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# Investigating the origin of the raw material of rag paper by Raman spectroscopy

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ABSTRACT

The analysis of a historical document of a registry office from nineteenth century through Raman spectroscopy was performed by comparing with an ensemble of standard samples synthesized from cotton and linen raps. Structural parameters of the fibers of the cellulose, such as crystallinity, chain length, intermolecular interactions and packing, were obtained by the measurement of intensity ratios of some marker features. The results suggested the historical document has a cellulosic support originated from cotton, probably produced without basic pH treatment of the raw material.

## 1. Introduction

The use of paper sheets of cellulose probably started in China in the first century B.C., by the use of fibrous materials from bark or cloth [1,2]. Since then, the process has been disseminated around the world, with paper being the principal support for document archiving as record of writing. Paper sheets were initially produced from fabrics of cotton or linen, having both materials high cellulose content and absence of lignin. Old papers produced from such materials were named rag paper and presented high quality, which can in fact be evidenced by their high resistance to the degradation, when compared with the modern wood paper [3–5].

The study for the conservation of cellulose-supported ancient documents requires a detailed and extensive historical search, checking important information such as date and place of its production, associating the investigation of its chemical nature. For this reason, the symbiosis involving the areas of chemistry and history has central role and complementarity in the field of restoration [6]. Considering the historical and cultural value of ancient documents for the analysis of the cellulose structure, it can be used either non-destructive techniques, which do not require a sampling of the object that is leaving in the same state after the study or micro-destructive techniques, which damage insignificant area of the material or requires the removal of a small amount of sample [6–10].

The micro-Raman scattering spectroscopy technique has the advantage of dispensing previous treatment of the sample, and depending on the use can be considered as a technique for non-destructive analysis, having been widely used in the characterization of historical artifacts, for purposes of archaeological findings [11–16], authenticity of paintings [17,18] or restoration of art works [19–22]. Edwards et al. showed that different resin specimens, found in historical artifacts from different archaeological sites, presented degradation patterns passable to be studied by Raman spectroscopy [21]. In the investigation of books and manuscripts, Raman spectroscopy is also capable to identify pigments and dyes in paintings [23]. Nastova et al. studied illuminated medieval old-Slavonic manuscripts, and found iron gall inks, sometimes mixed with carbon inks [24]. They also identified, by comparison of the pigments and paintings in such analyzed Slavonic manuscripts, a good correspondence with those used in Western Europe in the same period. The Raman spectroscopy can be used to identify the main vibrational modes observed in the spectra of cellulosic support of historical documents, allows verifying possible structural changes with time, since the deterioration is an inevitable process [25]. Among the changes, it is possible to mention the breaking of both intermolecular and intramolecular bonds, the oxidation of cellulose followed by change in its crystallinity and packaging. The processes of degradation can be accelerated by intrinsic or external factors as temperature, exposure time to luminosity [26,27], actions of oxidative agents [28] and biological organisms [29].

In this work we report an analytical methodology using Raman scattering spectroscopy for studying a historical document, originated from a registration office, supported in rag paper, dating from the nineteenth century, to discover the source of its raw material. Rag paper is a kind of material widely used until the middle of the 19th

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century [30], whose denomination is due to the use of cotton or linen rags. Textile tissue waste was used as raw material for the production of paper, after maceration and firing of the fibers in order to obtain the cellulosic pulp. The present study was carried out to determine if the fibers came from cotton or linen by comparing the spectral patterns, recorded from the original samples, with those obtained from standard materials synthesized by neutral and basic routes from cotton and linen rags.

## 2. Materials and methods

### 2.1. Historical document

The analyzed document is part of the Historical Collection of the Federal University of Juiz de Fora and was provided by the Laboratory of Conservation and Restoration of Paper belonging to the Museum of Modern Art Murilo Mendes in Juiz de Fora, Brazil. Such a manuscript dates from the nineteenth century and is referred to the registration of the property of slaves from the local aristocracy. Historical studies indicated the cellulosic support of the document was produced by rudimentary techniques, leading it to be classified as a rag paper.

### 2.2. Synthesis of the standard samples

Cotton and white linen fabrics were purchased in the local market. Calcium hydroxide was purchased from Sigma-Aldrich and distilled water was used for the preparation of solutions and baths. The standard samples were produced through two routes: at neutral or at basic pH by the addition of calcium hydroxide. The process for the production of the linen and cotton papers followed the below described steps, recorded in the Fig. 1:

- Fragmentation of cotton and linen fabrics in pieces with 1 $cm^2$ of area, followed by washing in distilled water by immersion for 100 min. and filtration;
- The material was hammering with wood hammer, as rudimentary procedure described in the past centuries, followed by fraying in a blender by adding approximately 500 mL of water to each 50 g of the dried material; after filtration and drying the process was repeated if the fiber was not enough cracked;
- The obtained cellulosic materials were immersed in distilled water baths for 120 min and under two different pH conditions: neutral or saturated calcium hydroxide solution with pH > 10, producing two distinct standard materials for each fabric sample;
- After washing and filtration, approximately 50 g of the cellulosic material was dispersed in a cubic container with 30 L of distilled water. It was stirred to favor the dispersion, and then with a thin rectangular sieve the cellulosic pulp was collected and retained in the screen of the sieve as a film;
- The film was compressed longitudinally by a mechanical press, in order to both the reduction of the thickness of the sheet and a better efficiency in the subsequent drying process at room temperature.

### 2.3. Equipment and methods

The Raman spectra was performed by using a Fourier-Transform micro-Raman spectrometer Bruker-RFS-100, with Nd-YAG laser source operating at a wavelength of 1064 nm, with a germanium detector cooled by liquid nitrogen. The spectra were recorded through the mapping of ten different points on each sample, by using 80 mW laser power, with 5000 accumulated scans and 4 $cm^{-1}$ spectral resolution. The samples were introduced between two glass slides to preclude change of the focus during the mapping record.

## 3. Results and discussion

Fig. 2 shows the ten Raman spectra obtained from the historical document sample through mapping tool. The signals recorded at different points on the sample have a similar spectral pattern, showed as an optical image in the insert of the Fig. 2. Such results indicate that in the investigated area there is an extended homogeneity. The comparative analyses of the spectral patterns from this sample and the

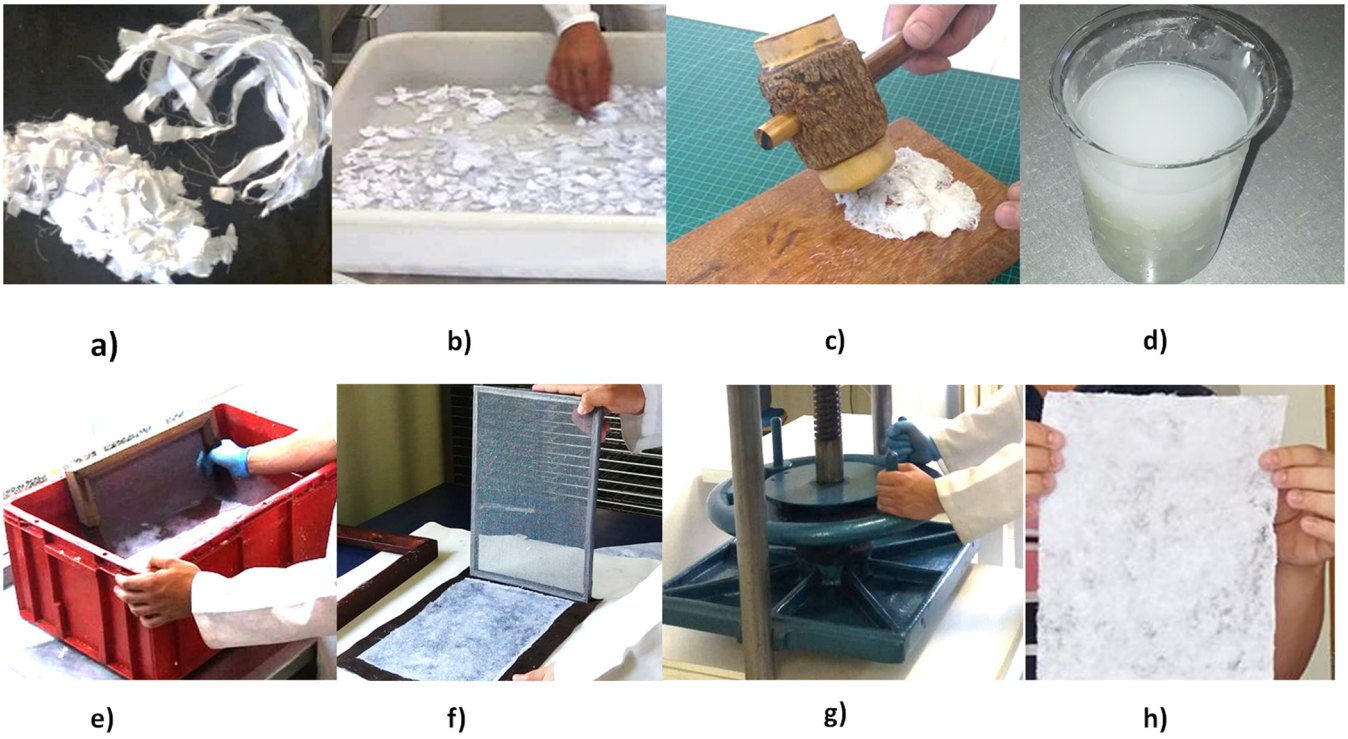


**Fig. 1.** The steps of the process for producing linen and cotton paper sheets: a) fabric clipping; b) washing; c) pounding; d) neutral or basic bath after grind; e) dispersion and collection with a sieve; f) humid film; g) compression; h) final paper sample.