NON-DESTRUCTIVE CHARACTERISATION AND DATING OF HISTORIC PARCHMENT USING NEAR INFRARED SPECTROSCOPY

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Summary: Parchment is a complex natural material made from animal skin, which has been used as a writing support and for bookbinding. Due to the historic value of objects made of parchment, understanding of their degradation and their conservation is of high importance to archives, libraries and museums. It was recently shown that lipid content in parchment may have an important influence on collagen degradation, probably via autoxidation. For parchment, a direct link between lipid content and degradation has, however, still not been demonstrated. The goal of this research presented here was to introduce NIR spectroscopy as a new non-destructive spectroscopic method of characterization of proteinaceous historic materials and to examine the relations between lipid content and degradation of parchment, measuring shrinkage temperature.

Keywords: Near infrared spectroscopy, Lipid peroxidation, Collagen

Introduction

Parchment has been used as a writing and drawing support since antiquity. Collagen is its principal component and has a unique triple helix structure, which is stabilised by hydrogen bonds and van der Waal's interactions between side chains [1]. The helix structure plays an important role in its mechanical properties. Numerous denaturation processes lead to degradation of the ordered structure, converting it into unfolded and disordered gelatine. This leads to fragility and brittleness of the object [2]. It was recently shown that lipid content in parchment may have an important influence on collagen degradation [3], probably via autoxidation [4]. Changes in the structure of collagen may be caused directly or indirectly [5]. However, a direct link between lipid content and degradation of parchment has still not been demonstrated.

In parchment research, shrinkage temperature is often used as an indicator of hydrothermal stability. The higher the shrinkage temperature, the more energy is needed to break the bonds between collagen molecules, thus indicating better condition of the parchment object [6]. Several other thermal methods to study the condition of parchment have been suggested and are in use [6,7]. Shrinkage temperature seems to remain the most widely understood parameter by the end-user community [7].

Classical methods for analysing historic materials are often time-consuming and destructive or at least micro destructive [8]. Near-infrared (NIR) spectroscopy, in conjunction with multivariate analysis, represents an attractive new option [9,10]. Overtones and combination vibrations, especially of NH, CH, and OH functionalities [11] lead to absorption of NIR radiation. For extraction of useful information from spectra, multivariate data analysis such as partial least square regression (PLS) is needed [12,13].

The goal of this research was to introduce NIR spectroscopy as a non-destructive spectroscopic method of characterization of proteinaceous historic materials [10]. In addition, we developed a dating model, based on NIR and multivariate analysis, allowing us to successfully date parchment documents from the collection of the National Archives of the Netherlands.

Materials and Methods

Samples. 24 historic samples of parchment, produced between 1480 and 1900, including a new goat parchment sample from 2005 (Talas, New York) were used in this research.
Lipids were extracted from samples with hexane (HPLC grade, J.T.Baker, USA) using Soxhlet extraction, the duration was 0 h (immersion only), 1 h and 4 h. After extraction, the samples were dried in vacuum and equilibrated at room temperature. The amount of extracted material was determined gravimetrically. Half of all samples (extracted and non-extracted) were then subjected to accelerated degradation in a climatic chamber (Vötsch Climatic chamber, Type VC 0020) at 80 °C and 65% RH for 18 days. The other half was not subjected to degradation.

Shrinkage Temperature. The shrinkage temperature of parchment samples was determined using a micro hot table (Caloris, Bucharest) and a stereo microscope Leica S4E (20-160x). The temperature was programmed using FLTK 1.1.9. Software (GNU Lesser General Public License). A high resolution Leica EC3 camera was used for visual determination of shrinkage temperature. The temperature programme was started at room temperature and increased at 2 °C min^{-1} until the temperature at which shrinking was just observed (this temperature was noted), and then continued until the process completed.

Spectroscopic Analysis. LabSpec 5000 ASD NIR spectrometer (Boulder, CO) with two separate attachments was used: ASD Chem Probe with a purpose-made accessory and ASD MuG-Light. The reflectance spectra were collected in the interval of 350-2500 nm, 100 scans per spectrum. Five measurements were taken on five different positions of the same sample, with a set of positions on the recto and another set on the verso side. As a background, a stack of pure cellulose filter paper sheets was used (Whatman No. 1, Maidstone).

Chemometric Data Analysis. Partial least square analysis (PLS) was performed using Unscrambler v.9.7 (CAMO, Trondheim).

Results and Discusion

The influence of lipids on parchment degradation

We used goat parchment from 2005 and another historic parchment from 1965 in the investigation of influence of lipid fraction on thermo-mechanical properties of collagen during degradation. We compared the shrinkage temperature of samples with and without lipids. Results presented in Figure 1 show the relationship between lipid content and degradation of parchment.

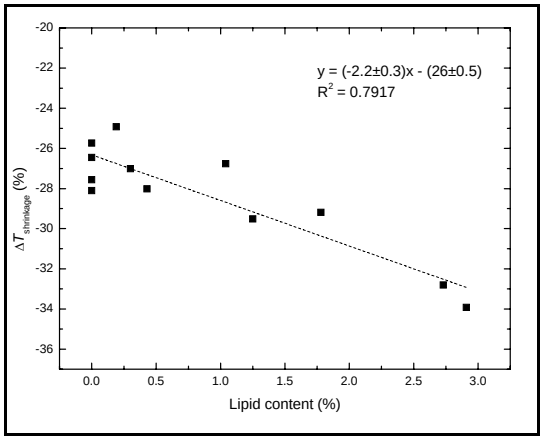

Figure 1. Decrease of shrinkage temperature of parchment samples during accelerated ageing.

The effect of lipids is considerable, taking into account that the removal of 3% lipids leads to a marked additional decrease of shrinkage temperature of 27%, compared to samples with no extracted lipids.

Determination of shrinkage temperature based on NIR spectroscopy and chemometrics

Shrinkage temperature is a good indicator of parchment condition [6] so it is important to develop non-destructive method for its determination. For this purpose, we collected VIS/NIR spectra (450-2000 nm) of all samples, including all the extracted and degraded samples. Using Partial Least Square regression [11,12], we investigated how NIR spectral information correlated with shrinkage temperature measurements.

A PLS model for determination of shrinkage temperature was successfully built and shrinkage temperature can be predicted from NIR spectra with RMSEV of 7 °C, which is sufficient for categorisation of parchment objects. The calibration curve for the PLS model is presented in Figure 2. All spectra were taken with the ASD Chem Probe with a purpose-made accessory on verso sides of parchment samples. Different pre-treatments were used in the optimisation process: baseline correction, Standard normal variate - SNV, derivation and Martens' uncertainty test for determination of significant wavelengths.

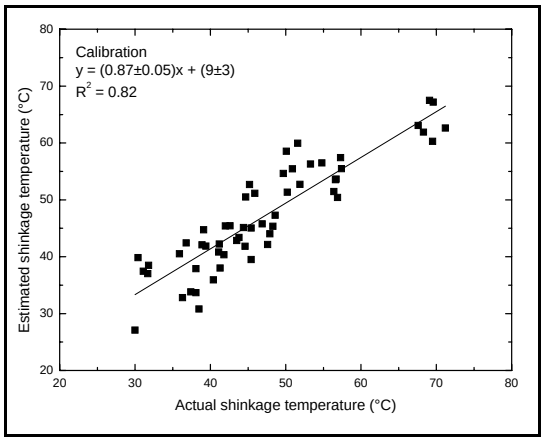

Figure 2. PLS calibration for determination of shrinkage temperature of parchment.

Dating of historic parchment

The historical parchment collection from the Nationaal Archief has been used to build a PLS model (Figure 3) for determination of the year of parchment production (i.e. for dating). All of the objects were dated between 1179 and 1793. A model was produced for prediction of the year of production for unknown historic parchment document with RMSEV 72 years.

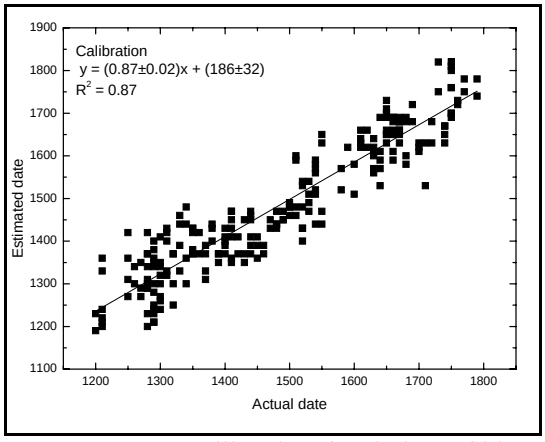

Figure 3. PLS calibration for dating of historic parchment.

Conclusions

The degradation and non-destructive characterisation of a large set of historic parchments was studied and a significant effect of the lipid fraction in parchment on its degradation was demonstrated. The higher the lipid content, the faster the degradation: a 3% lipid content led to 27% additional decrease of shrinkage temperature during accelerated ageing. Based on NIR spectroscopy and partial least square calibration, we developed a non-destructive method for determination of parchment shrinkage temperature. The method could be used for rapid condition assessment of historic objects. We also developed a method for non-destructive dating of parchment.
The research demonstrates the use of portable spectroscopic instruments for historic parchment characterisation and dating in non-laboratory environments, based on NIR spectroscopy and chemometrics.

Acknowledgments

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