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Original article

The effect of oil binders on paper supports via VOC analysis

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ABSTRACT

The effect of the presence of drying oils in paper supports on the rate of cellulose degradation is investigated in a novel manner using Solid Phase Micro-extraction (SPME), which is employed to analyse volatile organic compounds (VOCs), emitted from oiled paper. This technique is applied as a non-destructive means of analysing original works of art on paper, in order to detect volatile cellulose degradation products. It is also applied to artificially aged paper samples with and without oil, in order to investigate the extent to which the presence of drying oil accelerates the degradation of cellulose. Furfural and other volatile cellulose degradation products containing a furan ring are selected as representative cellulose degradation products to be measured for the purpose of the investigation. It is demonstrated, by the finding of increased emissions of the selected compounds, that the presence of drying oils accelerates the thermal and oxidative degradation of cellulose in cotton paper and two types of wood pulp based papers.

1. Research aims

We have been particularly concerned [1] with a collection of works in the National Gallery of Greece in Athens, which includes oil paintings on paper and oil-based ink prints on paper and contains works by important 19th century and early 20th century Greek artists, such as N. Gysis, N. Lytras, K. Volanakis, K. Parthenis and K. Maleas all of which present particular problems, associated with the absorption of the oil binder by the paper, such as; discoloration, reduction of mechanical strength and embrittlement of the support. We wished to investigate whether the presence of drying oils in paper accelerates cellulose degradation. Our approach in this current work was to use Solid Phase Micro-extraction (SPME), a solvent-free sample preparation technology for analysing volatile organic compounds (VOC).

This technology was applied as a non-destructive means of analysing works of art on paper to detect volatile cellulose degradation products and also was applied to mock-ups in order to investigate the extent to which the presence of drying oil accelerates the oxidative thermal degradation of cellulose. Furfural and other volatile cellulose degradation products containing a furan ring were chosen as marker compounds. The immediate aim here was to provide further information regarding paper degradation in the presence of oil, using SPME analysis of VOC and a comparison with changes in pH and mechanical strength of our samples.

2. Introduction

2.1. Drying oils on paper

Works of art on paper containing oil-based media degrade more rapidly than works where aqueous paint binders are used [2]. Problems, associated with the oil binder have been attributed to the oxidation of the paper support [3,4] or the oxidation of the oil medium [5]. Some scientific evidence has been added to these claims via pH measurements [6,7], which showed that the supports became notably acidic, even when there was no intense discolouration or embrittlement [6]. Vincent Daniels [8,9] showed by the Russell effect that free radicals were present around linseed oil stains in paper, demonstrating that oxidation was taking place.

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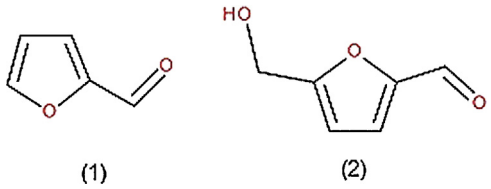

Fig. 1. Structures of furfural (1) and 5-(hydroxymethyl) furfural (2).

Elfecky and Hassan [10] measured; tensile strength, elongation on break, pH and colour by the 'CIELab' system, of mock up paintings on Fabriano paper. They compared paper coated with oil paint having a linseed oil coat before the paint and paper with animal glue based ground before the oil paint, the former being stronger at first but both deteriorating on ageing.

2.2. Volatile organic compounds as cellulose degradation products

It has been established [11] that oxidative and thermal degradation of cellulose can give furfural (1) and derivatives of furfural such as 5-(hydroxymethyl) furfural (HMF) (2) (Fig. 1). Fagerson [12] also lists other furans as degradation products including 2-methyl furfural, 2-methyl furan, 2-ethyl furan and 2-propyl furan, and he reports a possible route from carbohydrates to HMF during thermal degradation. Loss of formaldehyde from HMF then leads to 2-Furfural. More recently, Scheirs et al. [13] have reviewed other possible mechanisms for thermal degradation of cellulose to furfural and HMF, one via levoglucosan. They then propose an alternative mechanism for the acid catalysed hydrolytic thermal degradation of cellulose to furfural derivatives (Fig. 2) after demonstrating that the route via levoglucosan was not the most favoured route. Several researchers have studied the effects of mineral oils on Kraft paper, a combination used as an insulator in electrical transformers [14]. It is reported that furfural and related compounds could be used as indicators to detect the thermal degradation of cellulose and hemicelluloses within the paper. Interestingly, it is noticed that a combination of air, paper and mineral oil gave off the indicators at a greater rate than paper and mineral oil alone [14,15] and that oxygen was absorbed during the reaction, indicating that oxidative as well as thermal degradation was involved [14]. The presence of 4% moisture also increased the rate of degradation [14].

Contact and headspace-SPME has been successfully employed to track VOC emitted from pure cellulosic and ligno-cellulosic papers, both original and artificially aged, book and archival material [16–21]. The degradation products found [20,21] included aromatic hydrocarbons, an homologous series of alkanes, an homologous series of aliphatic aldehydes, an homologous series of aliphatic carboxylic acids, and several furan derivatives including furfural and 5-methyl furfural, the latter being more prevalent with ageing at 90 °C and 100% relative humidity than with dry ageing at 90 °C. Vanillin was also emitted as a lignin degradation product [20,21]. Clark et al. [22] recognised that paper contains some natural lipids. They claimed that the series of aldehydes found were derived from the fatty acids in the lipids. Other researchers have specifically measured furfural emissions [23] or furfural and acetic acid [24,25] emissions to monitor degradation in paper based collections. However, crucially, none of these studies had considered the effects of drying oils on paper.

Because of the problems associated with the collection being studied, we were particularly interested to see if the addition of drying oils to paper would accelerate cellulose degradation.

Here we chose to study several different papers and to age them at 90 °C and at a 77% humidity level. This humidity level was chosen for experimental reasons since it is given by saturated sodium chloride solution at 90 °C [26] and by dropping the paper samples into such a solution within the headspace vial after ageing we obtained a maximum recovery of VOC's for analysis. This is explained by the 'salting out effect' [27] which helps to expel the volatile organics, out of the aqueous phase, into the vapour phase from which they are then collected by the SPME needle. Also a 77% humidity level is expected to slightly exaggerate the results [28] compared to the standard 50% standard RH maintained in museum storage areas. We also sought to analyse works of art, containing oil on paper, in a non-destructive way for volatile organic compounds by SPME analysis to compare the emissions with that from old book papers [21] and with our own humid ageing tests.

3. Materials and methodology

3.1. Analysis of binding media in works of art

The nature of the binding media was established via methylation GC-MS techniques using TFTMTH as described and investigated by others [29,30].

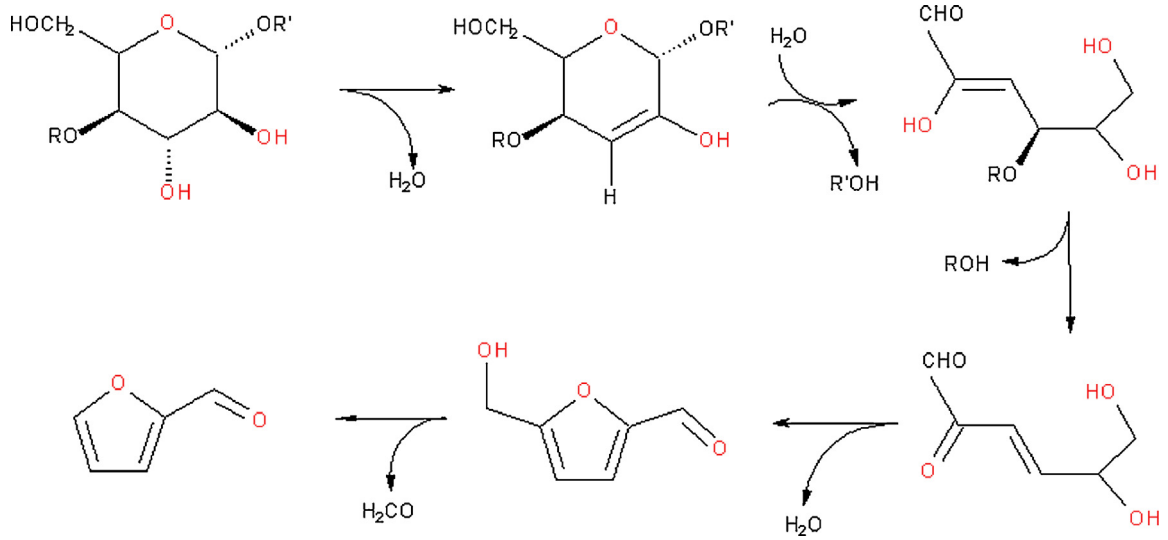

Fig. 2. Proposed route to 5-(hydroxymethyl) furfural and furfural from cellulose.

Adapted from Scheirs et al. [13].