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OIL BASED MEDIA ON PAPER: INVESTIGATING THE EFFECT OF OIL MEDIUM ON THE PAPER SUPPORTS VIA VOC EMISSION ANALYSIS.

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Abstract

The effect of oil binders on the paper support of an artwork is investigated through the analysis of volatile organic compounds (VOCs) emitted from artificially aged cotton and wood based paper strips impregnated with linseed oil, as well as areas of damage on original oil sketches, studies and b/w wood cut prints, using head space-solid-phase microextraction (HS-SPME) coupled with a gas chromatography/mass spectrometry (GC/MS). Considering that degradation of oil substances and paper results in common by-products, monitoring of certain furan and furfural derivatives, which are exclusively associated with paper degradation, is discussed.

Introduction

Oil binders have been widely used in various works on paper supports, such as oil sketches, oil studies, drawings and paintings, as well as, images and texts in books printed with traditional oil based inks. Certain problems recorded in these works appear to be related to the presence of the oil binder; discoloration of the paper varying in intensity, reduction of the mechanical strength and embrittlement of the support on areas where oil diffusion or absorption has occurred. Thus, the possible effect of the oil binders on the degradation of the paper support has raised an important research issue, since it is associated with conservation and preservation issues of the cultural heritage.

The effect of oil binder on the paper support degradation was investigated by the GC-MS analysis of VOC emitted both from mock ups and original art works, adopting research applications of solid-phase microextraction (SPME) method coupled with GC-MS, which have allowed the identification of volatile organic compounds (VOCs) emitted from paper

as it deteriorates [1,2]. The VOC profile produced depends on the nature of the paper, the degree of degradation, and the pathway by which it is degrading.

Pilot applications of this methodology on mock ups of cotton based paper impregnated with linseed oil have resulted in the production of volatile organic compounds, the majority of which could be attributed both to oil and paper degradation [3]. So, investigation was focused on compounds that are exclusively derived from paper degradation pathways. The extraction of VOCs from areas of damage on original works of art was performed with the application of a SPME needle, in an attempt to explore the identification of the extent of VOC emissions in relation to their condition and fibre content.

Experimental

Mock ups

Two types of paper were selected for the preparation of mock ups based on the paper supports of the original artworks in the collections of the National Gallery (see Table 3); a) *Munktel CxD pHoton paper*, a standard paper to model pure cellulose paper (100% cotton fibre from pure cotton linters), unbuffered, with no additives, fillers or sizing, and b) *Montval watercolour paper* by Canson, a (semi) chemical wood pulp with limited lignin content, cold pressed, acid free, with presence of fillers and additives. Linseed oil was selected to impregnate the mock ups, since it is the most common oil binder used in oil painting and traditional printing techniques, and it was identified as the binding media in most of the works of the National Gallery. Cold pressed linseed oil was selected, since it provided the purest form. Paper strips 1 x7 cm were cut, and the half of them were impregnated with equal volumes of linseed oil (0,06ml). Then, the oiled mock ups were left to air dry in dark conditions for 40 days.

Aging

Closed environment aging of the paper samples was performed, following the standard conditions used in analogous applications.[1,2] Studies have concluded that ageing in sealed vessels better emulate natural ageing.[4] The mock ups were placed in Head space vials, suspended over a saturated aqueous solution of sodium chloride (NaCl) in deionised water. The aqueous solution of sodium chloride could provide controlled conditions of relative humidity in the close environment of a vial during aging, less extreme than 100% RH provided by the addition of water solely [5] and would also, after ageing provide a solution, in which the samples could be immersed, that would facilitate emission of the VOC's trapped in the paper. Headspace vials (screw top, rounded bottom, size 20 mL, clear glass, thread 18, O.D. × H 22.5 mm × 75.5 mm) were covered with stainless steel screw cap (magnetic, open-top), thread 18 and PTFE/silicone septum, thickness 1.3 mm. Accelerated aging procedure was carried out in a *Solar climatic chamber Atlas SC 600.* All samples were aged at 90^{o}C and at 77.8% RH (78% RH) for 1,4,7,14,21 and 28 days.

Original artworks

Six works were selected for this experimental procedure, providing different case studies regarding the technique, the materials and the presence of characteristic phenomena and problems related to absorption and diffusion of the oil binder. These works were: a 19th c. oil sketch by N. Gysis, "The Sewing studio" (Π3434), that presented oil absorption and discoloration in certain areas on the verso: a 19th c. oil study by K. Fanellis, "*Figure of*

Christ" (Π 2985), that presented oil diffusion and absorption on both sides of the support; three mid 20th c. black and white woodcuts by G. Economides, *Livadia* (Π9822), *Mykonos* (Π9823) and *Katohi* (Π9812) that presented oil diffusion and discoloration beyond the limits of the printed lines and intense absorption of the oil binder only evident on the verso, and finally, an album, *Sachsische Scheriz* (Π9740), where the area of interest is the discoloration on the opposite page in contact, that responds to the printed image.

VOC extraction procedure

For both mock-ups and original art works, a SPME needle with 50/30μm divinylbenzene-carboxen/poly(dimethylsiloxane) fibre was used, which has been found to be the most appropriate for extraction of the variety of VOCs emitted from paper [6]. The needle cartridge was preconditioned by heating to 230°C in the injection port of the GC-MS instrument and retracted.

Mock ups

The preconditioned SPME needle was inserted into a headspace file containing the paper sample in 5ml of 15% sodium chloride solution and thus exposed to the vapours given off from each sample for 40 minutes (which was held at 40°C in an incubator, so as to absorb the VOC emissions). In addition, the salt solution, an ionic solution, provided a non-friendly environment for the low molecular mass, non-ionic, volatile organic compounds, so it would aggravate their emission.

Original art works

The experimental procedure was carried out in the Paper Conservation studio of the National Gallery in Athens. It involved encasing both the artwork and the SPME needle in a glass set up to track the VOCs emitted, confining additionally the area of interest with a petri dish [3]. The capacity of the selected methodology and set up to extract and identify chemical compounds related to the degradation of the paper support, as well as the background environment interference, had been initially assessed in preparatory experimental trials [3,7].

The SPME needle was placed on the verso of each work, over a specific area that presented oil absorption, diffusion or discoloration. The absorbing part of the needle was exposed just before being covered with a glass lid of a *petri* dish and a glass tray. The needle was exposed for 24 hours. The SPME needle was then retracted and transferred back to the lab. The needle was conditioned between runs by heating to 230°C for 10mins. The procedure was repeated in the exact same way for the six works.

GC-MS analysis

After being exposed to the VOCS emitted by the mock-ups or the original artworks, the SPME needle was then reopened in the injection port of the GC-MS and heated to 230°C for 10 minutes to release the volatile components and trap them at the beginning of the column. The compounds were then separated and identified by GC-MS. GC-MS analyses were carried out in an Agilent Technologies 7890A GC gas chromatograph coupled with an Agilent Technologies 5975 C MSD (mass selective detector) with triple-axis detector, and an Agilent 1909/S capillary column (30 m×0.25 mm i.d.; coating thickness 0.25 μm). Carrier gas used was He with a flow rate 1 mL/min at linear velocity 40 cm/s; split 1:10; ionization: EI 70 eV. and the temperature of the column was held at 40°C for 10 mins. and then raised from 40°C to 250°C at a rate of 5°C per minute and held at 250°C for 15 mins.

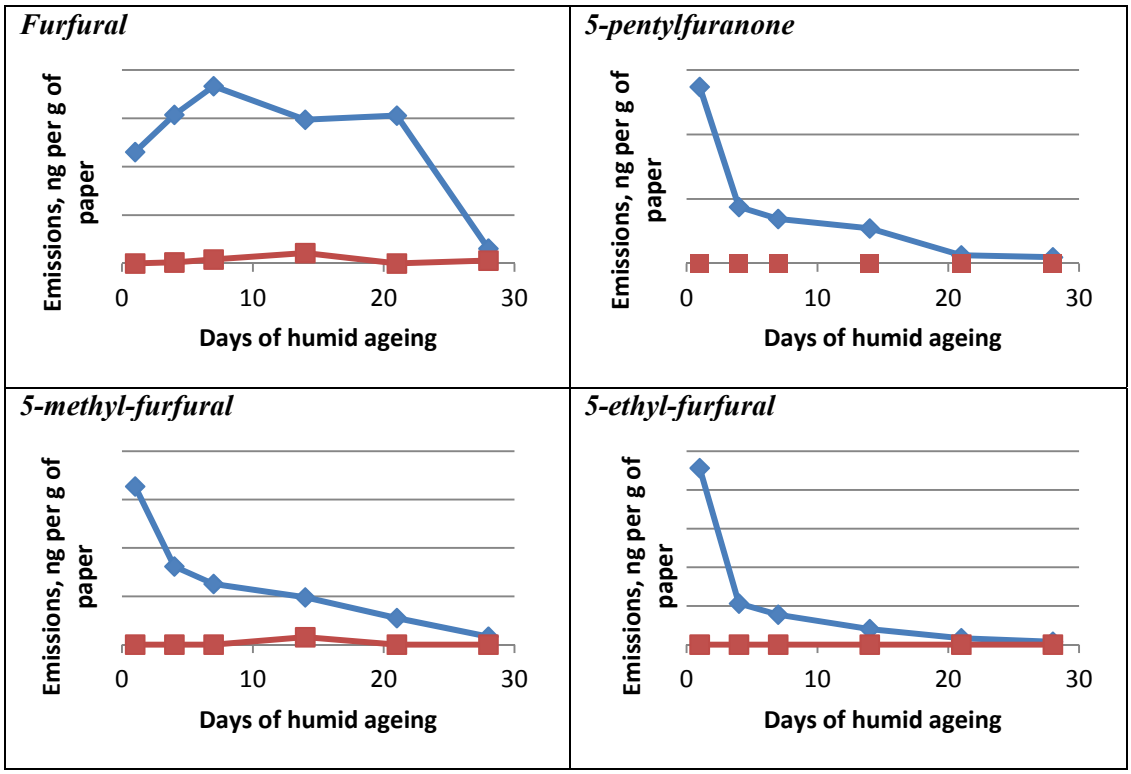
Results and Discussion

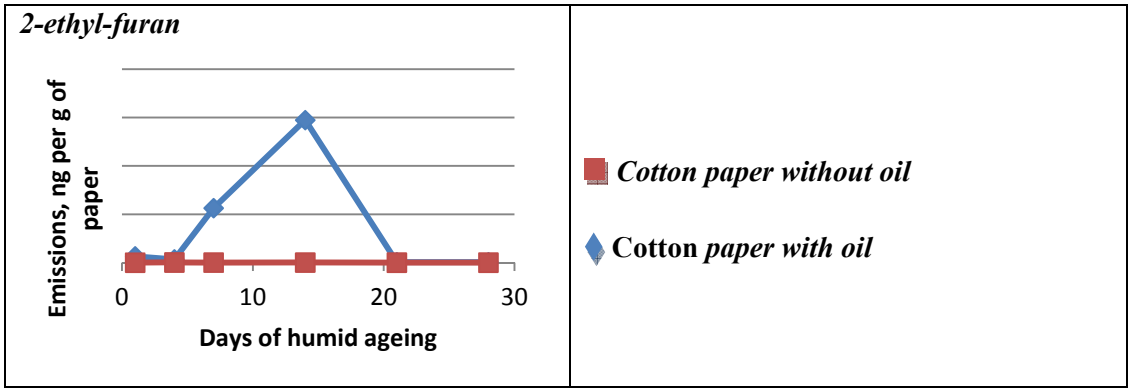
For the mock ups, five compounds had been chosen for monitoring: 2-ethyl furan, furfural, 5-methyl furfural, 5-ethyl furfural and 5-pentyl furanone. These are known volatile cellulose degradation products [1,2] and had been shown to be produced on ageing of paper but not during the ageing of oil films containing a manganese oxide drier[7].

Mock ups - Cotton paper

2-ethyl furan was emitted from the cotton paper impregnated with oil even after 1 day and three days of ageing. The emission then begun to increase at 7 days and peaked at 14 days. None of this compound was detected at 21 days or at 28 days of ageing. In contrast, a comparatively minor emission of this compound was recorded from the paper without oil only at 21 days. Furfural is emitted fairly steadily over the first 7 days from the cotton paper impregnated with oil and then emission peaks decline to a low level by the 28 days. The emission of this compound is much lower for the paper without oil and seemingly they peaked insignificantly after 14 days. 5-methyl furfural and 5-ethyl furfural emissions, from the cotton paper impregnated with oil, peak on the first day of ageing and drop to only a very low level by the 28 days. The emission of these two compounds from the cotton paper without oil are low: peaking at 14 days for the 5-methyl analogue and zero throughout for the 5-ethyl analogue. A result similar to the last two is shown by 5-pentylfuranone. Again there are no detectable emissions from the paper without oil within the 28 day period.

Table 1. VOC emissions of furfural, 5-methyl-furfural, 5-ethyl-furfural and 5-pentylfuranone over 28 days of ageing from pure cotton paper with or without oil application. Plot shows absolute peak areas against number of days aged.

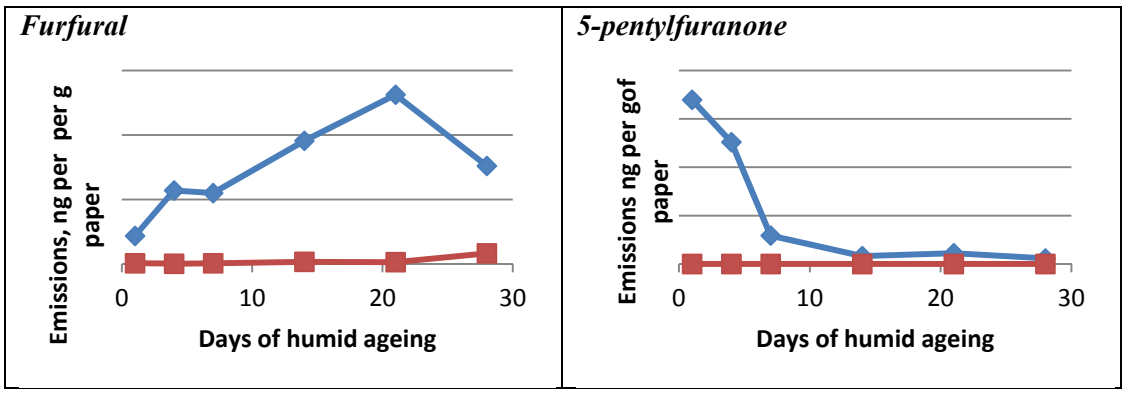


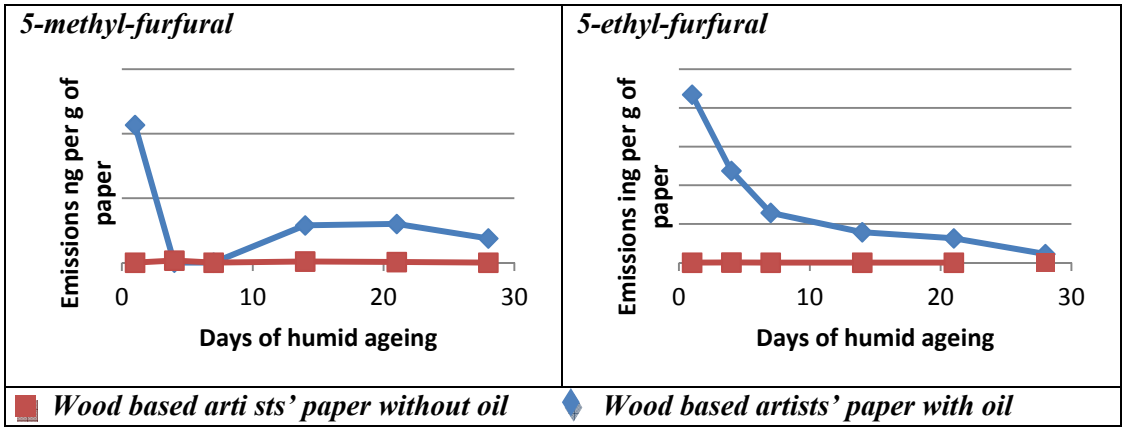


Mock ups - Wood based Artists' paper

2-ethyl furan emission from the wood based artists' paper was very low whether the paper was impregnated in oil or not. Furfural emission appears to increase over the first 21 days from the wood based artists' paper impregnated with oil that peaks at 21 days, while it declines to the half amount of the emission at 28 days. This compound emissions by the paper without oil are much lower and increase by the 28th day. For 5- methyl furfural emissions, from the wood based paper impregnated with oil, they appear to peak on the first day of ageing and drop to a lower level, by 28 days. An equivalent outcome is noted for 5-ethyl furfural except that emissions are slightly higher than the methyl analogue and after 28 days the emission is even lower than that of the first day of ageing. The emissions of these two compounds from the wood based paper without oil appear to be low: peaking at 3 days for the 5-methyl analogue and zero throughout for the 5-ethyl analogue. Interestingly the peak emissions of these two compounds are a little lower in the case of the wood based paper with oil than with the cotton paper with oil. A result similar to the last two is shown by 5-pentylfuranone. Again there are no detectable emissions from the paper without oil within the 28 day period. Also the peak emissions of this compound are a little lower in the case of the wood based paper with oil than with the cotton paper with oil.

Table 2. VOC emissions of furfural, 5-methyl-furfural, 5-ethyl-furfural and 5-pentylfuranone over 28 days of ageing from wood based artists' paper with or without oil application. Plot shows absolute peak areas against number of days aged.





Original Works of art

Several VOCs were identified in the gas phase emission. The compounds found to be given off by the objects include: aromatic hydrocarbons (m-xylene, toluene, 1,2,4-trimethyl-benzene, naphthalene); aliphatic hydrocarbons (n-nonane, n-decane) , straight chain aliphatic aldehydes (n-octanal, nonanal, decanal), straight chained aliphatic carboxylic acids (ethanoic acid, pentanoic acid, heptanoic acid, octanoic acid, nonanoic acid), esters (isopropyl myristate, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate) all of which can be oil or paper degradation products [1, 2, 8], while phenol, mono terpenoids such as verbenene, limonene, trans-verbenol, menthol and I-verbenone, and significantly, furan derivatives, such as furfural, 5-butyldihydro -2(3H) furanone and 5-pentyl-2(5H)-furanone), which are known paper degradation products and not oil degradation products [1, 2]. Also vanillin was found, which is a known lignin degradation product [1, 2]. Three of the mono terpenoids , verbenene, trans verbenol and 1-verbenone are also known oxidation products of α-pinene [9], from turpentine and therefore may originate; either from pine resin size in the paper or, more probably, turpentine solvent used in the oil paint or oil based inks

Table 3. Data on the fibre content, oil medium, sizing and lignin content of all the works studied, and the pH values of the areas of the VOC extraction.

Object	Date	Description	Fibre content	Findings	pH
3434	Late 19th c.	*Oil sketch*	Cotton, linen rag and softwood	*Drying oil, rosin, alum, lignin*	*4.70*
2985	Late 19th c.	*Oil study*	Cotton and linen rag and softwood	*Drying oil and beeswax, rosin, alum*	*4.70*
9812	20th c.	*B/W woodcut*	Kozo and softwood	*Non-drying oil and rosin*	*5.88*
9822	20th c.	*B/W woodcut*	Linen, cotton	*Non-drying oil, rosin, alum*	*5.20*
9823	20th c.	*B/W woodcut*	Linen and cotton	*Mixture of drying oil and non-drying oil and rosin*	*5.10*
9740	20th c.	*B/W woodcut*	Cotton rag mixed with softwood	*Mixture of drying oil and non-drying oil and rosin*	*5.53*

Table 4. Peak Area (to 2 Significant figures) responses of the target VOCs emitted from original works of art.

Target Compounds	Typical retention time	Object 3434	Object 2985	Object 9812	Object 9822	Object 9823	Object 9740
furfural	8.7	710	1400	1100	1400	1000	0
5-butyldihydro - 2(3H) furanone	27	76000	100000	25000	101000	66000	256000
5-pentyl-2(5H)-furanone	29	12000	1500	0	1500	1800	21000
vanillin	31	130000	42000	31000	42000	2400	370000

Focusing to the degradation products of holocellulosic and lignocellulosic papers exclusively, furfural, 5-butyldihydro-2(3H), 5-pentyl-2(5H)-furanone and vanillin were selected to be studied, which are in accordance with those selected for the study of the mock-ups in the various stages of aging. Furfural emission has been recorded in all the original works. However, the values of furfural peak areas are relatively lower than those of the furanone derivatives and vanillin. Although it could be suggested that furfural values are analogous to vanillin values for objects 2985, 9812 and 9822, values of objects 3434 and especially 9740 are inconclusive respectively. In the case of object 9740, there is no furfural emission recorded, while the values of the peak areas of the other compounds are comparatively high. The outcome is really interesting, since the sampling area responds to the offsetting of slow drying oil medium to the opposite page. For all the works, 5-butyldihydro-2(3H) furanone emission is recorded as being the most intense than all the selected compounds studied. The values of 5-butyldihydro-2(3H) furanone are extremely higher than those of furfural. This may reflect an increase in the rate of oxidation of the paper in contact with the oil in these objects. The values of the peak areas of 5-pentyl-2(5H)-furanone varies among the works, they are relatively low, occasionally close to those of furfural, while object 9812 presents no emission.

Vanilin values are associated with the lignin presence and appear to respond to the amount of wood fibres included in the paper pulp of each work. Taking into consideration the background interference, the value of vanillin in object 9823 is regarded insignificant, and it could not indicate the presence of wood fibres, a fact confirmed by the fibre content identification. The surface pH values of the areas of extraction cannot really correlate with the emission of any of the compounds studied. However, the late 19^{th} century objects present slightly lower pH values. Accordingly, the drop of the pH values on the 20^{th} c. prints, cannot really associated with the type of the paper support or the woodpulp content. Finally, a comparison between the values of the peak areas of the compounds monitored for mock ups and original art works is not possible because of the different conditions used to collect the VOCs. However it is interesting that a similar range of compounds were discovered in similar proportions as this validates our ageing procedure for the mock ups.

Conclusion

It was concluded that the presence of drying oil in paper greatly accelerates and increases the emission of volatile cellulose degradation products both for cotton based and wood based papers. Comparison of the results from the two different paper type of mock-ups, provide indications on the input of the paper type on the rate of deterioration of support caused by the oil binder, wood based papers degrading more quickly than cotton based.

Furfural emissions are greater from wood based paper impregnated with linseed oil compared to furfural emissions from cotton paper impregnated with linseed oil. The increased levels of furfural are an indication that the lignin and/or hemicelluloses present in the wood based papers are accelerating the degradation even further in the presence of oil. Perhaps the increased levels of furfural are an indication that hemicelluloses degrade favourably to furfural. However it seems that both in cotton and wood based paper the amount of furfural produced is increased whereas the levels of the other four compounds studied seems to decrease. It could be perhaps speculated that furfural is a favoured product of cellulose degradation in the presence of oil.

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