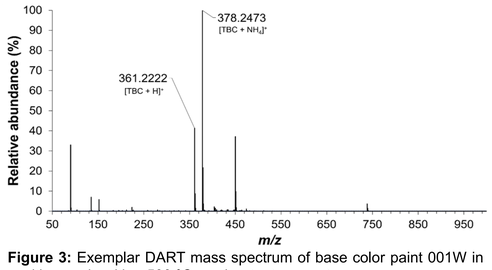

Figure 3: Exemplar DART mass spectrum of base color paint 001W in positive mode with a 500 °C gas heater temperature.

- A characteristic ion for black base paint (*m/z* 162) was detected in mixed paint replicates containing ≥10% 002Bk (**Figure 5**).

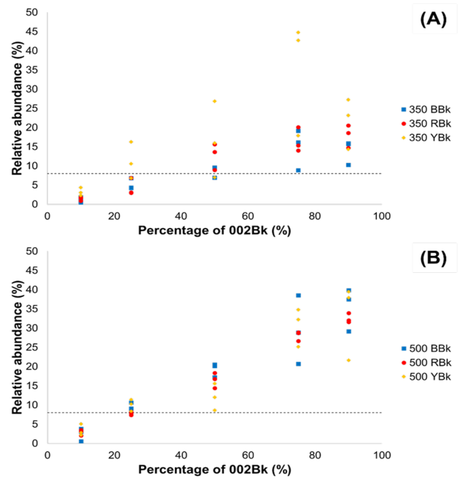

Figure 5: Comparison of the relative abundance of the ion at *m/z* 162 as a function of percentage of 002Bk paint in mixed paints containing base color paints 003B and 002Bk (blue square), 004R and 002Bk (pink circles), and 005Y and 002Bk (yellow diamonds) at 350 °C **(A)** and 500 °C **(B)**.

- DART-MS spectra of 001W (**Figure 3**) were generally characterized by a base peak at nominal *m/z* 378, with an additional ion at nominal *m/z* 361.
- These ions were determined to be the ammoniated and protonated molecules, respectively, of tributyl citrate (TBC), a common plasticizer.
- Positive mode DART mass spectra, indicated substantial differences between base color white (**Figure 3**) and the other four base color paints (**Figure 4 A-D**).
- Positive mode DART mass spectra shown in **Figure 4 A-D** were generally characterized by a base peak at nominal *m/z* 341, which was determined to be the protonated molecule of dioctyl maleate (DOM), used both as a plasticizer and a comonomer in paints.

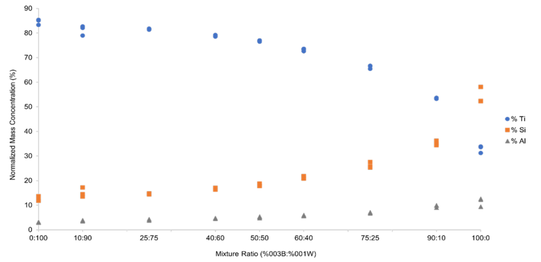

Figure 6: Plot of normalized mass concentrations for titanium (blue circles), silicon (orange squares), and aluminum (gray triangles) in mixed paints containing base color paints blue and white.

- **Figure 6** indicates that, based on SEM-EDS analysis, as the mixture composition transitioned from predominantly 001W to predominantly 003B, titanium concentrations decreased while silicon concentrations increased.

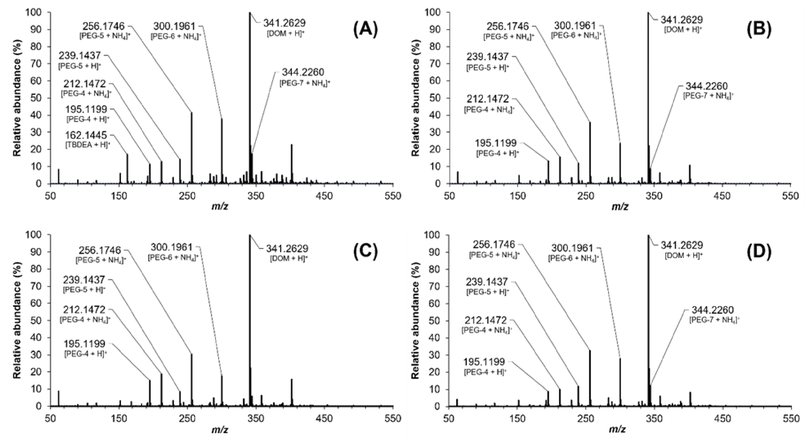

Figure 4: Exemplar DART mass spectra of base color paints 002Bk **(A)**, 003B **(B)**, 004R **(C)**, and 005Y **(D)** in positive mode with a 500 °C gas heater temperature.

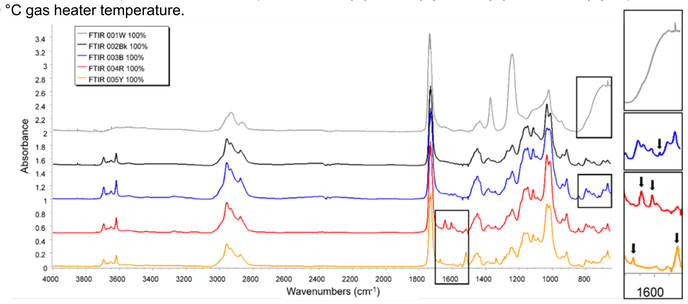

Figure 7: Spectra of base color paints. The gray spectrum represents 100% Ultra White paint (001W), the black spectrum represents 100% Noir paint (002Bk), the blue spectrum represents 100% Classic Royal Blue paint (003B), the red spectrum represents 100% Classic Red paint (004R), and the yellow spectrum represents 100% Sunny Jonquil paint (005Y). Insets on the right highlight notable absorption bands in the spectra.

- As shown in **Figure 7**, characteristic absorption bands were observed in the base paints, including talc at 1023 cm^{-1} and TiO_2 at 700 cm^{-1} (001W), PR 254 at 1646 and 1608 cm^{-1} (004R), and PY 74 at 1674 and 1518 cm^{-1} (005Y).

CONCLUSIONS

- DART-MS successfully detected a range of organic compounds commonly present in architectural paint, including plasticizers, additives, and solvents, which were not identified using FTIR spectroscopy or SEM-EDS.
- DART-MS demonstrated the capability to detect a characteristic ion at a nominal *m/z* 162, associated with the black base paint, in mixtures containing concentrations above 10% at both 350 °C and 500 °C, unlike FTIR and SEM-EDS.
- FTIR spectroscopy proved effective in identifying both organic and inorganic components within the base paints and their mixtures, including binders, pigments, and extenders.
- SEM-EDS demonstrated enhanced sensitivity for trace-level inorganic compounds, also informative of pigments and extenders.
- The complementary chemical information provided by all three techniques underscores the added value of DART-MS in forensic paint analysis, particularly for detecting organic components and enhancing mixture discrimination.

REFERENCES

[1] M. Marić, J. Marano, R.B. Cody, C. Bridge, DART-MS: A New Analytical Technique for Forensic Paint Analysis, Anal Chem 90 (2018) 6877–6884. https://doi.org/10.1021/acs.analchem.8b01067.

[2] T.-H. Chen, S.-P. Wu, Forensic applications of direct analysis in real time (DART) coupled to Q-orbitrap tandem mass spectrometry for the in-situ analysis of pigments from paint evidence, Forensic Sci Int 277 (2017) 179–187. https://doi.org/10.1016/j.forsciint.2017.06.001.

ACKNOWLEDGEMENTS

The authors would like to thank the SHSU Department of Forensic Science for the use of their laboratory and equipment and the SHSU Microscopy Center and Daniel Doucet, Microscopy Lab Coordinator, for their help with the SEM-EDS data collection.

Interested in learning more about this study?

Department of Forensic Science
College of Criminal Justice
forensics.shsu.edu