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Non-destructive determination of cellulose functional groups and molecular weight in pulp hand sheets and historic papers by NIR-PLS-R

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ABSTRACT

A fast and non-destructive method to evaluate the condition of pulp and paper was developed. Partial least square regression (PLS-R) models based on near infrared (NIR) spectra and reference values for molecular weight, carbonyl group content and carboxyl group content were calculated for pulp hand sheets and rag papers.

In this study, 110 pulp hand sheets were used and gave satisfactory models with high correlation coefficients (up to 0.97) during validation; whereas the test set validation (external validation) results were always better than those of cross-validation.

Modeling of 267 historic rag paper samples was more demanding due to inherent variability of the material. Nevertheless, PLS-R models for the carbonyl group content, carboxyl group content and molecular weight with good correlation coefficients (up to 0.93) and low errors for cross-validation using average spectra of different paper samples were obtained. For carbonyl group content models with good correlation coefficient was also obtained without previous averaging. Joint models using both pulp hand sheets and rag papers were calculated for carboxyl and carbonyl group contents resulting in lower correlation coefficients then the single models.

1. Introduction

Functional groups such as carbonyl and carboxyl groups, and molecular weight are important parameters in cellulose characterization. Even though the oxidized functionalities are only present in rather low amounts in the μmol/g scale they play a crucial role in brightness stability and molecular weight correlates to strength properties (Zou, Uesaka, & Gurnagul, 1996). Formation of chromophores in pulp can be directly associated with the amount of functional groups such as carbonyls (Potthast, Kostic, Schiehser, Kosma, & Rosenau, 2007). Hence a fast and still accurate determination is of great importance. Common pulp and paper testing methods require one gram of paper or several sheets of paper for chemical and mechanical paper testing (Pedersoli, 1999). Additionally, wet chemical analysis is time consuming and thus costly. This fact makes fast and straightforward qualitative and quantitative testing very desirable for cellulose characterization.

When the quantitative analysis of cellulose and its condition is needed in conservation science sample material is not as readily available. The use of destructive methods for historic material is generally problematic and material on a gram scale is hardly ever available from an archive or library. Alternatively conservation-relevant topics might be investigated on freshly produced mock-ups, whose preparation is expensive and does not necessarily reflect naturally aged material. Contemplating this issue, Porck and Teygeler (2001) stressed in an overview of conservation developments that the development of non-destructive or micro-destructive analytical tools is strongly recommended in conservation science, especially in order to monitor naturally occurring degradation processes, such as ongoing oxidation and chain scission of the cellulose molecule.

Since then, conservation scientists have made big efforts and advances in reducing the sample amount needed to investigate the condition of paper-based material, such as work of arts and documents. The pH of paper is considered to be a very important parameter to decide upon the need of deacidification treatments, therefore several techniques for the micro-determination of pH have been suggested (Saverwyns, Sizaire, & Wouters, 2002; Strlič et al., 2004). Unfortunately the pH value does not yield any information about strength properties or oxidative damage; it only allows a rough estimation of the stability perspectives.

The use of miniaturized fluorescence labeling of oxidized functionalities in paper has been applied to investigate subtle changes in carbonyl and carboxyl group content within small distances like 1 mm steps to determine deterioration gradients. For this type of analysis about 5 mg of paper have to be provided (Henniges,

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Prohaska, Banik, & Potthast, 2006). Even though this is already a small amount of sample material, it is rather an exception in paper conservation to obtain fragments like this from precious originals. As non-destructive analysis is preferred on original material, this method, although already miniaturized, might be unsuitable in other cases. Another suggestion was the use of micro-size exclusion electro chromatography (SEEC) on single paper fibers to assess the deterioration state of paper works of historic value (Stol, Pedersoli, Poppe, & Kok, 2002). However, the authors have pointed out one big drawback, namely that a single fiber cannot be representative for the whole paper sheet. Again, even though with very little sample demand, the method itself is destructive and sample material has to be provided from the original.

One option for a truly non-destructive analysis might be the application of chemiluminescence to assess the degree of polymerization of paper (Rychlý, Strlič, Matisova-Rychlá, & Kolar, 2002). Another method introduced in paper conservation science is solid phase micro-extraction coupled with gas chromatography and mass spectrometry (SPME-GC–MS). The highly sensitive SPME fibers have been used to detect volatile degradation products of paper and define marker substances that indicate deterioration of paper. Although SPME-GC–MS is highly sensitive and completely non-destructive, such marker substances were found to be difficult to determine and to quantify (Doering, Fischer, Binder, Liers, & Banik, 2000; Lattuati-Derieux, Bonnassies-Termes, & Lavédrine, 2004).

In the paper industry, the demand for non-destructive and fast pulp and paper testing has been met by near infrared (NIR) spectroscopy combined with multivariate calibration (Antti, Alexandersson, Sjöström, & Wallbäcks, 2000; Fardim, Ferreira, & Duran, 2002; Marklund, Hauksson, Edlund, & Sjöström, 1999). As NIR spectroscopy is completely non-destructive and may be applied on originals without a need for sample preparation it would also be an attractive analytical option for paper conservation science. Recently it was shown that non-destructive determination of the degree of polymerization of cellulose, and pH (Trafela et al., 2007) as well as mechanical properties (Lichtblau, Strlič, Trafela, Kolar, & Anders, 2008) is possible in historical papers. Being an indirect method, reference methods are necessary to obtain the reference values for calibration. These reference methods may be time consuming, expensive or not applicable to the material discussed above. Consequently, they are used only for calibration, and will then be replaced by NIR spectroscopy which thenceforward provides the same parameters in a fast, inexpensive and non-destructive way.

In the present study, the application of NIR spectroscopy combined with multivariate calibration for pulp hand sheets and historic rag papers as encountered in a paper conservation context is described. Group-selective fluorescence labeling of carbonyl and carboxyl structures with subsequent gel permeation chromatography (GPC) analysis was used as (destructive) reference method to provide three chemical parameters: the carbonyl group content, the carboxyl group content and the molecular weight, which were correlated with the NIR data.

2. Experimental details

2.1. Samples

For the 110 pulp hand sheet samples pulp was weighed to 2 g portions and processed to lab hand sheets according to ISO 3688 "Preparation of laboratory hand sheets for the measurement of diffuse blue light reflectance factor" by Lenzing AG (www.lenzing.com) without fillers or sizing material.

The 267 rag paper samples were provided from different sources and were of different ages, covering a range from the 16th to the 19th century. They are considered to be representative for typical historic European rag papers. The historic storage conditions of these papers are unknown.

Microscopic analysis of some fibers from historic rag papers and literature study support the assumption that the chosen historic papers were mostly produced from flax (McCrady, 1992). These fibers are characterized by their low lignin content, usually below 3% (Klemm, Schmauder, & Heinze, 2002). Rag papers are completely soluble in DMAc/LiCl and behave like dissolving pulps during CCOA and FDAM analysis.

2.2. Chemical analysis – Determination of the carbonyl and carboxyl groups content and of the molecular weight

2.2.1. Labeling

Carbazole-9-carbonyl-oxy-amine (CCOA) labeling of carbonyl groups was performed as described earlier (Potthast et al., 2003; Röhrling et al., 2002a, 2002b). Fluorenyl-Di-Azo-Methan (FDAM) labeling of carboxyl groups was performed as described by Bohrn et al. (2006). After labeling of a 20 mg sample for each parameter, i.e. carbonyl and carboxyl group determination, dissolution in *N,N*-dimethylacetamide/lithium chloride 9% (v/w) (DMAc/LiCl) is achieved by solvent exchange to DMAc in the case of CCOA. In the case of FDAM the solvent exchange step is omitted as the labeling is performed in DMAc. Measurement is performed with a GPC–MALLS (multiple-angle laser light scattering) detector system that yields molecular weight and molecular weight distribution in addition to the content of the respective oxidized group (C═O or COOH).

The suitability of the chosen cellulose solvent (DMAc/LiCl 9%) in combination with gel permeation chromatography for the analysis of pulp containing various additives typically found in historic papers was studied thoroughly and approved (Dupont, 2003).

2.2.2. General analytics

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; autosampler, HP 1100 column oven, Gynkotek STH 585, fluorescence detectors TSP FL2000 by Spectra Physics (CCOA) and Agilent FLD G1321A (FDAM); MALLS detector, Wyatt Dawn DSP with argon ion laser (λ_0 = 488 nm); refractive index (RI) detector, Shodex RI-71; Data evaluation were performed with standard Chromeleon (Softron), Astra (Wyatt) and GRAMS/32 (Thermo Fisher Scientific) software.

2.2.3. GPC method

The following parameters were used in the GPC measurements: flow, 1.00 mL min^{-1}; columns, four Polymer Laboratories PLgel mixed-A LS, 20 μm, 7.5 × 300 mm; fluorescence detection, λ_{ex} = 290 nm, λ_{em} = 340 nm (CCOA), λ_{ex} = 280 nm, λ_{em} = 312 nm (FDAM); injection volume, 100 μL; run time, 45 min. *N,N*-dimethylacetamide/lithium chloride (0.9% w/v), filtered through a 0.02 μm filter, was used as the mobile phase.

2.3. NIR measurements

Spectra were taken on different days using the FTIR spectrometer MPA™ form Bruker Optics (www.brukeroptics.de) with an integration sphere with a PbS – detector for measurement in diffuse reflection mode (15 mm diameter) covering a wavenumber range from 12,000 cm^{-1} to 3700 cm^{-1}. Following acquisition parameters were chosen: spectral resolution: 8 cm^{-1}, number of scans for a single sample spectrum: 100, zero filling factor: 2.

As pulp hand sheets were assumed to be of sufficient inherent homogeneity only one spectrum was recorded per sample; in total 110 spectra were acquired. Not all spectra were finally used for

calibration as for some of them no reference values were obtained. Details about the number of spectra used for calibration can be found later.

For historical sample papers 267 single spectra have been acquired before applying the respective reference method. It was attempted to use the same position for wet chemical analysis as that from where the NIR-spectra have been taken. For spectroscopic and wet chemical analysis only areas without visually perceivable inhomogeneities have been recorded.

2.4. Data processing

2.4.1. Wet chemical analysis

Evaluation of wet chemical analysis was done by ASTRA for molecular weight distribution and CHROMELEON for carbonyl and carboxyl group content determination.

2.4.2. Multivariate calibration

Partial least square regression (PLS-R) models were calculated using Bruker OPUS QUANT 2 software. For calibration (cross-validation) the infrared data sets were regressed against molecular weight (M_w), carbonyl group content and carboxyl group content, respectively, to find models with high correlations (i.e. high correlation coefficient r) and low root mean square error of cross-validation (RMSECV). The pulp hand sheets data set was divided into a calibration (cross-validation) set and a test set. The cross-validated models were then tested through test set validation. The test set was generated automatically using OPUS QUANT 2 software in the following way. After principal component analysis the number of principal components and the percentage of samples to be selected from the whole data set for the test set has to be defined. Then the selection by the software is done from the aspect of covering the whole concentration range in the best possible way to obtain a robust model.

Except for calibration of rag paper M_w, spectra were processed (smoothed and derived) according to Savitzky and Golay (1964) by means of 25-points smoothing filter and a second order polynomial to obtain first and second derivatives, respectively, using OPUS software.

3. Results and discussion

3.1. NIR spectroscopy

Band assignment of NIR-spectra (Fig. 1a) is rather complicated due to many broad and overlapping bands corresponding to overtones and combinations of fundamental vibrations appearing in the mid infrared region.

Pre-processing (Fig. 1b) of spectral data is useful to account for differences within the set of sample paper, especially for historic rag papers that are obviously different in color and thickness. Derivatives, multiplicative scattering correction, vector normalization and straight-line subtraction or combinations thereof, were found to be appropriate for the present problem. Before and after pre-processing, the spectra have been visually examined for unusual features. Three spectra (nos. 55, 57 and 117) of pulp hand sheets that deviated noticeably from the majority have been removed from the data set (Fig. 1b). Depending on visual pre-selection, and further detection of unsuitable samples (called outliers) that were later found during modeling, different numbers of spectra for each parameter were used for the models. Details will be given later at each model description.

3.2. Pulp hand sheets

The pre-processed (first derivative + multiplicative scattering correction) NIR-spectra in the wavenumber range from 7500 cm^{-1} to 4250 cm^{-1} and the molecular weight (M_w) determined for 98 samples by GPC (FDAM) were used to calculate a PLS-R model (73 spectra for calibration and cross-validation) and to validate it (19 samples for test set validation). During modeling six samples (outliers) were removed from the calibration (cross-validation) data set. The cross-validation and test set validation results using 10 PLS components for the model are shown in Fig. 2 and the errors are listed in Table 1.

From the 93 samples, whose carbonyl group content was determined by fluorescence labeling using CCOA-label, 75 samples were used for calibration. The pre-processed (first derivative + multiplicative scattering correction, selected wavenumber ranges: 7155–5970 cm^{-1} + 5340–4945 cm^{-1} + 4500–3775 cm^{-1}) NIR-spectra were modeled by 7 PLS components. During cross-validation six samples (outliers) were removed. The test set validation with 18 samples was also calculated with 7 PLS components (Fig. 3). For errors, see Table 1.

Carboxyl group content was determined on 102 samples by fluorescence labeling using FDAM-label. The pre-processed (first derivative + vector normalization) NIR-spectra in the wavenumber range from 7525 cm^{-1} to 3820 cm^{-1} and the carboxyl group content determined were used for modeling during which six samples (outliers) were removed. Ten PLS components were obtained during the cross-validation with a sample set containing 76 spectra,

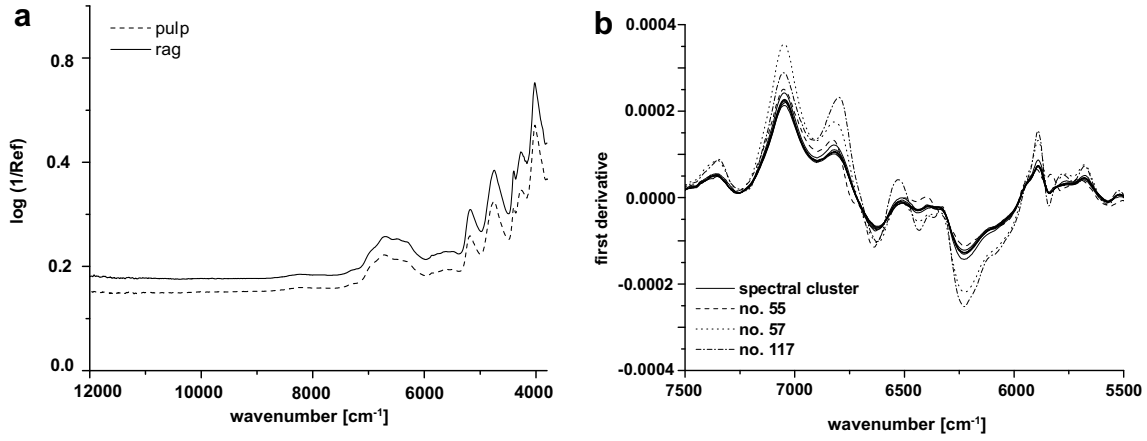

Fig. 1. (a) NIR-spectra of pulp hand sheet (dashed line) and rag paper (solid line). (b) First derivative of pulp hand sheets NIR-spectra (detail) showing visually deviating pulp samples nos. 55, 57 and 117 that have been excluded from multivariate calibration.

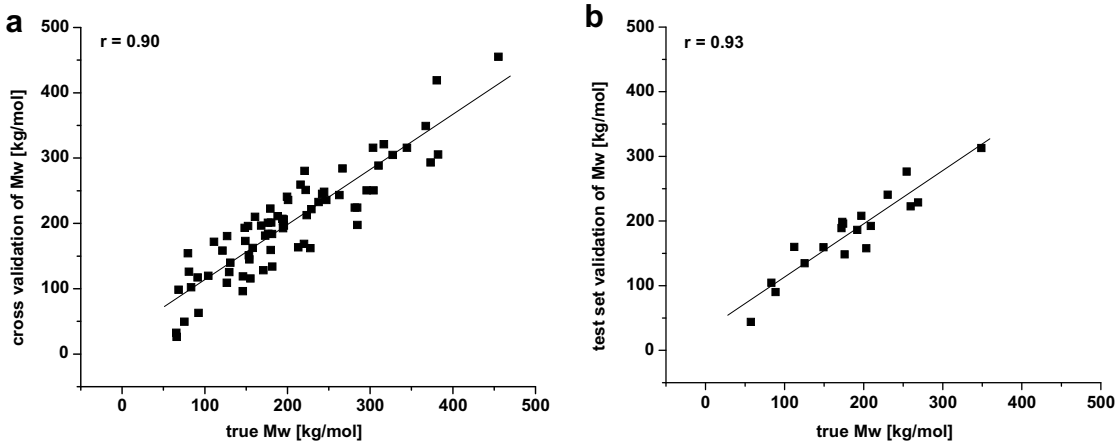

Fig. 2. Cross-validation (a) and test set validation (b) results of the molecular weight (M_w) of pulp hand sheets.

Table 1
Parameters of cross-validation (CV) and test set validation (TS) on pulp hand sheets.

Parameter		Offset	Slope	r^a	RMSECV[b]/RMSEP[c]
Molecular weight	CV	29 kg/mol	0.84	0.90	37 kg/mol
	TS	20 kg/mol	0.87	0.93	23 kg/mol
Carbonyl group content	CV	1.3 μmol/g	0.91	0.96	2.7 μmol/g
	TS	0.7 μmol/g	0.87	0.97	2.2 μmol/g
Carboxyl group content	CV	5.8 μmol/g	0.64	0.77	3.3 μmol/g
	TS	1.3 μmol/g	0.88	0.91	2.2 μmol/g

[a] *r*, correlation coefficient.
[b] RMSECV, root mean square error of cross-validation.
[c] RMSEP, root mean square error of prediction.

and test set validation (20 samples). The results are shown in Fig. 4. Errors are listed in Table 1.

In Table 1, the results for the prediction of the M_w, carbonyl group content and carboxyl group content of pulp hand sheets are given. It is remarkable that test set validation yielded better results than cross-validation. Especially for carboxyl group determination the cross-validation model is not very satisfying at the first glance. Nevertheless, according to Rodrigues et al. (2006) it is possible to have a relatively bad cross-validation while still a good prediction can be obtained, which is due to the fact that PLS-R is an inverse calibration method that assumes that the deviation form a perfect correlation between reference values and spectra is due to the reference method. In this case we decided to use the suggested model, not only because the satisfactory test set validation, but mainly because it was possible to use these parameters for rag papers as well. Another advantage of these parameters was that the number of samples that have to be removed is very low compared to other models tested.

3.3. Rag papers

Variations in color, paper surface structure, paper thickness and visual appearance found within and among the analyzed paper were obviously quite large. While pulp hand sheets contain cellulose in a reasonable pure and uniform form, historic rag paper contain different fillers and sizing material, while also aging does its part in changing paper parameters and inflicting inhomogeneities in an uncontrolled way. Visual inspection of the rag paper spectra revealed considerably differences regarding their absorption even though several spectra represented one single reference value. In order to account for this, several spectra with almost identical reference values were averaged to give one spectra representing the desired parameter. Due to this averaging process of historic paper objects only a small number of samples (48 for M_w, 38 for carbonyl group content and 30 for carboxyl group content) could be used for the study. Therefore, no test set was available and the validation was restricted to cross-validation of the models.

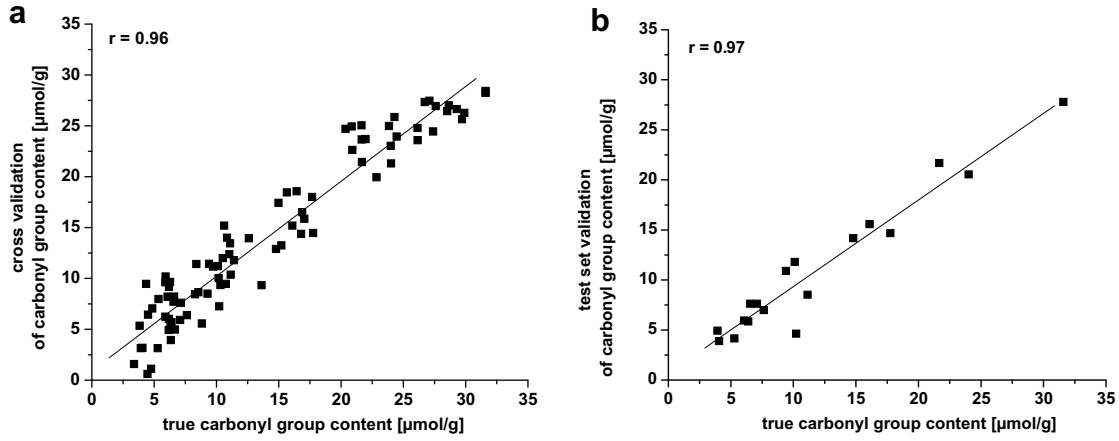

Fig. 3. Cross-validation (a) and test set validation (b) results of carbonyl group content of pulp hand sheets.

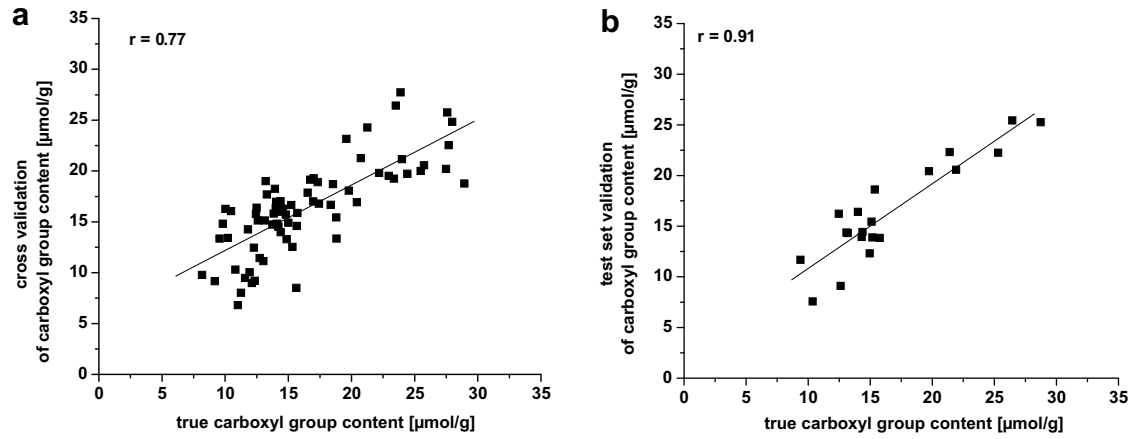

Fig. 4. Cross-validation (a) and test set validation (b) results of carboxyl group content of pulp hand sheets.

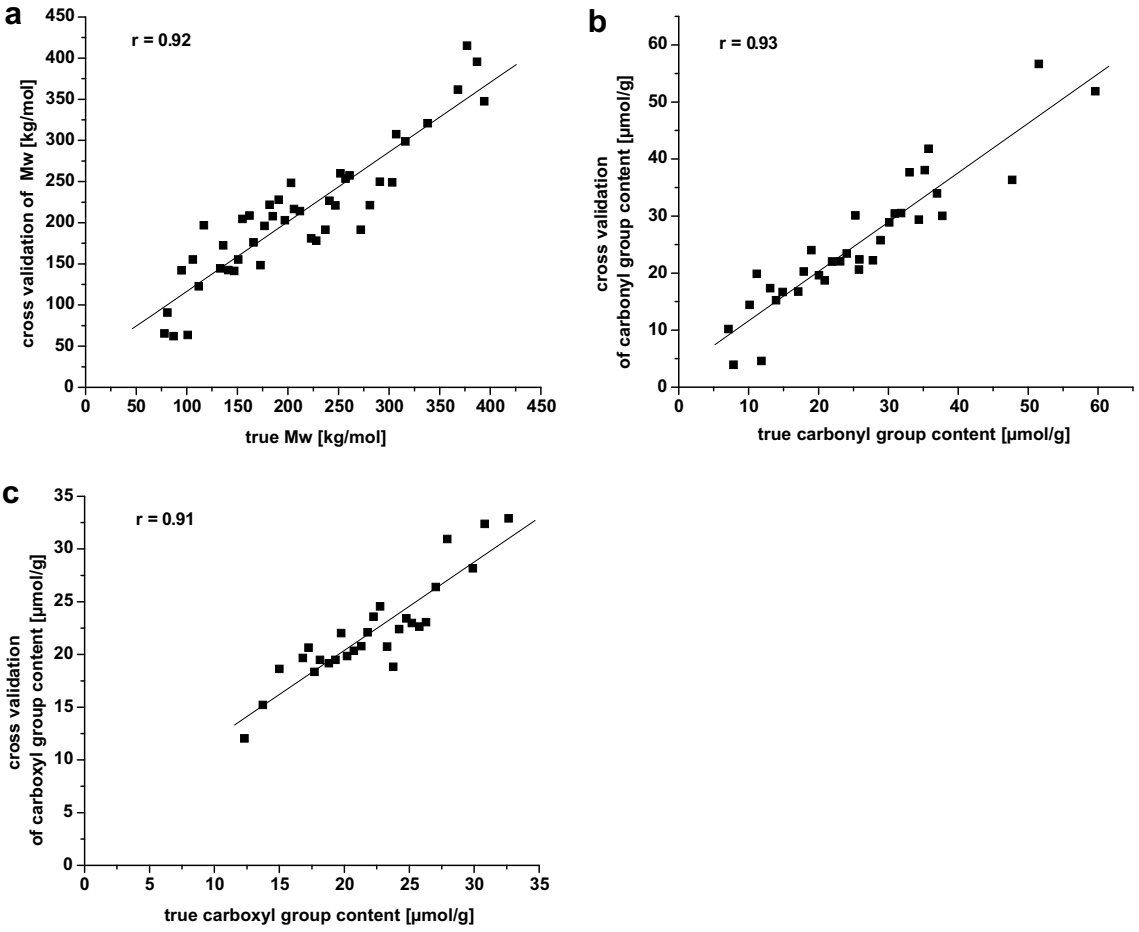

Fig. 5. Cross-validation results of molecular weight using 44 averaged spectra (a), carbonyl group content using 34 averaged spectra (b) and carboxyl group content using 28 averaged spectra (c) of rag papers.

Fig. 5 show the cross-validation results of rag papers for the M_w, carbonyl group content and carboxyl group content, respectively. Two samples for carboxyl group content and four samples for both, M_w and carbonyl group content were marked as outliers and removed during modeling. Despite the higher variability of these materials as described above the quality of the prediction was quite satisfying, being only slightly lower than for the pulp hand sheets. The averaging process that helps to level out inhomogenities within the paper matrix explains this. The corresponding data are summarized in Table 2.

As for both, carbonyl and carboxyl groups, identical wavenumber ranges and pre-processing procedures lead to good models when predicting pulp hand sheets and historic rag papers the two sample sets were combined to one set and joint models were calculated. All pulp hand sheet spectra and historic rag paper spectra were used. The rag paper spectra were not averaged this time.

Table 2
Parameters of cross-validation on rag papers.

Parameter	Pre-processing	Wavenumber range [cm^{-1}]	Offset	Slope	r^a	RMSECV[b]
M_w	Straight-line subtraction	7500–6800	32 kg/mol	0.85	0.92	34.6 kg/mol
Carbonyl group content	First derivative + multiplicative scattering correction	7155–5970 + 5340–4945 + 4500–3775	3.0 μmol/g	0.87	0.93	4.7 μmol/g
Carboxyl group content	First derivative + vector normalization	7525–3820	3.6 μmol/g	0.84	0.91	2.1 μmol/g

[a] *r*, correlation coefficient.
[b] RMSECV, root mean square error of cross-validation.

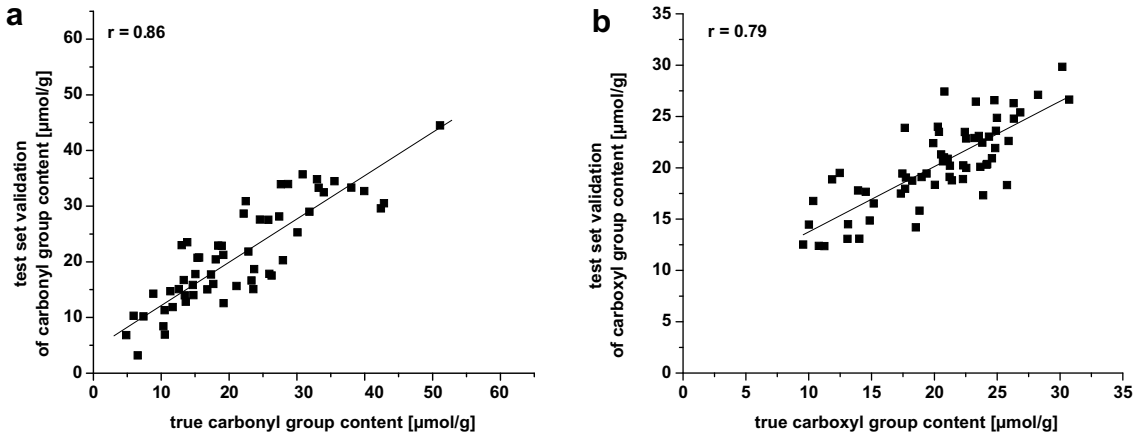

Fig. 6. Joint models of pulp hand sheets and historic rag papers applying the same pre-processing parameters and identical wavenumber regions as for the single models. (a) Test set validation of carbonyl group content (251 calibration spectra, 57 test set spectra and 69 outliers, number of PLS components: 16). (b) Test set validation of carboxyl group content (255 calibration spectra, 63 test set spectra and 13 outliers, number of PLS components: 6).

A test set was selected as described above. Identical pre-processing procedures and spectral regions as described for the single models were used for calibration and validation of the joint models. Test set validation of the carbonyl group content gave a correlation coefficient of 0.86 (Fig. 6a) needing 16 PLS components, while the model for carboxyl group content has a lower correlation coefficient of 0.79 (Fig. 6b) with 6 PLS components. Obviously the model for carbonyl group content prediction leads to a higher correlation coefficient. Corresponding data are summarized in Table 3.

However, it has to be noted that more PLS components were necessary for carbonyl group content prediction and the number of outliers removed as suggested by the software (51 CV and 18 TS) was considerably higher as for carboxyl group content prediction (6 CV and 7 TS). The outliers found during validation of the carbonyl as well as carboxyl group contents in the joint models were spread over the whole ranges. Most of the pulp sample outliers are identical with those already removed in the pulp models; therefore the majority of the detected outliers were among rag paper samples. The latter was expected because it was not possible to develop acceptable models using non-averaged single rag paper spectra. Contrary to that, the joint models were calculated using single rag paper spectra.

As the carbonyl group content of about 95% of the outliers could be predicted with the joint model the problem seem to be the naturally occurring inhomogeneities. When aiming to include outlier rag papers into the model they have to be reanalyzed. Special care has to be taken that the whole area from which the spectra are collected is also analyzed by the reference method to rule out the variance within historic paper sheets as a disturbing factor in the modeling procedure.

Table 3
Parameters of test set validation of joint models obtained from pulp hand sheets and rag papers.

Parameter		Offset (μmol/g)	Slope	r^a	RMSECV[b]/RMSEP[c] (μmol/g)
Carbonyl group content	CV	4.5	0.77	0.86	4.5
	TS	4.4	0.78	0.86	5.3
Carboxyl group content	CV	8.4	0.58	0.74	3.2
	TS	7.4	0.64	0.79	3.1

[a] *r*, correlation coefficient.
[b] RMSECV, root mean square error of cross-validation.
[c] RMSEP, root mean square error of prediction.

4. Conclusion

A simple, fast and non-destructive method based on NIR spectroscopy and multivariate calibration for the determination of the molecular weight, carbonyl group content and carboxyl group content of pulp hand sheets and rag paper was developed for the first time. The quality of the obtained predictions was based on accurate reference methods (CCOA and FDAM).

The developed models allow testing on different sites of a paper to obtain the analytical parameters and gain insight into inhomogeneities of those parameters without damaging the paper. This is important for historic rag papers which have an inherently higher variability of the paper material, such as discolorations, varying thickness and surface textures. This deliberately incorporated variability could be modeled using average spectra of different historic paper samples as confirmed by cross-validation of the key chemical parameters. For the prediction of the carbonyl and carboxyl group content joint models of pulp hand sheets and historic rag papers without previous averaging were obtained. Both models provided acceptable correlation coefficients.

The presented method can reasonably be expected to find acceptance as a supporting tool in conservation science, helping

to assess the damage state of cellulosic objects and to decide on conservation treatments, but also its applicability in cellulose chemistry as well as pulp and paper science appears to have future perspectives.

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