Application of Raman Imaging to the Analysis of Old Paper Samples

E. Pigorsch, Papiertechnische Stiftung (PTS) Heidenau, Germany

Motivation & Objectives

The knowledge of the exact and detailed chemical composition of old papers can be important and useful for different purposes. It can give information on historic paper making practices and can help paper conservators to evaluate the preservation state of old papers and to find suitable measures for paper conservation or restoration. Furthermore, the chemical analysis of paper can help to reveal forgeries of works of art or of documents.
By using the Raman imaging technique, the chemical structure, that means the presence and distribution of different paper components on the surface or along the cross-section, can be visualized. This includes different fibers, filler pigments, sizing compounds and also other substances that came as trace particles with the main components in the paper or were formed during the production process.

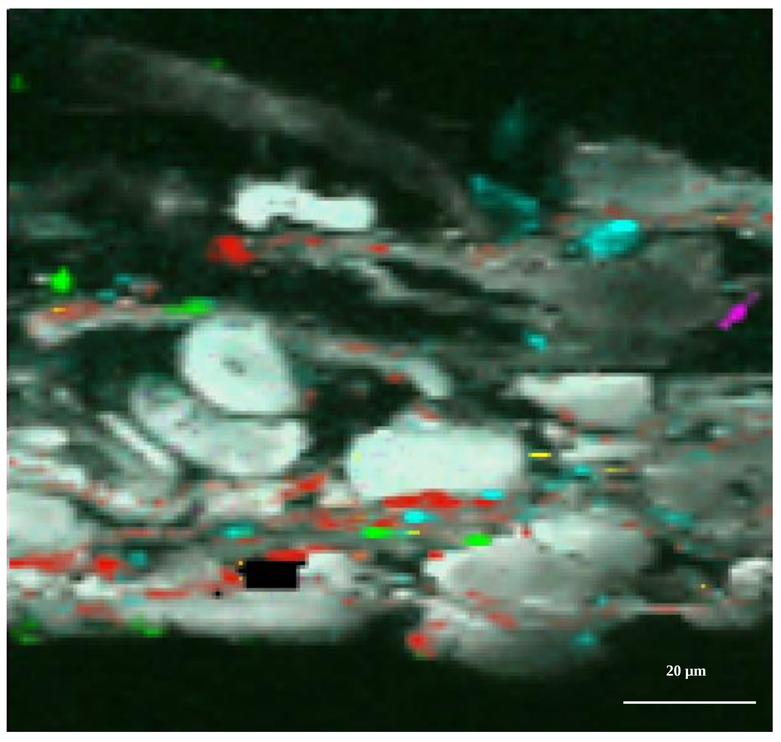
The working hypothesis behind our studies is that the presence and the distribution of different paper compounds including the trace particles contain information about the potential production year and production place of the paper and its treatments.

Source: Le Monde (2011 & 2015)

Experimental

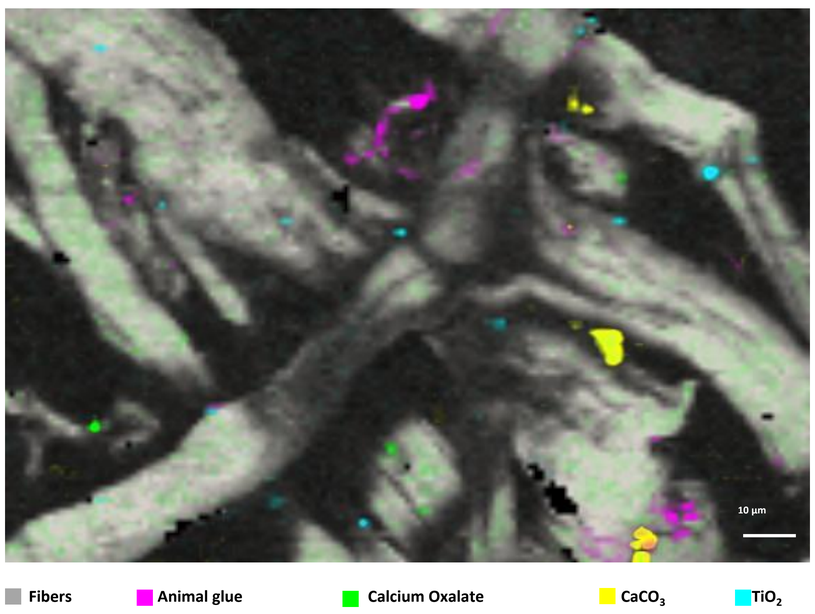
The Raman measurements were done with a Raman Microscope WITec alpha 300M+ with a 532 nm laser. The laser power at the sample was about 10 mW. The spectra were acquired with an integration time of 500 ms. The step size of the mapping measurements was 1 micron. Data analysis was accomplished by an in-house developed spectral imaging software based on MATLAB (The MathWorks Inc.).

Cross-Section of a Writing Paper from 1890

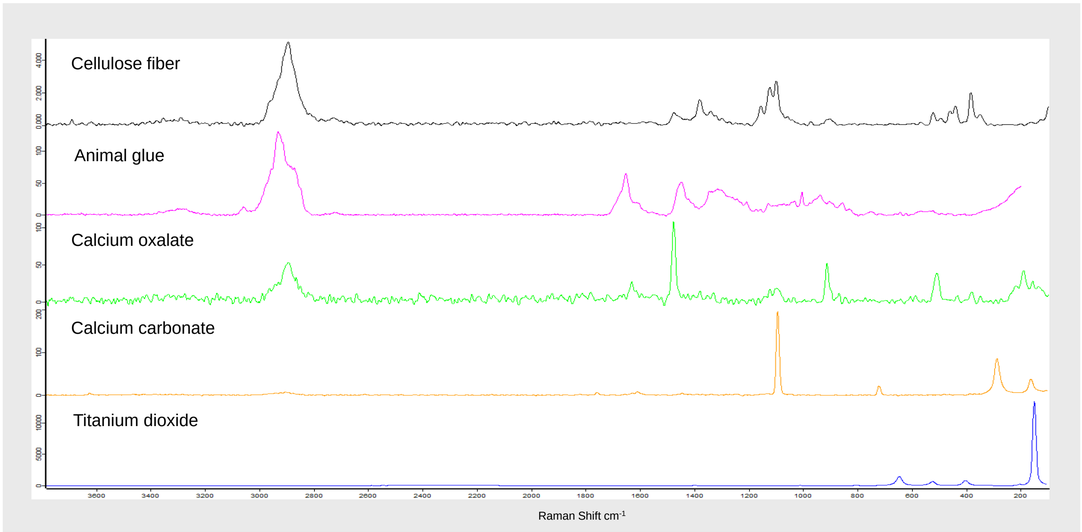


The paper consists of rag fibers and clay as filler and it is internally rosin sized. Additionally to the main paper components one observes starch which was added with the rosin to the paper. The gypsum particles in the paper were formed under acidic conditions by the sulphate ions of alum which was added to precipitate the rosin on the fibers and the calcium ions of the process water.

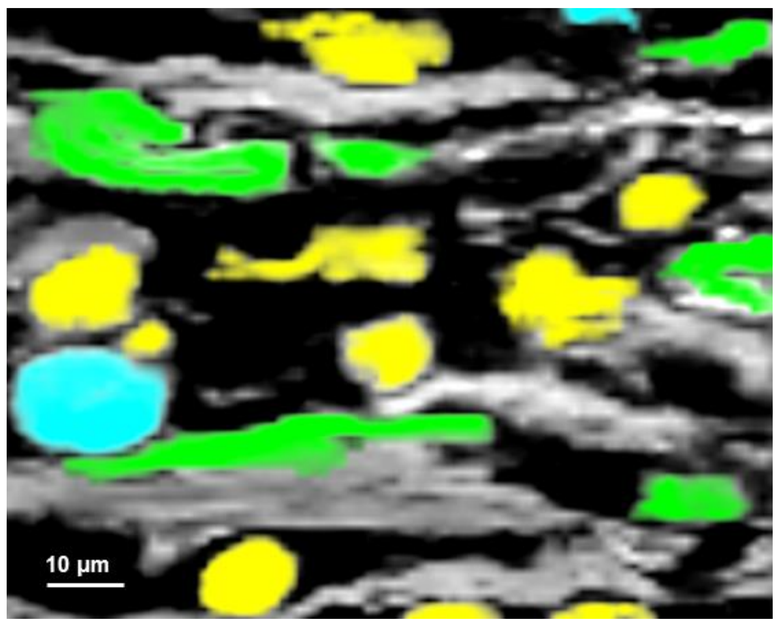
Writing Paper from 15th Century

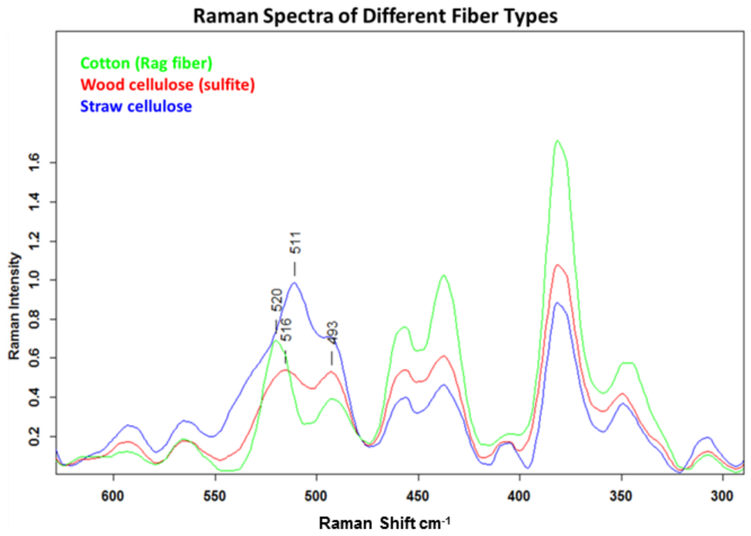


In the Raman image from the surface of a 15th century paper we see the fiber structure and regions with animal glue. The fibers are partially covered with calcium oxalate $CaC_2O_4 \cdot 2H_2O$ (weddelite) which was very likely produced by fungal activity. There are also calcium carbonate particles which precipitated during the processing of the rag fibers with lime. Especially interesting are the many small particles of titanium dioxide (anatase). This quantity of titanium dioxide in an old paper is unusual and must come from certain clay minerals or sediments which came with the process water in the paper.



Detection of Different Fiber Types





Acknowledgements

This work has been financially supported by the German Federal Ministry of Economics and Technology BMWi. We would like to thank Gangolf Ulbricht (Werkstatt für Papier, Berlin, www.papiergangolfulbricht.de) for providing the old paper samples.

Research Project IK-MF 150045 „Neue spektroskopischen Analyseverfahren zur Authentifizierung von Dokumenten und Kunstwerken auf Papier“ Contact: Dr. Enrico Pigorsch · Phone +49 (0)3529 551 678 · Mail: enrico.pigorsch@ptspaper.de
PTS · Pirnaer Str. 37· D-01809 Heidenau · Internet: www.ptspaper.com