Chromatography-free analysis of pigments by high resolution mass spectrometry with direct sample introduction

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Introduction

Analysis of paint and pigment samples can give detailed information as to the origin and history of the object. Frequently these samples can be very limited in quantity; whether from a valuable painting or historical object, or from a forensic sample. Therefore, a method that can quickly analyze these samples with a limited amount of sample prep is desirable. The absence of chromatography decreases the time needed for analysis, while increasing the possible solvents and solutions used.

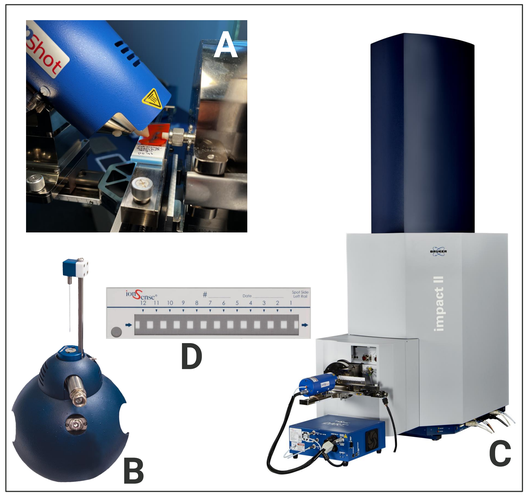


Fig. 1) A – JumpShot DART source with 45-degree module for ionizing surfaces. B – APCI source with Direct Ionization Probe (DIP) attachment. C – Bruker impact II QTOF mass spectrometer with DART attached. D – QuickStrip card used for spotting liquid samples for DART introduction.

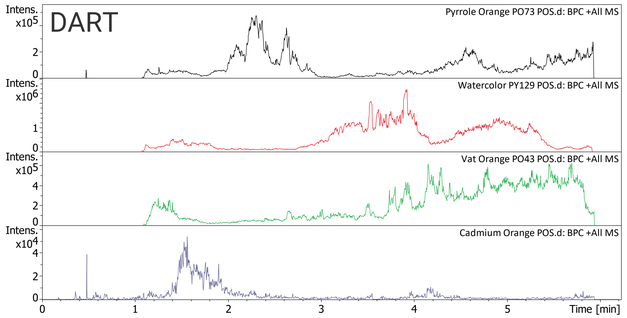
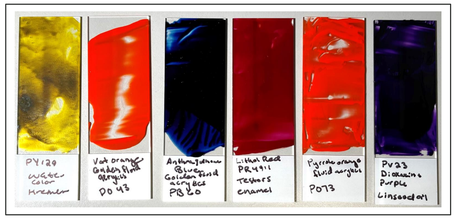


Fig. 2) Chromatograms from DART scanning across the painted slides. The DART was scanned at 0.3 mm/s across the slide with a gas temperature of 450° C. Samples showed heterogeneity with spectra changing across the length of the slide.

Methods

Sampling was conducted by introducing both solid paint and pigment samples and samples in solution. For solids, a small amount of sample is applied to a glass capillary (consumable) and introduced to the ion source. Atmospheric pressure chemical ionization (APCI) and direct analysis in real time (DART) sources were used. Vaporizer temperature is set between 200 and 470 ˚C to facilitate desorption off the capillary and gas phase introduction to the instrument. Ionization of paint directly from glass slides was possible with the DART source. Ionization occurs through coronal discharge or plasma generated metastables for APCI and DART respectively. All spectra were collected with a Bruker impact II quadrupole time-of-flight mass spectrometer.



Slides painted with a variety of paints with different pigments. Watercolors, linseed oil, enamel, and acrylic paints were all tested. Slides are standard glass 1x3" microscope slides.

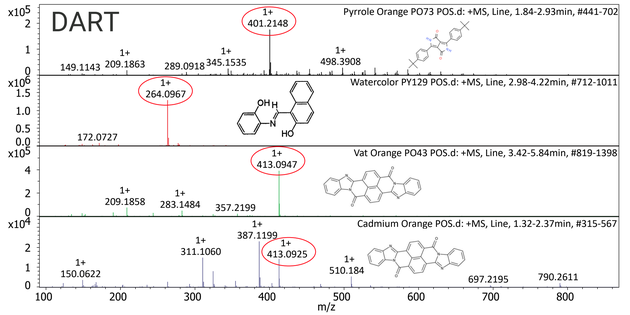


Fig. 3) Spectra from 4 different paint samples collected with DART ionization. In each the parent [M+H]+ ion is present from the main pigment, as well as other peaks that come from the binders and other materials in the paint samples.

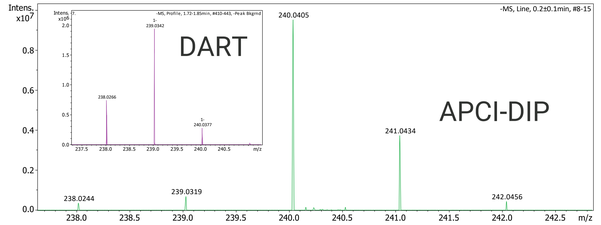


Fig. 4) Spectra of Alizarin collected with the APCI-DIP source and DART (inset) in negative ion mode. The parent [M-H]- peak is present at 239.0319, but the pattern is a combination of various other ions including M-. A similar pattern is seen in the DART spectrum.

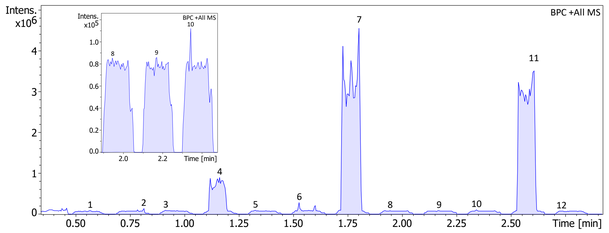


Fig. 5) 12 samples can be collected in one run using the DART QuickStrip module. Inset shows the spacing between subsequent DART pulses, enabled by the JumpShot source. The intense signals at 4, 7, and 11 are carminic acid, purpurin, and quinacridone respectively.

Results

>DART QuickStrip with Pigment Solutions

Pigments were dissolved or suspended in methanol and spotted onto a DART QuickStrip. The anthroquinone pigments gave the best result from a solution in both positive and negative ion modes.

>DART Direct Ionization of Paints

The linear rail was set up to hold glass slides directly under the entrance to the MS source for maximum signal. A slow scanning speed across the slides demonstrated differences in the spectrum based on paint thickness and the amount of heat applied to the slide. Some paints showed a consistent base peak while scanning, while others showed distinct peaks in the chromatogram. A high temperature of 450° C was used to achieve ionization from the paints; however, this temperature may be too high for some classes of paint such as watercolor and caused some burning of the samples.

>APCI Direct Ionization Probe

APCI using direct probe also showed good results, particularly for small solid samples. This is a good option for analysis of real historical objects as sample is often very limited. Either a solid or liquid applied to the DIP capillary produced spectra for select pigments. A mixture of different ions, including [M-H]-, M-, and others can make interpretation of spectra difficult due to overlapping isotope patterns. However, these patterns are consistent and indicative of the pigment present. Spectral library matching can be used to identify these patterns.

Summary

- APCI-DIP and DART are both viable methods for direct analysis of pigments and can be swapped quickly on the same instrument
- DART can be used to ionize directly from surfaces, simplifying sample preparation
- APCI-DIP works well for small sample amounts
- High resolution mass spectra collected from both sources enables accurate identification of pigments

DART/APCI QTOF MS