Degradation of paper-based collections is a consequence of a variety of factors, from endogenous (paper acidity, lignin content, etc.) to exogenous (pollutants, humidity, etc.). Environmental influences during long-term storage are undoubtedly important parameters. Studies have shown that increased humidity leads to higher rates of degradation of acidic paper, while the influence on mildly alkaline paper is less straightforward. The role of temperature is also crucial – it is possible to calculate how many times the lifetime of paper can be changed if the temperature of storage is increased or decreased by one degree Celsius. Volatile organic compounds (VOCs) are another subject which deserves attention, especially since they are both emitted and absorbed by paper. Studies have shown that such emissions can be substantial.

In any case, long term monitoring of large collections is needed to assess the influence of the storage environment and of the inherent material properties on the ageing behaviour of a collection. For such a task, a simple instrument is needed, which would allow us to survey a collection in a non-destructive, non-invasive and chemical-free manner. In the frame of the SurveNIR project, co-funded by the European Commission 6th Framework Programme, a consortium of research institutions and end-users set out to build a dedicated near infra red (NIR) spectroscopic instrument, which would enable the user to determine a variety of chemical and mechanical properties of paper, including naturally aged paper. The approach will be validated in several European collections in the British Library (London), Victoria and Albert Museum (London), National Archives (The Hague), National Archives (Stockholm), National Museum of Denmark (Copenhagen), National and University Library (Ljubljana), and State Archives of Dubrovnik.

**Introduction**

Paper-based documents have long been, and still are, the most important record of human activity. Fortunately, paper is a long-lived material provided that the production technology favours its stability and provided that it is stored in a favourable environment. However, most of the paper produced between 1850 and 1990 is likely not to survive more than a century or two due to the inherent acidity auto-catalysing the degradation of paper. Cellulose is the most important structural element of paper and it is well-known that the rate of its degradation depends on the pH of its environment [1].

Traditionally, the condition of a paper-based object or a whole collection is assessed visually, and simple physical and chemical tests are performed, such as the folding test [2] or determination of pH of paper using pH-indicator pens. While the folding test is performed in such a way that a paper corner is actually torn away, the pens leave some of the dye used as a pH indicator on the object. Neither of the two tests can be described as non- or micro-destructive. Even determination of paper pH using flat surface electrode, which is probably the most often used methodology in paper conservation workshops, is destructive as an area of paper has to be wetted in order that the measurement can take place at all. After drying, degradation is likely to proceed faster along the wet-dry boundary [3]. In addition to all of the above tests, surveying methods are also highly individual [4]. In any case, surveys are necessary in order to reveal the condition of a collection, the general conservation needs and in order to plan preservation activities.

Mid-IR spectroscopy is widely used to study cultural heritage material. In general, near-IR spectroscopy is gaining in importance in material studies [5-7]. However, aged paper is a complex material and an analytical interpretation of mid-IR spectra is often difficult.

Near-IR spectra often exhibit fewer particular features than mid-IR and Raman spectra. NIR spectra are characterised by overtones and combination vibrations, especially of NH, CH and OH functional groups.

Chemometric analysis of data is a widespread approach to spectral analysis, instead of analytical band assignation [8]. It enables us to compare the whole spectrum (or part of it) with chemical information obtained with the same set of samples. To develop a model for determination of pH of paper, we first
need to determine the pH using traditional methods and compare the obtained data with the spectra of the same set of samples. This approach can be successful under certain conditions [9]. A large enough sample set is needed and the method should be carefully validated. For this purpose, partial least squares (PLS) is often used for correlation of spectral and chemical information [10-12]. From these correlations we can deduce the chemical information for an unknown sample from its spectrum. However, the quality of these correlations depends on a number of factors, among which the quality of spectra and the quality of chemical analytical data play a decisive role.

In this paper, we report on the development of a non-destructive NIR instrument which promises to replace the traditional destructive methods of determination of mechanical properties [13] and pH [14] of historical paper. It should be noted that a developed PLS method is only useful for analysis of the same paper types as was used for building the correlation. A method developed for estimation of pH of rag paper will likely lead to erroneous results if applied to transparent paper.

**Experimental**

Paper samples were taken from books dated from 1800 till the present. Parts with evident damage due to biodegradation, water-related damage or with damage evidently caused by excessive use were disregarded. Excessively soiled and densely printed samples or laminated, transparent and other specialty papers were not considered either. Margins (3 cm) were cut away to exclude areas degraded due to environmental influences.

Tensile strength (ISO 1924-2:1994) was determined using Zwick Proline Z0.5 TS (load cell nominal force 500 N type II, pneumatic grips, modified jaw faces).

To determine the pH of the paper, cold extraction of microsamples was performed in the following way: 5 µL of deionized water was added to 20-50 µg of sample, and left overnight. pH was determined in the extract using a micro-combined glass electrode (MI 4152, Microelectrodes, Bedford, NH).

A Perkin-Elmer Spectrum GX (Waltham, MA) equipped with a 76-mm Labsphere RSA-PE-200-ID (North Sutton, NH) integration sphere coated with Infragold, with a DTGS detector, was used. The reflectance spectra were collected in the interval 6500 - 500 cm⁻¹, 128 scans per sample. Spectra were taken using 4 layers of sample paper.

Spectrum Quant+ software (Perkin Elmer, Waltham, MA), partial least squares analysis (PLS) was used to build correlations and deduce the chemical properties. The quality of correlations was optimized through selection of the most appropriate pretreatment of spectra (derivation, smoothing, etc.) and of the wavenumber intervals used.

**Results and Discussion**

NIR spectroscopy in combination with chemometric data evaluation has already been used for evaluation of cellulose degradation during accelerated ageing experiments [7]. The intention of the SurveNIR project is to provide museums, libraries and archival collections with a non-destructive, chemical-free, low-cost surveying tool that would provide more in-depth information than the traditional methods but would also be user-friendly and would not require extensive technical knowledge by the surveyor [15].

Using the PLS approach, we were able satisfactorily to relate NIR spectral information to determinations of mechanical properties [13] and pH [14] of a variety of historical paper. The results are shown in the following graphs:

**Figure 1.** PLS calibrations for estimation of tensile strength [13] and pH [14] of historical paper.
of historical papers (figure 1). This enables us to propose the methodology for rapid determination of the most important information on historical paper needed by conservators and collection managers. In addition to this, we also developed methods for determination of ash content, aluminium content, carbonyl group content, lignin content [14] and tensile strength after folding [13], all from a single spectrum taken in less than a second.

As a part of the dedicated SurveNIR instrument (figure 2), software will be developed which will incorporate the chemometric data evaluation. Chemometry will allow the analysis of a large amount of information – represented by the large number of reflection NIR spectra taken in a collection. The concept of the software will be to allow the user to survey whole collections of paper for chemical and mechanical information, and thus propose actions needed for its optimal preservation.

Case studies in seven collections from European countries in three different types of paper-based collections – museum, library and archive – will be performed to validate the approach.

CONCLUSIONS

A new dedicated NIR instrument has been built, which is designed to enable rapid and safe measurement of spectra from paper. The spectra will be used to describe paper properties of interest, such as pH and mechanical properties. These data are needed in order to decide the most appropriate conservation treatment for the object in question.

In addition, the SurveNIR software will enable the user rapidly to measure spectra of selected items from a collection in order to perform a survey. The traditional techniques, which are destructive and inconclusive, can thus be successfully replaced by this new non-destructive instrument. The SurveNIR instrument will allow us to survey a collection in a non-destructive, non-invasive and chemical-free manner and it will be easy to use by non-professionals.

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