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Non-destructive characterisation of iron gall ink drawings: Not such a galling problem

Matija Strlič[a,*], Linda Cséfalvayová[a], Jana Kolar[b], Eva Menart[c], Joanna Kosek[d], Caroline Barry[d], Catherine Higgitt[d], May Cassar[a]

[a] Centre for Sustainable Heritage, University College London, Gower Street, London WC1E 6BT, UK
[b] Morana RTD d.o.o., Ivančna Gorica, Oslica 1B, SI-1295, Slovenia
[c] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva cesta 5, 1000 Ljubljana, Slovenia
[d] British Museum, Great Russell Street, London WC1B 3DG, UK

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ABSTRACT

Iron gall inks are of extraordinary historical significance considering their widespread use for over a millennium. Due to their corrosiveness, which is a consequence of their acidity and content of transition metals, iron gall inks accelerate the degradation of the writing or drawing support, which in this study is rag paper. Characterisation of acidity (pH) and degree of polymerisation (DP) of cellulose in paper is thus of high interest as it enables the estimation of material stability and assessment of risks associated with its handling. Based on a well-characterised set of samples with iron gall ink from the 18th and 19th centuries, we developed a near infrared spectroscopic method with partial least squares calibration for non-destructive determination of pH and DP of both inked areas and paper. Using this method, 27 18th and 19th century iron gall ink drawings from the British Museum collection were analysed and in all cases, inked areas turned out to be more acidic and degraded than the surrounding paper. Based on the obtained DP data, we were able to estimate the time needed for the inked areas to degrade to the point when they become at risk of damage due to handling. Using the average uncertainty of the calculated lifetime, we propose a quantitative stability classification method which could contribute to the curatorial and conservation decision-making process.

1. Introduction

Drawings in iron gall ink on paper are undoubtedly among the most exquisite artworks. Apart from their artistic value, they are very complex also from the chemical point of view [1,2]. The ink, generally a mixture of an Fe(II) compound, gallotannins, gum Arabic and water, was often prepared by the artist him/herself [3,4], and hundreds of recipes were passed down, and probably hundreds were forgotten. Once exposed to air, the fresh ink starts oxidising [5,6], rendering the ink insoluble, but this process also gradually leads to decomposition of the cellulosic support as well [7].

The complex reaction system includes acid-catalysed hydrolysis of cellulose and autoxidation of the many organic compounds present in the ink and in the paper. Due to its high variability, the chemistry of iron gall inks is still not entirely understood, although it is known that its acidity, the amount of ink applied, as well as the composition and grammage (or weight) of the paper support are important factors affecting degradation [8].

Although drawings prior to 1850 may have been made on rag paper, which would by itself withstand several millennia [9], the chemical degradation along ink lines results in loss of mechanical properties of the support and its lifetime drastically reduced. In order to assess the condition of drawings and potential risks of damage or information loss, it is therefore vital to know the acidity of paper along an ink line and the remaining degree of polymerisation of cellulose providing mechanical strength to paper. The procedures for their determination include viscometry for determination of the degree of polymerisation (DP) of cellulose in paper [10], size exclusion chromatography for DP of cellulose [11] in ink lines and determination of pH using micro-combined pH electrodes [12].

The drawings by Ubaldo Gandolfi (Fig. 1), John Everett Millais, Luca Giordano, Cosmas Damian Asam and of other celebrated 18th and 19th century artists, however, can certainly not be subjected to destructive chemical analyses. While their artistic and historic value is immense, so is our desire to understand their condition in order to be better able to preserve them. Spectroscopic methods are particularly suitable for the analysis of artworks *in situ*, as often

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* Corresponding author. Tel.: +44 20 7679 5994; fax: +44 20 7916 1887.
E-mail addresses: m.strlic@ucl.ac.uk (M. Strlič), jana.kolar@morana-rtd.com (J. Kolar), eva.menart@ena.si (E. Menart), chiggitt@thebritishmuseum.ac.uk (C. Higgitt).

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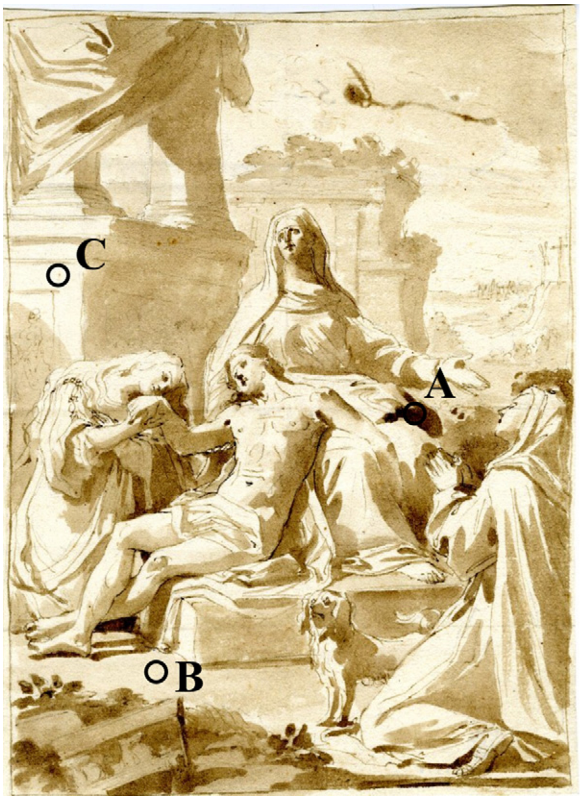

Fig. 1. Ubaldo Gandolfi's drawing (BM registration number PD 1946,0713.929) used in the study. The areas indicate where non-destructive analyses using NIR/chemometrics have been performed. ©Trustees of the British Museum.

no sample preparation is necessary and portable instruments are becoming increasingly available. Near infrared (NIR) spectroscopy is particularly suitable as the spectra are characterised by overtones and combination vibrations and are thus information-rich since absorptions of a single bond type appear in the spectrum several times [13]. Due to the overlapping bands, the spectra are complex and difficult to interpret analytically [14]. In order to extract the information, multivariate analysis is necessary [15].

Chemometric methods, in particular the partial least squares (PLS) method enable us to interpret NIR spectra quantitatively [13,15–17]. In the process of method calibration, a well-characterised and representative set of samples must be used, and for method validation, a separate sample set is needed. NIR spectroscopy in combination with chemometric data analysis has become increasingly used in material characterisation [18] and also heritage science [19], wherever a sufficiently large set of historical samples can be collected and characterised using conventional methods of analysis to provide the calibration data. This is not a trivial issue due to the variability (and availability) of historic samples.

Here we report on the development of an NIR method for characterisation of iron gall ink drawings. We developed PLS methods for determination of pH and degree of polymerisation/molar mass of both ink and rag paper, and propose a procedure for comparison of both sets of data to establish which drawings are at most risk from handling, which could result in mechanical damage.

2. Experimental

2.1. Samples and analyses

For calibration, 285 18th and 19th century rag papers and 85 18th and 19th century rag paper samples with iron gall ink applications were collected through donations and acquisition. For determination of paper and ink pH, many arbitrary methods for determination are available and some have been standardised [12]. However, due to sample size, a modified cold extraction method was used: to 20–50 μg of sample (extracted from a paper sample using a hollow, perpendicularly cut and sharpened surgical needle), 5 μL of deionised water was added and left overnight. pH was determined in the resulting extract using a micro-combined glass electrode (MI 4152, Microelectrodes, Bedford, NH).

Table 1
Drawings from the British Museum collection characterised non-destructively using NIR/chemometrics.

Drawing no.	Registration no.	Artist	Date
1	1946,0713.941	Gandolfi, Ubaldo	1728–1781
2	1946,0713.929	Gandolfi, Ubaldo	1743–1781
3	1946,0713.1528	Gandolfi, Ubaldo	1743–1781
4	1946,0713.1472	Gandolfi, Ubaldo	1743–1781
5	1946,0713.925	Gandolfi, Ubaldo	1743–1781
6	1946,0713.879	Busiri, Giovanni Battista	1698–1764
7	1946,0713.876	Busiri, Giovanni Battista	1725
8	1946,0713.875	Busiri, Giovanni Battista	1725
9	1980,0628.1	Fancelli, Pietro	1779–1850
10	1997,0712.39	Schmidt, Martin Johann	1770–1780
11	1982,1211.1	Millais, John Everett	1854
12	1997,0712.38	Asam, Cosmas Damian	1726–1727
13	1897,0505.603	Delany, Mary	1772–1782
14	1897,0505.77	Delany, Mary	1776
15	1897,0505.664	Delany, Mary	1774
16	1897,0505.39	Delany, Mary	1775
17	1875,0508.1231	Bergmüller, Johhan Georg	1703–1762
18	1995,0121.21	Frey, Johann Jacob	1681–1752
19	1981,0516.10	Deveria, Achille	1800–1857
20	SL5223-54	Giordano, Luca	1647–1705
21	2000,0929.12	Diziani, Gaspare	1704–1767
22	1980,1011.5	Calletti, Giuseppi	1615–1660
23	2003,0730.2	Carriera, Rosalba	1734
24	1928,1016.11	Mengs, Anton Raffael	1743–1779
25	1946,0713.1452	Gandolfi, Ubaldo	1743–1781
26	1995,0121.4	Millais, John Everett	1853
27	1981,0516.8	Deveria, Achille	1800–1857

For determination of the degree of polymerisation of cellulose in paper, the standard viscometric method was used [10]. DP was calculated from intrinsic viscosity using the Mark–Houwink–Sakurada equation [20]:

$$\mathrm{DP}^{0.85} = 1.1 \times [\eta].$$

Due to sample consumption, this method is not suitable for inks. The molar mass of cellulose in iron gall inked area was determined using size exclusion chromatography of carbanilated cellulose, based on a previously published method [21], which was slightly modified [11]. Approximately 200 μg of the material was necessary to determine relative average molar masses, using the universal calibration approach. The weight-average molar masses of CTC (MW) relative to polystyrene standards were converted to absolute molar mass using the established calibration [11]. The MW values (absolute mass average molecular weights) were recalculated to DP by dividing the MW by 537 g/mol (the MW of a fully carbanilated glucose monomer).

2.2. Historic drawings

Twenty seven 18th and 19th century iron gall ink drawings from the British Museum collection were analysed (Table 1). The measurements were performed on ink areas where the ink was most thickly applied and where degradation has been shown to proceed fastest [8], on areas with thinner ink application and on areas without ink.

2.3. NIR spectroscopy

Near infrared reflectance spectra were measured using a LabSpec 5000 spectrometer (Analytical Spectral Devices, USA) with three separate holographic diffraction gratings and three separate detectors; 512 element silicon photo-diode array for the spectral region 350–1000 nm, and two TE-cooled InGaAs for spectral regions 1000–1800 nm and 1800–2500 nm. The spectra were measured with a purpose-made accessory which could be used in a manner which was safe for the drawings and which allowed for collection of spectra in the 45°/45° geometry (spot diameter ca. 2 mm), using a 1 m fibre-optics jumper cable to interface with the LabSpec instrument. UV–vis–NIR spectra were measured over the range 350–2500 nm, using 300 scans. Several layers of Whatman filter paper no. 1 (Maidstone, UK) were used as the background. A Spectralon 99% reflective standard (Labsphere, North Sutton, NH) was used for calibration.

Each paper and ink sample was analysed three times and spectra were averaged to reduce the sampling error. For inks, spectra were taken on the verso and on the recto side. Spectra were subsequently manipulated with GRAMS 8.0 software (Thermo Scientific). All the measurements were performed under controlled temperature and relative humidity.

2.4. Data analysis

The goal of building a multivariate calibration model is to predict paper and ink properties from a NIR spectrum. A good NIR multivariate calibration model could replace the destructive reference method.

Multiple algorithms were available for analysing experimental results, *e.g.*, PCA (principal component analysis), PCR (principal component regression), PLS (partial least squares), Discriminant Analysis or various distance functions (*e.g.*, Mahalanobis distance) [22,23]. We chose the PLS spectral decomposition technique to correlate the target property of rag paper and ink samples (pH, DP, and MW) with NIR spectra. PLS regression was performed using Grams 8.0 software with an add-on PLS algorithm [24]. Separate calibration models were generated for each property. The methods for reduction of the light scatter effect, multiplicative scatter correction (MSC), standard normal variate (SNV) with or without detrending and differentiation using Savitzky–Golay algorithm, were considered as primary pre-treatments for spectral data to help remove undesirable variations from data and to optimize the PLS models [25–27]. The optimal complexity of the PLS models was determined by the leave-two-out cross validation procedure and corresponded to the number of latent factors resulting in the lowest root mean squared error of cross validation (RMSECV). Model accuracy was assessed using root mean squared error of prediction (RMSEP) using a validation set of samples separate from the calibration set.

Before applying quantitative calculations for the drawings we used Discriminant Analysis, the PCA/MDR method as a pre-filter to determine if the unknown spectrum matched the calibration well enough to give an accurate prediction [28]. The PCA/MDR method combines the PCA scores and spectral residuals for each spectrum, representing the spectral data not fit by the PLS calibration model, and uses them all for the Mahalanobis group matrix calculations. Including the sum squared spectral residual as a discriminating factor sets the maximum allowed variation in the factors, and also limits the range of variation in the residual for a sample. This is particularly important in the application for drawings because the outliers could easily be determined during prediction giving us best assurance of the result. If an unknown is an outlier, i.e. sample of which spectra differ significantly from those of the calibration set, the PLS-predicted value for the parameter of interest cannot be considered reliable.

3. Results and discussion

Prior to ca. 1850, paper production was a manual process, using rags as a source of raw materials. Even after defibration, and occasionally bleaching, cellulose fibres remained long and of high quality. After drying, the freshly made sheets were gelatine sized to make them suitable for writing/drawing. Despite the use of alum as a ‘hardener’ for gelatine, which lowered the pH of the size, the bulk of a rag paper sheet was still saturated with $CaCO_3$ and $MgCO_3$. This is ideal from the viewpoint of long-term preservation, as cellulose is most stable in a mildly alkaline macromolecular environment.

During degradation of paper, various acidic degradation products, and absorption of acidic pollutants lead to acidification. The more acidic a paper is, the faster it degrades, as the dominant degradation process of cellulose in an acidic environment is acid-catalysed hydrolysis.

3.1. PLS model development

With the reference samples, following the determination of pH of paper and ink, degree of polymerisation of paper, and molar mass of cellulose in inked areas, partial least square calibration using the same samples was attempted. The PLS methods for determination of pH of rag paper and of ink (verso) are presented in Fig. 2 and are highly satisfactory. The standard errors of prediction are the same order of magnitude as those of the pH measurement method, which is typically 0.2–0.3 pH units. For ink, two calibrations were done, both for the recto and for the verso side, with the predictions slightly better for verso side measurements. The pH as determined here represents bulk measurements, with the cellulose and size layers averaged. Considering that the PLS calibration can be obtained on the basis of NIR spectra at all, it is likely that pH depends on the content of organic acids and other degradation products which should give rise to absorption in NIR spectra.

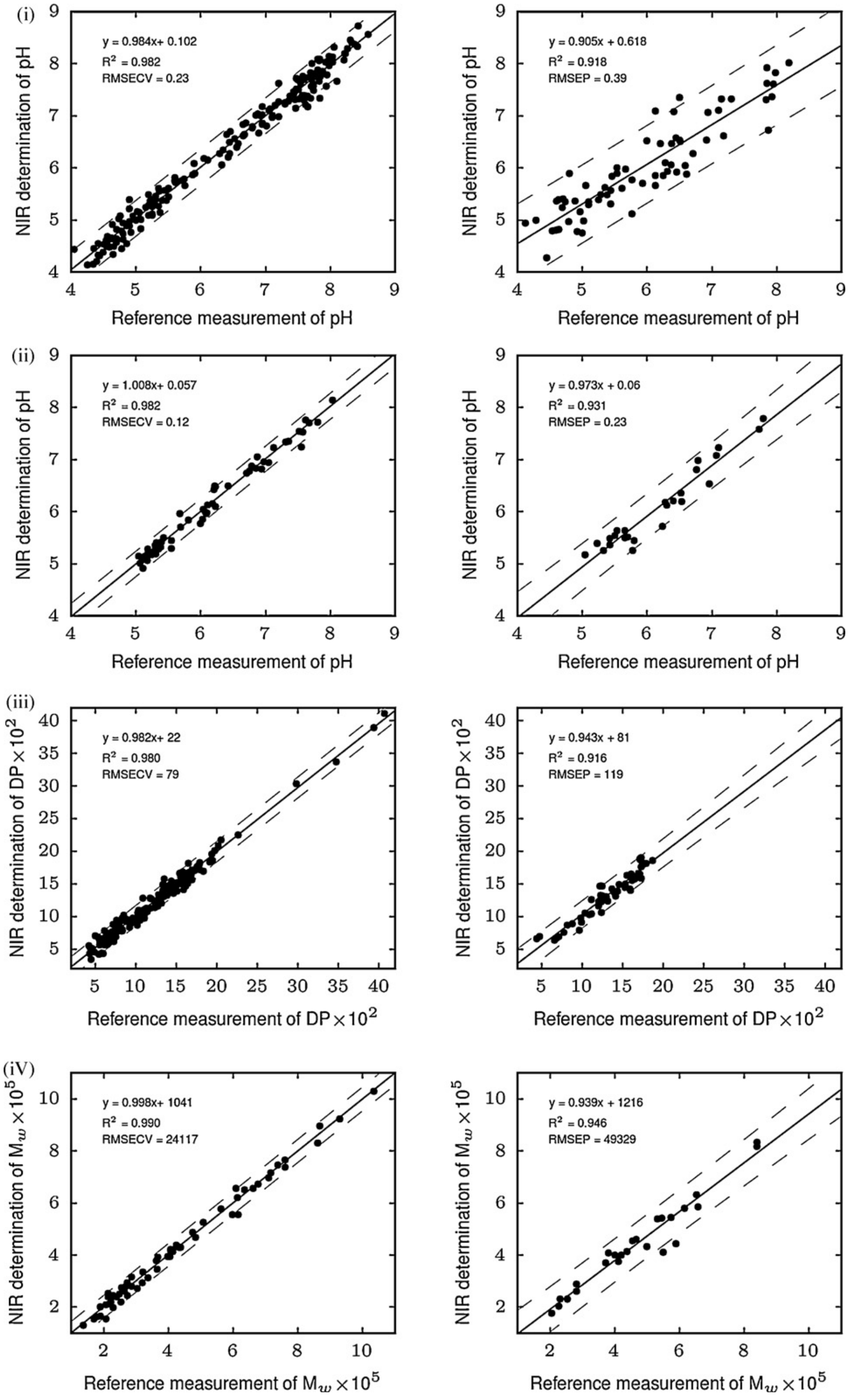

Fig. 2. The PLS calibrations (left) and validations (right) for (i) pH of rag paper, (ii) pH of iron gall ink, (iii) DP of cellulose in rag paper and (iv) MW of cellulose in iron gall ink areas (from top to bottom), based on verso measurements for inked areas. The PLS models for rag paper were calibrated on the set of 180 samples and validated on 50 samples, and those for ink were calibrated on the set of 60 samples and validated on 25 samples. The full lines and the broken lines represent the regression line and 95% confidence interval of regression, respectively.

The degree of polymerisation of cellulose, as well as the molar mass of cellulose, is crucially important for mechanical properties of paper. For bleached pulp, it has been shown that retention of folding endurance correlates with degree of polymerisation [29]. Paper with no mechanical resistance, which is difficult to handle without inflicting mechanical damage has been shown to have DP of about 250–300 [30]. In lifetime calculations, this DP value is often used as the cut-off value [31].

The PLS methods show excellent correlation between the measured and modelled values. The SEP values are approximately tenfold higher than the uncertainties of measurement, which are ca. 1%. Due to the raw materials used, inhomogeneity of rag papers

Table 2
The values of pH and DP determined using PLS methods, for the areas indicated in the drawing in Fig. 1. All NIR spectra were taken on the verso side.

	A	B	C
pH	6.2	6.4	7.3
DP	800	1000	1400

is usually much higher than that of industrially made paper. Therefore, the SEP and typical measurement errors cannot be compared directly, since the area of sample used for chemical measurement was approximately 1 mm in diameter, while the area of measurement of NIR spectra was 2 mm in diameter, and additionally, three measurement spots were averaged. For this reason, the uncertainty of prediction typically combines uncertainties associated with material inhomogeneity with that of measurement uncertainty. Also, while every effort was made to make NIR measurements as close to the spot where chemical measurements were made, material inhomogeneity can still have an impact on predictions. The data and results derived below should therefore be evaluated considering the RMSEP values in Fig. 2.

3.2. Non-destructive analyses of iron gall ink drawings

Having developed the PLS methods, it was then possible to determine pH and DP/MW of iron gall ink drawings. Spectra were collected on triple measurement spots on rag paper with and without ink application. In the inked areas, spectra were collected on the recto and on the verso side and for calculation of stability, their average was calculated.

For the drawing of Uberto Gandolfi in Fig. 1, the resulting values of pH and DP are given in Table 2. The areas with ink application (A and B) exhibit significantly lower pH than the area with no ink (C). Despite the rather thin ink application in spot B, the pH is not significantly higher than that of the other inked spot. The differences in DP show a similar picture: the area of thick ink application (A) exhibits significantly lower DP than that of paper, while the DP of the thin ink application is intermediate in value.

For all drawings used in the study, the values for pH and DP of areas with ink applications calculated using models for recto and verso give similar values, which is not surprising given that NIR radiation in the spectral region of interest was shown to penetrate through at least four layers of paper [19]. As a rule, the values of pH and DP obtained for areas with ink applications are significantly lower than those without. While this is probably expected, it is of interest as it offers the possibility to calculate how fast the degradation of inked areas is likely to proceed relative to the areas without ink.

3.3. Classification of stability

If the time necessary for iron gall ink to degrade until paper along the ink line loses all mechanical strength can be determined, it would then be possible to estimate which drawings are most stable and therefore least at risk of mechanical damage during handling. It is possible to obtain an estimate of this time using the Ekenstam equation [31] for degradation of linear polymers (see below). Surprisingly, the pH of all ink areas and that of paper areas is similar: the pH of papers without ink was on average 7.3 ± 0.5 and that of ink areas 6.1 ± 0.2. The rate of paper degradation crucially depends on paper acidity [32].

In calculations of the above average pH, we excluded drawings 19, 22, and 27, which have been subject to conservation intervention, and 11 and 26, which are considerably more acidic than the other drawings in the group studied. In the following discussions, we also excluded the Delaney collages (13–16), as they exhibited no areas without ink applications and a measurement of the DP of paper without ink was not possible. Collage 15 was already in an extremely degraded state and exhibited cracks along the edges – the determined value of DP of this paper was 250. Collages 13, 14 and 15 were also considered to be at risk – the average modelled value of DP of paper of these three objects was 400. This was therefore taken as the DP value of paper where the risk of damage during handling was considered to be high.

Table 3
DP and pH of papers and paper with ink for drawings included in study, ordered by the time remaining until the iron gall ink area with most ink application degrades to DP 400, rounded to 100 years. The divisions between lines in the table represents three possible risk categories.

Drawing	Ink		Paper		Time to DP 400 (years)
	DP_i	pH	DP_p	pH	
1	570	6.2	1180	7.3	200
25	590	6.0	1190	7.4	200
2	660	6.0	1420	7.0	300
17	610	6.1	1090	6.9	300
6	630	6.4	960	7.9	500
18	610	5.8	910	5.7	500
9	750	6.4	1160	7.4	500
7	690	6.1	1100	8.0	500
21	720	5.9	1140	7.4	600
4	800	6.2	1250	7.5	700
3	860	6.2	1400	7.3	700
10	860	6.1	1230	8.1	900
23	850	6.2	1220	7.3	1000
24	940	6.4	1360	6.9	1100
8	790	6.2	1020	7.7	1200
5	710	6.2	830	7.0	1300
20	870	5.9	1150	6.8	1600
12	950	6.3	1010	7.6	6500

Following from the Ekenstam equation [31] for degradation of linear polymers:

$$\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP}_0} = kt$$

where k is the rate constant of chain scission and t is time, and not knowing DP_0 (which was the same for paper without ink and with ink), we can write two equations for ink (i) and paper (p), and subtract them, to obtain:

$$\frac{1}{\mathrm{DP}_i} - \frac{1}{\mathrm{DP}_p} = (k_i - k_p)t$$

If we now assume that the degradation of ink proceeds at a significantly higher rate than that of paper, i.e. $k_i \gg k_p$, we obtain:

$$\frac{1}{\mathrm{DP}_i} - \frac{1}{\mathrm{DP}_p} = k_i t$$

and thus, we can calculate k_i, based on the measured DP_i, DP_p and based on the age of a drawing, which is known, at least approximately. Using k_i, we can now calculate the time needed for an ink line to become fragile ($\mathrm{DP}_i = 400$) under similar conditions of storage as they have been until the present time:

$$t_{400} = \frac{1}{k_i}\left(\frac{1}{400} - \frac{1}{\mathrm{DP}_i}\right)$$

The values calculated for individual objects are provided in Table 3 and while a number of assumptions have been made and the errors on the DP and t values need to be considered, the values seem reasonable, based on the observations of iron gall ink drawings from even earlier periods than 18th–19th centuries. The value of 6540 years for the drawing 12 is less reasonable and originates in the two determinations, i.e. for DP_i and DP_p being very similar. In this case, the assumption $k_i \gg k_p$ is probably not correct.

A conservator's assessment of condition of a drawing will examine the object as a whole and will depend on a range of factors. Based on the calculated lifetime it is now possible to add a quantitative stability criterion and gain some insight into which objects are most at risk. Therefore in Table 3 the drawings are ordered by the time for the object to reach the critical DP value of 400. Given the uncertainty in these values, it is perhaps more useful to consider classification into categories rather than the absolute values of time. We propose such a classification based on the average propagated uncertainty [33] of the time for the object to reach the critical value of DP, which is $s = 170$ years (based on uncertainties in age and determinations of DP_i and DP_p), *e.g.*, category 1: <2*s*, category 2: 2*s* to 4*s* and category 3: >4*s* (Table 3). However, it is possible to estimate which objects are most at risk regardless of the classification used, and in Table 3 they are ordered by the time for the object to reach the critical DP value of 400.

The above calculation can be used to inform decisions about which drawings would benefit most from a deacidification treatment, if it were considered. To counteract acid-catalysed hydrolysis, conservators sometimes use solutions or suspensions of calcium or magnesium compounds, which convert into the respective carbonates upon drying and lead to neutralisation of acids present in paper and ink, and often, antioxidants are added for further protection [1]. Such deacidification treatments would have a higher benefit in the case of drawings, which are not most at risk of mechanical damage. For drawings at high risk of mechanical damage, material consolidation would be of greater benefit.

The non-destructive analyses and modelling of the crucial parameters defining paper stability and mechanical strength can thus inform decision-making by those who are entrusted with the care of unique works of art.

4. Conclusions

Near infrared spectroscopy with chemometric data evaluation was used to model the degree of polymerisation (and molar mass) and pH of paper with and without iron gall ink. Based on the destructive analyses of 285 rag papers and 85 rag paper samples with iron gall ink applications, partial least square methods were built with highly satisfactory validation. Once the calibrations were obtained, pH and DP of a selection of 18th and 19th century iron gall ink drawings from the collection of the British Museum were modelled based on non-destructive collection of NIR spectra.

In all cases, pH and DP of areas with ink was lower than those of paper without ink application, which confirms the corrosive effect of the ink. However, based on the data, it was also possible to approximate the time remaining until an inked area of paper becomes so degraded as to be considered at risk. Based on the measurements of four objects (where ink lines exhibited signs of embrittlement) which already reached such a state, a value of DP 400 was considered as the critical value at which mechanical damage may occur during handling.

Such evaluations offer the possibility to categorise drawings in terms of stability, which informs their safe use in the collection. They also allow prioritisation if a conservation intervention were to be considered. The proposed quantitative stability classification could also become part of condition assessment of iron gall ink drawings.

The proposed NIR/chemometrics approach to non-destructive characterisation of iron gall inks has been shown to have considerable potential and could find widespread application in heritage science.

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