Specac

Application Note

Watching Paint Dry, ultra-long duration experiments using the Arrow consumable ATR

Specac Quest and Arrow ATR

Introduction

Oil based paints dry by a process of autoxidation, where an oxygen molecule is added between two unsaturated fatty acid chains to form a polymeric structure. The paints themselves are complex mixtures of chemicals, including pigments, oils and other components. FTIR spectroscopy allows for these components to be probed and can be used to gain insights into the drying process.

The ASTM method STP1119 [1] describes various methods for the analysis of paint by FTIR spectroscopy. One such method looks at time-resolved spectroscopy of samples painted onto KBr windows, with spectra recorded of the drying paints every two hours over multiple days. Until recently, transmission spectroscopy offered clear advantages over ATR spectroscopy for the study of such long duration experiments. The use of multiple KBr windows allows many similar experiments to be run side by side, whilst the cost of a diamond ATR puck would limit the analyst to one sample at a time. The advent of low-cost consumable ATR slides opens the door to apply the methods describe in the standard to ATR spectroscopy. Here we investigate the drying of linseed oil based paints with various colour pigments.

Silicon ATR consumable technology helps you zero in on your analysis. Designed for the Quest™ ATR accessory, Arrow™ allows rapid assessment of a range of liquid analytes.

- Long duration ATR experiments.
- Batch sample preparation.
- Archive samples.
- Prevent sample cross contamination.
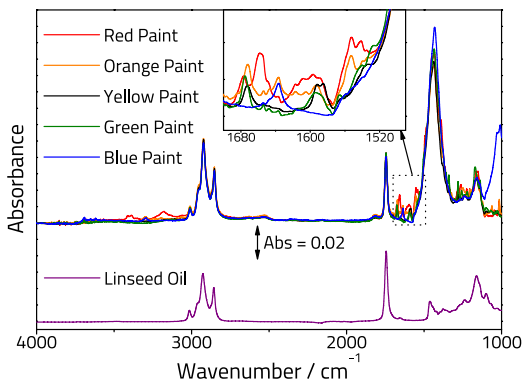- Remote sample preperation.

Figure 1: *Spectra of linseed oil based paint with various different pigments immediately after application. Shown on an offset scale is a spectrum of pure linseed oil. Inset: zoomed in section showing unique differences between the pigments in the region 1500-1700 cm⁻¹.*
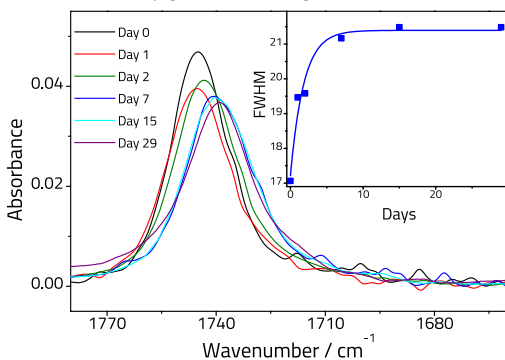

Figure 2: *Time resolved spectra showing the evolution of the carbonyl peak from the linseed oil over multiple days as the oil polymerises. Inset: Peak width vs. time showing a broadening as the paint sets. The blue line is an exponential fit line with negative preexponential factor.*
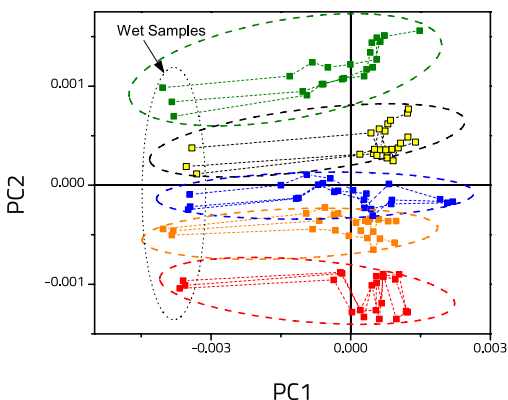

Figure 3: *Principal Component plot showing 3 samples of each pigment recorded on an Arrow slide over 1 month.*

Experimental

A set of five linseed oil-based paints were obtained with different coloured pigments. A small amount of each was painted onto the silicon chip of an Arrow slide, taking care to fully cover the chip with sample. Each pigment was prepared 3 times (15 samples total). Spectra were then recorded over multiple days as the paint sample set. A reference arrow slide (chosen at random) was used as a background measurement immediately before each measurement. Spectra were recorded on a commercially available spectrometer fitted with a Quest ATR accessory at a resolution of 4 cm^{-1}. For each time point, spectra of the Arrow slides were recorded in a randomized order.

Lorentzian band fitting regression analysis was performed using a standard statistical analysis package to extract the full-width half-maximum (FWHM) for the carbonyl peak, whilst a different analysis package was used to perform principal component analysis. Spectra were pre-processed first by performing EMSC correction, and then obtaining the second derivative. Analysis was restricted to the region of 2000-1500 cm^{-1}, which was found to give a good correlation of the components to experimental parameters.

Results and Discussion

Figure 1 shows the spectra of 5 paint samples immediately after they were applied to the Arrow ATR system. For reference, a pure linseed oil sample is also shown on an offset scale. The major spectral features of the paint samples correlate to the linseed oil base, with a saturated C-H Stretch at 3000-2800 cm^{-1} and a C=O stretch at 1744 cm^{-1}. An intense band at 1461 cm^{-1} is common to all paint samples but is not present in Linseed oil. This peak is tentatively assigned to a carboxylate group, although it is not clear which component of the paint it comes from.

ASTM method STP1119 describes a method of collecting time-resolved spectra. Figure 2 demonstrates how a similar method can be applied to these paint samples, showing the evolution of the carbonyl peak from the linseed oil component over one month of drying time, at room temperature, for a blue paint sample. As the linseed oil polymerises via oxidation the chemical environment becomes more heterogenous owing

to many possible oxidation pathways. Consequently, the C=O peak broadens and there is a slight shift to lower wavenumber, indicative of a weakening of the carbonyl bond. This agrees with previous literature reports from transmission measurements [2]. The inset figure shows the FWHM extracted by regression analysis, fitting to a linear peak shape. Most of the changes occur within the first week of drying, although the paint will continue to oxidise for a long time after.

Spectra were recorded for all the different paint pigments over the course of one month. PCA analysis was then performed on these spectra as shown in **Figure 3**. PC1 was found to correlate well with drying time. Wet samples start on the left-hand side and the dashed lines show their progression towards the right-hand side of the plot by day 29. PC2 was found to correlate to the colour pigment, and the dashed circles indicate the distribution of points from each colour.

Conclusion

We have demonstrated the suitability of the Arrow silicon ATR system for batch, long-duration experiments on paint samples following the same principles as ASTM STP1119, a commonly used transmission method. Arrow makes preparing sample batches for ATR measurement feasible for the first time and is a simple and cost-effective alternative to using multiple KBr windows for this task. We have also shown that spectra recorded on Arrow are amenable to spectral processing using chemometric tools such as PCA.

References

[1] W. Golton, ed., Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems. (West Consho-hocken, PA: ASTM International, 1992), https://doi.org/10.1520/STP1119-EB

[2] J. Weerd, A. Loon, & J.J. Boon, *Stud. Conserv.*, **50**, (2005), 3-22, https://doi.org/10.2307/25487713
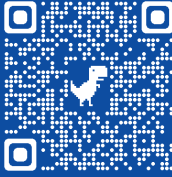
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