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Spectral Classification of Paper Fixatives: A Case Study on Thomas Fearnley's Drawings

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Abstract

Drawing materials, such as soft graphite or charcoal applied on paper, may be prone to smearing during transport and handling. To mitigate this effect, it was common practice among 19th century artists to apply a fixative on drawings made in friable media. In many cases, the fixative has been imperative in preserving the drawings, although it may also have altered the appearance of the paper and/or the media. It is rarely possible to identify the type of fixative used, without using analytical techniques that require sample taking. As the fixative layer is very thin, any sample will often also contain small fragments of the paper. In this article, we are proposing a non-invasive approach for recognizing fixatives based on their spectral signatures in the visible and near-infrared range, collected with a hyperspectral imaging device. Our approach is tested on mock-up samples designed to contain fixatives of animal and vegetal origin, and on two drawings by the Norwegian artist, Thomas Fearnley.

Introduction

Historical paper is at its core an organic material that might contain additional elements of varied nature. The complex composition of paper makes it susceptible to different aging agents, from the presence of insects to acid chemical reactions and photo-oxidation [1].

The complexity of paper also interacts with the layers on top of the paper. Moreover, common drawing materials, such as graphite and charcoal, are fugitive and smudging. Aware of these challenges, and in an attempt to protect paper-based drawings, 19th century artists used to apply coatings of fixating material, such as casein, starch, egg white, or gum Arabic. However, even fixatives transform with time, leaving visible and noticeable traces that interfere with the appearance of a paper-based artwork.

Thus, a major part of the paper conservation field is dedicated to preserving cultural heritage items manufactured on paper by first recognizing and examining the underlying materials. Many times, scientific investigation demands the use of multiple analytical techniques to reach consensus. Some of these techniques, for example gas-chromatography with mass spectrometry (GC-MS), are invasive, even though highly precise.

The purpose of this article is to explore to what extent optical non-destructive methods, in particular, hyperspectral imaging in the visible and near-infrared (VIS-NIR) range can help to identify different types of fixatives applied on paper drawings. The rationale of this work stems from a previous case study [2] on two 19th century pencil drawings: *St. Sebastian, Ramsau* and *Tree, Ramsau*, created by Thomas Fearnley (1802-1842), a Norwegian romantic artist. Reissland et al. [2] discovered with GC-MS that milk was used as fixative in both drawings, contrary to the discrepancy in the colour appearance: the former drawing appears to be heterogeneously whitish while the other more homogenously brownish (Figure 1). Thus, the first research question arises: can the VIS-NIR spectral signatures reveal that the two drawings are coated with the same fixative notwithstanding the different colour change behaviour? In order to have a broader testbed, we prepared a mockup containing paper swatches with various fixatives of animal and vegetal origin in different concentrations: skimmed milk, whole milk, gelatin, sturgeon glue, egg white, rice starch. With the mockup samples, we are also targeting another research question: are we able to separate the various fixatives according to their vegetal and proteinic origin given the VIS-NIR spectroscopic data?

Figure 1: The two drawings by Thomas Fearnley. Left: St. Sebastian, Ramsau, where the milk applied in the church area gets more discoloured than the rest of the paper. Right: Tree, Ramsau, where the drawing is more homogeneously yellowed, with the milk fixative applied in the tree area locally protecting from discolouration.

Related Work

Reissland et al. [2] analyzed the two Fearnley drawings with photographic techniques under various light conditions (daylight, ultraviolet light, raking light, transmitted light) and with several analytical techniques (microchemical tests, X-Ray fluorescence, GC-MS, polarization microscopy, scanning electron microscopy with energy dispersive X-Ray analysis). As hypothesis behind the different colour behaviour of the milk fixative, they propose the paper type: the more homogenously browner-looking drawing - *Tree, Ramsau* - is made on a substrate with more iron-particles, that in combination with the chlorine-bleach commonly employed in the paper fabrication process at the time, is known to lead to a darker yellowish-brown tone in the long term.

As a matter of fact, in conservation science, the understanding of fixatives applied on graphite drawings is an active topic. Weir et al. [3] used spectroscopic measurements in the mid-infrared region to identify fixatives in a collection of drawings by British artist John Constable. They were able to detect protein peaks characteristic to a wide series of fixatives: rabbit skin glue, flour paste, isinglass, milk, egg, fish glue, gum Arabic and mastic resin. In order to check the impact of application methods on the appearance of drawings, Weir [4] recreated three such methods, spraying, dipping and brushing for three types of varnishes: skimmed milk, egg white and sturgeon gelatin (isinglass). In her experiments, she discovered that the brushing technique was the best at preventing the smearing of the graphite. Moreover, she noticed difference in appearance effects of the three fixatives. While skimmed milk gives a rather matte finish and accentuates the black of the graphite, the egg white is glossier and casts a yellowish hue. With the naked eye, the fish gelatin seems to be the most imperceptible, even though at a microscopic scale, isinglass is made of crystals that could disperse the white light colours. The work highlights the complexity of fixatives, showing how they can affect various optical properties of the surface they cover.

While no hyperspectral imaging analysis was ever carried out on the two specific drawings included in our case study, there are few works that approach the study of paper varnishes with this non-invasive optical technique. Martinez et al. [5] investigate the change in colour distribution of a set of paper varnish samples before and after undergoing artificial aging. In addition, they generate renderings of the samples under various illuminants, showing how this increases the discernibility of the aging effects. In a later work, Martinez et al. [6] elaborate their colour and spectral analysis, focusing only on the aging process of water-soluble varnishes, i.e. gum Arabic and egg white. The authors also propose a spectral yellowing index to characterize the colouration of varnish, as an improved variant of the yellowing index in only the colour domain.

Our study also draws inspiration from the chemometrics field, where spectroscopic data is processed towards material and chemical composition identification. For example, Tsenkova et al. [7] use derivatives of the spectral absorbance in the near and short wave infrared to detect the chemical content of unhomogenized milk.

Materials and Method

Drawings

Two 19th century drawings by Thomas Fearnley drove the case study in this article: *St. Sebastian, Ramsau* and *Tree, Ramsau.* The drawings belong to the collection of the National Museum in Oslo, Norway. Previous conservation studies [2] identified that milk was applied as a protective layer on top of the graphite figures in both drawings. Although the same, the fixative developed a different colour behaviour in the two cases, as shown in Figure 1.

Mockup design

For the mockup preparation, we selected fixatives that span the common materials used by artists for protecting graphite-based paper drawings. Egg white, milk, gelatine, and sturgeon glue are all of animal origin, from hen, cow, pork, and sturgeon (fish), respectively. Rice starch is of vegetal origin. Egg white, whole milk and skimmed milk were applied in 1-layer and 2-layer configurations. Gelatine and sturgeon glue were each mixed in 5% and 10% concentrations. Lastly, the rice starch was mixed in 10% and 20% solutions.

The main chemical components that vary in the content of the fixatives are fat, proteins and carbohydrates. They also contain multiple vitamins and minerals. Although the list is too long and it's beyond the scope of the article to mention all chemical compounds, it is important to consider that vitamins and minerals might also stand as ground for variation between the fixatives.

Figure 2: Details of the two drawings scanned with the hyperspectral camera. The red rectangles highlight areas with and without fixative, selected for spectral analysis.

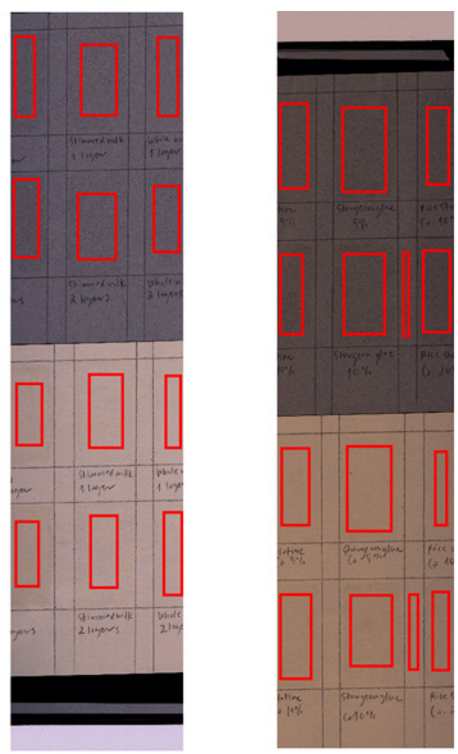

Figure 3: The fixative samples in the white and blue mockups captured with the hyperspectral camera. The areas highlighted in red represent the regions of interest selected for analysis.

From our mock-ups, the whole milk is the sample richest in fat with 4g/100g. There is a very small amount of fat in skimmed milk (0.1g) and even less in egg white, gelatine and sturgeon glue (practically none), and there is no fat at all in rice starch. When it comes to carbohydrates, milk contains lactose (mostly, about 4.5g/100g) and starch a mix of amylose (20-25%) and amylopectin (75-80%). Egg contains a very small amount of carbohydrate, while gelatine and sturgeon glue contain none.

As far as proteins are concerned, starch contains none. Sturgeon glue contains about 80% (collagen mainly) and gelatine contains about 86%. Egg contains about 11% (mix of many different proteins), milk about 3.5% (casein about 80%, whey protein about 20%). If mixed in 5% solutions, sturgeon glue and gelatine have a similar protein content to milk (4.28 and 4 versus 3.5%), while egg has a higher content (11%). The fixatives were applied with a brush on two different papers, that from this point on will be referred to as the white mock-up and the blue mock-up. By using two different substrates, we can better isolate the properties of the fixatives without unmixing between the protective layer and the paper underneath.

Data Acquisition

The two drawings by Fearnley and the fixative samples were scanned with a hyperspectral imaging system (HySpex VNIR-1800 by Norsk Elektro Optikk AS) in-situ at the museum. This push-broom camera captures a stack of 1800-pixel lines while the object is moved by a translation stage. For every pixel, the camera acquires 186 spectral bands, with sensitivity between 400 and 1000 nm. A 30-cm lens was coupled with the camera, 22 cm away from the object, resulting in a spatial resolution of 0.05 mm. The radiance captured by the camera was converted to reflectance using dark-current correction and the ground-truth reflectance of a Spectralon 99% white tile that was placed next to the object and covered the entire field of view of an acquisition line.

Data Processing

Patches representing significant areas were selected for each drawing (Figure 2) and fixative (Figure 3), and the reflectance spectra were spatially averaged. Based on the average spectra, first-order and second-order derivatives were computed using Savitzky-Golay filter [8] with window size 7 and polynomial order 2 to find significant inflection points in the VIS and NIR reflectance. Afterwards, several spectral metrics such as spectral angle, spectral correlation and Euclidean cumulative spectrum were determined to compare the different representative spectra. The spectral angle distance computes the angle between two discrete signals s_1 and s_2, by using the inverse cosine function:

$$SA = \cos^{-1}\frac{\sum s_1 s_2}{\sqrt{\sum s_1^2}\sqrt{\sum s_2^2}}$$

Smaller values of spectral angle correspond to signals more similar in shape. The spectral correlation is a modified expression of Pearson correlation [9] and is mathematically similar to the spectral angle, but it applies mean centering on the signals.

$$SC = \frac{\sum(s_1 - \bar{s_1})(s_2 - \bar{s_2})}{\sqrt{\sum(s_1 - \bar{s_1})^2}\sqrt{\sum(s_2 - \bar{s_2})^2}}$$

Spectral correlation varies from -1 to 1, with the maximum indicating perfectly resembling signals. However, it is possible to express the spectral correlation as a distance, using either the inverse cosine function or a subtractive formulation. This way, the higher the metric, the higher the divergence between the signals. We opted for the subtractive formulation:

$$SCD = 1 - (1 + \frac{SC}{2})$$

All computational experiments were implemented in Python programming language.

Results and Discussion

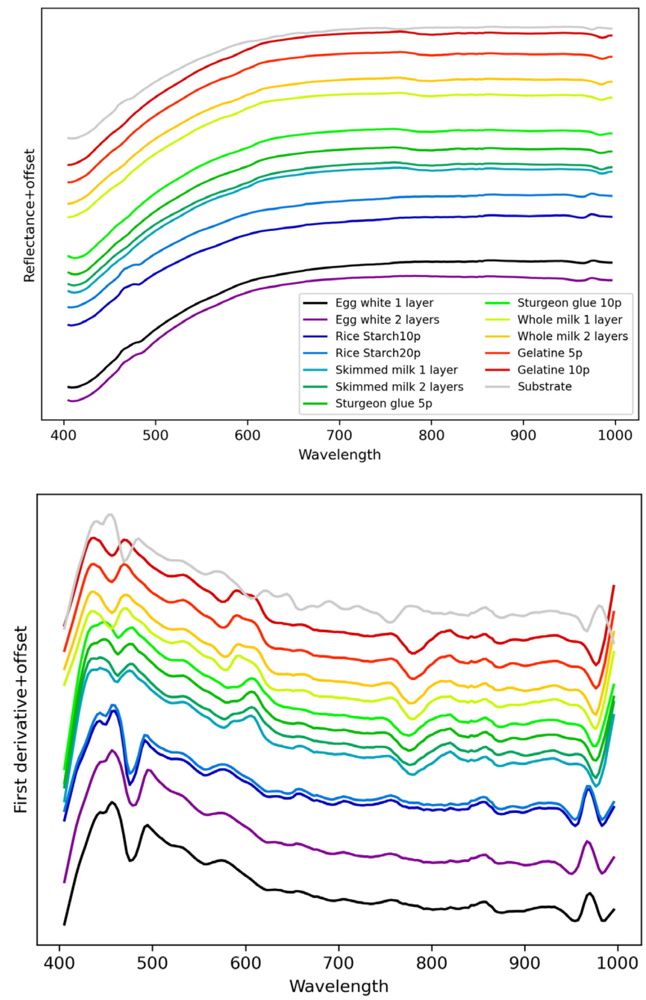

Figure 4: The reflectance spectra (top) and first derivative for the white mockup fixatives. Variable offsets were added for visualization purposes in order to focus on the reflectance shapes rather on their intensities. While particularities that group together the fixatives are only slightly visible in the reflectance curves, they become more enhanced in the derivative.

The visual examination of the VIS-NIR reflectance and the first order derivatives indicate a certain grouping of the fixatives in the mockups. For example, in the white mockup spectra displayed in Figure 4, it seems that the rice starch and egg white are more similar to each other than they are to the rest of the fixatives, sharing two inflection points (a rapid change in the reflectance of the signal, either a local maximum or a local minimum) at approximately 475 nm and 967 nm. Likewise, the rest of the fixatives share two absorption peaks at around 780 nm and 975nm. The peaks are more noticeable in the first derivative than in the reflectance signals.

The grouping trend of the fixatives is consistent among the two different substrates. The spectral plots of the blue mockup samples in Figure 5 point to the same two clusters: 1) egg white and rice starch; 2) milk, gelatine and sturgeon glue. Moreover, the typical inflection points in the NIR for these groups show up at the same

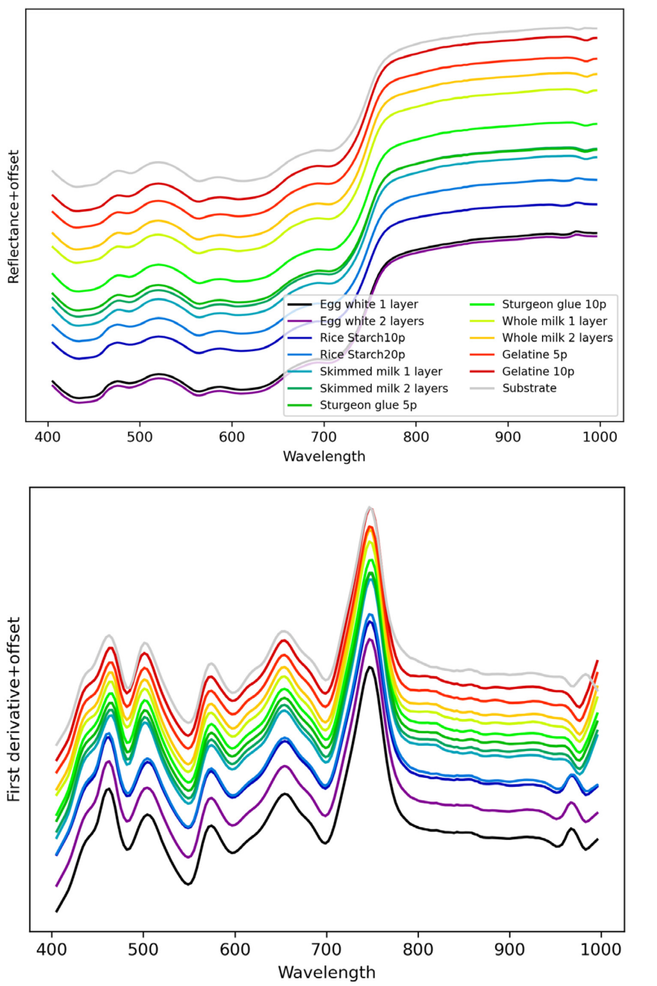

Figure 5: The reflectance spectra (top) and first derivative for the blue mockup fixatives. Offset was added for visualization purposes. The two inflection points in the NIR, the minimum at 975 nm for milk, gelatine and sturgeon glue, and the maximum at 967 nm for rice starch and egg white are consistent with the ones in the white mockup.

wavelengths as before. For both mockups, the signals of the fixatives are correlated with that of the paper. This should ideally be accounted for by applying an unmixing procedure. However, the fact that the similarity between fixatives is preserved notwithstanding the different substrates implies that this behaviour is idiosyncratic to the fixatives, and not the paper.

Interestingly, the inspection of the drawings' spectra reveals an absorption peak at 975 nm (see Figure 6), common to the milk, gelatine and sturgeon glue fixatives in the mockups. Knowing that indeed milk was the fixative employed by Thomas Fearnley, this finding seems valid. Although it is difficult to name the chemical component that provokes this absorption peak for milk, as well as gelatine and sturgeon glue without further analysis, we will try to contextualize our result with those of Tsenkova et al. [7]. In their investigation, Tsenkova et al. perform spectroscopic measurements of liquid dairy samples and identify the spectral bands that give the highest correlation coefficient with the chemical content. Among

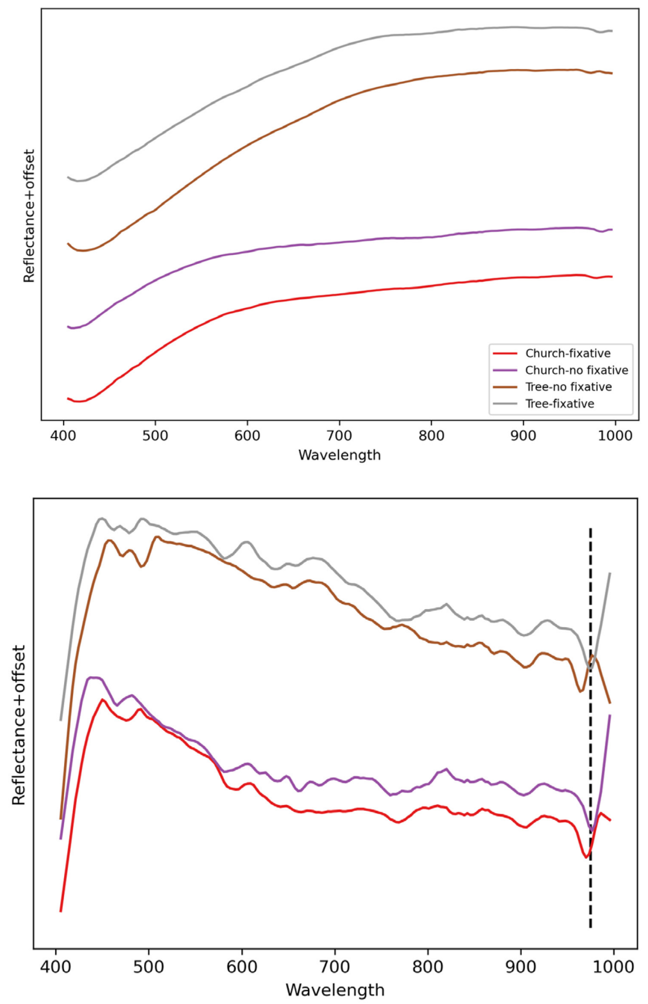

Figure 6: The reflectance spectra (top) and first derivative for the two drawings. Offset was added for visualization purposes. There is an absorption peak at 975 nm (dashed line), common for the area in the tree drawing treated with fixative and for both areas in the church drawing, with and without fixative. This absorption peak is present in the milk-based mockup samples as well.

others, their findings are that one of the most informative bands for fat is 968 nm and for lactose 974 nm. Connecting this with our experiments, we can hypothesize that the inflection point at 968 nm characteristic to rice starch and egg white might be explained by the low amount of fat in these two fixatives. Furthermore, we expect that the turning point at 975 nm for our milk samples is given by the lactose content. However, following this hypothesis one question remains unanswered: knowing that gelatine and sturgeon glue contain no lactose, why do they also have an absorption peak at 974nm? Such questions can be more precisely addressed in future work, by extending the range of the spectroscopic analysis to short-wave infrared.

It is important to mention that the minimum at 975 nm appears for the areas with fixative in the tree, as well for both areas in the church drawing, with and without fixative. It is uncertain why this occurs for both fixative and no-fixative area in the church drawing, but one possible explanation might be that traces of residual material are present in the area considered to have no fixative.

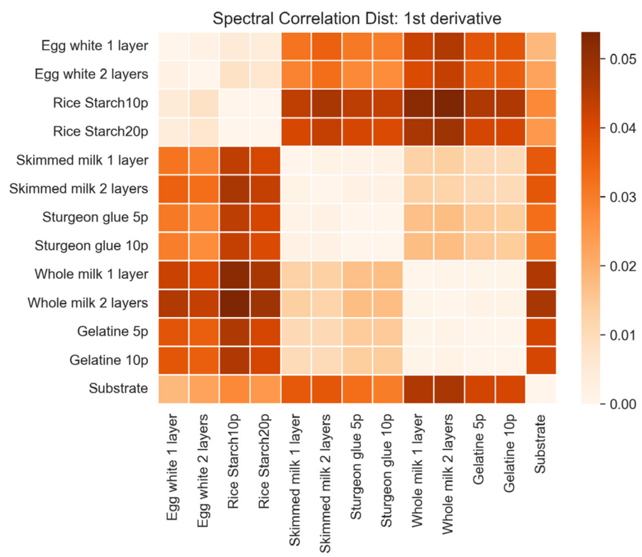

Figure 7: Spectral correlation distance between all the samples in the white mockup computed for the first derivative over the entire spectral range (VIS+ NIR), visualized as confusion matrix. The lower the numeric values, the lighter the colour, and so the higher the similarity.

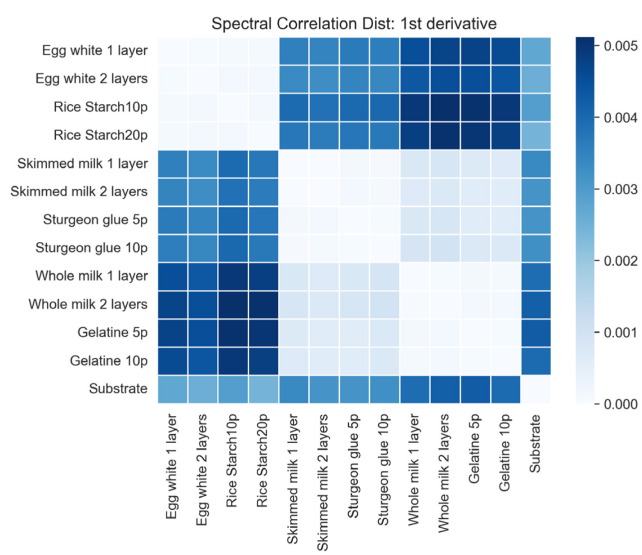

Figure 8: Spectral correlation distance between all the samples in the blue mockup computed for the first derivative over the entire spectral range (VIS+ NIR), visualized as confusion matrix. The lower the numeric values, the lighter the colour, and so the higher the similarity.

The quantitative analysis with spectral angle and spectral correlation distances confirms the insights gathered through visual examination. To begin with, we noticed that the distances are more meaningful when computed on the first and second derivative rather than directly on reflectance. Then, the difference between first order and second order derivative is negligeable. It is in the first and second derivative that the grouping of the mockup samples is more evident. This is valid for both metrics, as well as for both mockups.

Figure 7 and Figure 8 show the spectral correlation computed as a distance between the first derivative spectra of all the samples in the white and blue mockup, respectively. Higher values represent higher dissimilarity and are graphically represented by darker colours in the confusion matrix. The spectral correlation distance computed over the full spectral range subdivides the milk, gelatine and sturgeon glue group into two subgroups: skimmed milk and sturgeon glue, and whole milk and gelatine.

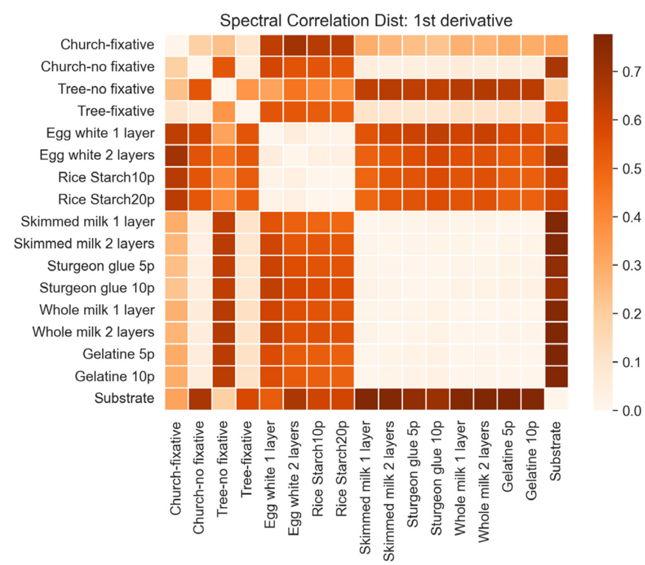

Figure 9: "Figure 9: Spectral correlation distance between all the white mockup samples and representative areas in the drawings computed for the first derivative in NIR only (750 nm to 1000nm), plotted as a confusion matrix. The lower the numeric values, the lighter the colour, and so the higher the similarity.

As observed in the graphical analysis, the NIR range is more informative for the classification of the fixatives. Indeed, in the visible colour domain, the fixatives are rather transparent, especially given the fact that the samples were not aged. As far as the drawings are concerned, spectral correlation in the NIR finds a high similarity between the spectral signatures of areas treated with fixatives in both drawings (distance lower than 0.2 units), as portrayed in Figure 9. When comparing the drawings with the white mockup samples, the highest similarity corresponds to the milk-gelatine-sturgeon glue group, in agreement with the spectral curves. At the same time, this is true for the comparison with the blue mockup samples, which can be observed in Figure 10. However, at the scale given by all NIR distances, the difference between the mockup fixatives is less perceptible for the blue paper than it is for the white paper. In the latter case, we can still see the two nuclei egg white-rice starch and milk-gelatine-sturgeon glue. This means that the inter-class separation for the sample fixatives is lower for the blue substrate with respect to the white one.

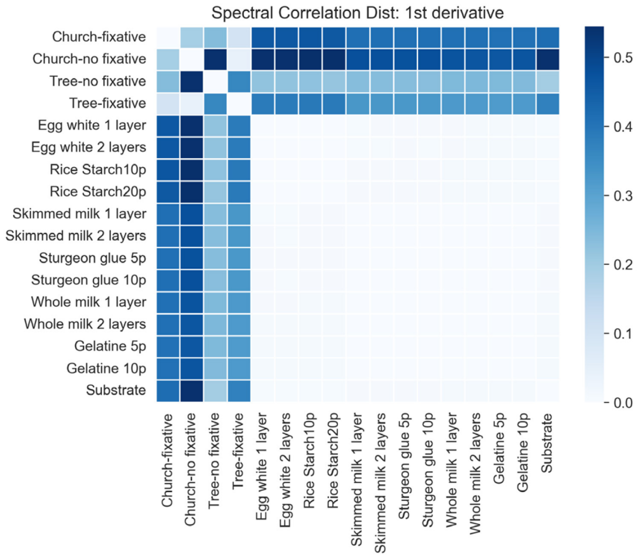

Figure 10: Spectral correlation distance between all the blue mockup samples and representative areas in the drawings computed for the first derivative in NIR only (750 nm to 1000nm), plotted as a confusion matrix. The lower the numeric values, the lighter the colour, and so the higher the similarity.

Conclusion

In this article, VIS-NIR hyperspectral imaging analysis has been used to classify paper fixatives typically employed by artists to protect friable media. It was shown that, although with a limited spectral range for accurate determination of chemical compounds, VIS-NIR spectroscopy is able to distinguish among various fixatives. Particularly, two main classes have been distinguished: egg white-rice starch and milk-gelatine-sturgeon glues. In the latter, there seems to be a slight further split: skimmed milk-sturgeon glue and whole milk-gelatine. While this grouping does not target the animal vs. vegetal origin, it holds against different paper substrates. As a matter of fact, through our analysis, we were able to draw a link between the fixatives used by Thomas Fearnley in two of his drawings and the milk-gelatine-sturgeon glue cluster from the control samples. Nonetheless, to specifically pinpoint to the chemical component that causes these similarities, further analysis is needed, extending the optical analysis deeper into the infrared region and combining it with other analytical techniques.

As future work, we would like to explore more the spatial capabilities offered by hyperspectral imaging. This would be particularly useful for generating appearance maps of the drawings that extract other meaningful descriptors than spectra such as yellowing index and glossiness.

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