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Original article

Evaluation of the volatile organic compound emissions in modern and naturally aged Japanese paper

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ABSTRACT

Volatile organic compounds (VOCs) can have a strong effect on cellulose degradation, contributing in decreasing the lifetime expectancy of the paper materials, widely employed in the field of conservation. In this work, we investigated several industrial and homemade Japanese papers, as well as fibers, evaluating VOCs emission by using solid-phase micro extraction coupled with gas chromatography–mass spectrometry (SPME-GC/MS). Acetic acid and 1-butanol were highly detected in industrial and homemade papers rather than fibers, suggesting that the emission of these compounds is influenced by the production process more than by the raw material itself. Conversely, N-N dimethyl formammide was peculiar of industrial processes. Ketones, aldehydes and heavier alcohols were preferentially emitted by fibers and homemade papers. The higher emission of furfural from fibers rather than on papers place new questions about the use of this compound to evaluate the degradation state of the paper material that should be carefully evaluated.

1. Introduction

It has been recognized that volatile organic compounds (VOCs) can have a strong effect on degradation of cellulose, in particular for those organic compounds that contain acidic or oxidizable functions, whose removal has been estimated to positively contributing in increasing the lifetime expectancy of the paper [1,2]. It has also been observed that the main source of VOCs in libraries and archives consists in the paper itself, as a consequence of the degradation process that, in turn, depends on the stability of the paper materials, as well as the environmental conditions [3,4]. In the perspective of developing a suitable strategy to storage paper-based heritages, a wider understanding of VOCs emission by papers is desirable. However, although a few of studies were recently carried out for evaluating VOC emissions from historical papers in European libraries [3,5], to the best of our knowledge, VOCs emission from Japanese papers is still unexplored.

Japanese paper is used for conservation and intervention on a wider range of cultural heritage artifacts [6] in force of its high mechanical properties combined with a high stability, mainly due to the length of the fibers and the low presence of lignin [7,8]. Nowadays, the term 'Japanese paper' is rather ambiguous as it includes materials made using oriental fibers, chemical wood pulp as well as non-oriental fibers, such as Manila hemp, that are sometimes used by several producers for containing the production costs [9,10]. These non-oriental fibers typically contain higher amount of lignin with respect to Japanese fibers. Higher lignin content in papers used for conservation should be avoided because it can accelerate degradation processes of the paper itself as well as the restored artifacts [7].

Traditional Japanese paper, oftentimes indicated with the Japanese word '*Washi*', uses oriental fibers as Mitsumata (*Edgeworthis chrysantha*), Kozo (*Broussonetia kazinoki*) and Gampi (*Diplomorpha sikokiana*) [11], with low lignin content [12]. *Washi* paper is traditionally produced following the so-called *Nagashi-suki* technique that includes the use of an aqueous solution containing a starchy substance (Neri) obtained from Malvaceae plants (*Abelmoschus manihot*) [13,14]. Next to the length of the fibers and the low lignin content, as previously stated, the higher mechanical and chemical quality of Japanese paper is also affected by the production process employed. For example, Uyeda et al. [15] demonstrated that the stability of papers produced with Kozo fibers can vary as a function of the type of alkaline solution used in the cooking step (i.e.

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sodium rather than calcium hydroxide). As a consequence, the production process could also influence the VOCs emitted by the paper materials once employed in conservation interventions. In this work, we aim to investigate several industrial Japanese papers from the VANGEROW Catalogue and two types of homemade papers made by the *Washi* paper Master Yuko Isozaki, using Mitsumata and Kozo/Gampi fibers. Since paper samples are naturally-aged and, although not declared by the manufacturers, they may differ in the raw material employed and/or in the papermaking process, we preliminarily characterized the papers using microscopy observations, attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetry and differential scanning calorimetry (TG-DSC). Next to the paper samples, we also investigated the declared raw materials employed for their production (i.e. Mitsumata, Gampi and Kozo fibers). Solid-phase micro-extraction–gas chromatography/mass spectrometry (SPME-GC/MS) was also employed for detecting the VOCs emitted from the papers and the fibers considered in this study.

The availability of naturally-aged papers from the VANGEROW Catalogue (1986) and homemade papers (2005), as well as modern (2015) analogues, provides the unique opportunity also to investigate potential differences in the emission of volatile organic compounds in relation to the natural aging, the production processes and/or the raw material employed. Therefore, in view of their over the time stability and related potential conservation issues in particular for paper interventions, we evaluated the potential use of SPME-GC/MS – a totally non-invasive approach–for shedding light on the composition of Japanese paper VOCs emissions.

2. Materials and methods

2.1. Paper samples

Samples of naturally-aged industrial Japanese papers were taken from an original catalogue of VANGEROW (Bolzen, Italy) *Japanische Handapapiere* of the 1986, and kindly provided by Rosanna Chiggiato. From this catalogue, five paper samples were selected in accordance to their use in the field of conservation. New samples, sold with the same code and characteristics, were purchased from Vangerow (2015). The selected papers differentiate not only for their thickness, but also for their composition. Vangerow catalogue papers will be afterwards labeled as V where the sub- and super-scripts indicate the catalogue number (500, 508, 523, 517 and 561) and the ages, corresponding to 2015 and 1986, of these samples.

Fibers and handmade papers, both new and old, were provided by the *Washi* master Yuko Isozaki. The naturally-aged paper samples date back to 2005, while the more recent samples were produced in 2015. Homemade papers were labeled as Y-KG and Y-Mit to indicate the declared raw material used: 30% kozo/70% gampi and 100% mitsumata fibers, respectively. The sub-script refers to the age of the samples (i.e. 2015 and 2005).

2.2. Preliminary characterization

Paper samples were stained with Herzberg's reagent to assess the presence of lignin, following the protocol reported elsewhere [16]. The presence of lignin was detected accordingly to the coloring of the paper material [16]. Lugol's test [17] was also employed to reveal the presence of starch that turns blue due to the reaction with the reagent, in accordance with TAPPI standard T 419 OM-11. The paper samples were observed for both tests under the microscope and images were taken using a digital camera (CANON PC1049 Powershot G5) both for lignin and starch stains. pH measurements were carried out in laboratory conditions, by cutting approximately 1 g of paper in small fractions and leaving them in 70 mL of distilled water for one hour. Then, the pH value of the cold extracted was analyzed without filtration under stirring by using a Crison GLP 21 pH meter, in accordance with TAPPI standard 509 [hydrogen ion concentration (pH) of paper extracts-cold extraction method].

2.3. TG-DSC analysis

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed simultaneously using a Netzsch 409/C apparatus. The temperature program was set from 30 C to 500 °C at 5 °C/min and the instrument was purged in an atmosphere containing a mixture of air and N_2. The sample mass ranged between 0.5 and 2 mg and were weighted in an aluminium crucible using a TG internal balance. Alumina was used for internal calibration and data were collected with STA Netzsch software. Before analysis, samples were stored in a dessicator (20 ± 2 °C; 60 ± 5% RH) for at least 48 hours in our laboratory.

2.4. ATR-FTIR and SEM analysis

Infrared spectra were obtained by a Thermo Nicolet Nexus 670 FTIR spectrophotometer combined with a Smart Orbit Single Reflection Diamond ATR accessory, from 4000 to 400 cm^{-1} for 128 scans with 4 cm^{-1} resolution. Spectra were elaborated with Omnic 10.0. Surface characterization of the papers and fibres was performed using a Jeol JSM 6300 Scanning Electron Microscope operating with a Link-Oxford-Isis Energy Dispersive X-ray microanalysis system in low vacuum conditions (20 kV, back – scattered electrons, 2.10–9 A beam current and 15 mm working distance). The analysis mainly focused on the morphology of the raw fibres to highlight their characteristics and on the paper samples for observing the possible presence of additives related to the production process.

2.5. SPME – GC/MS

Solid phase microextraction (SPME) was performed using 50/30 μm, divinylbenzene/carboxen/polydimethylsiloxane (DVI/CAR/PDMS) fibers (Supelco, Bellefonte, PA). These types of fibers are suitable for a wide range of chemicals and were successfully used for studies on paper materials [18]. Before the first use, each fiber was conditioned in order to remove contaminants and to stabilize the polymeric phase. Conditioning was conducted by heating the fiber in the injection port of the GC system for 1 h at 260 °C before every extraction. The extraction was performed adapting methods available in the literature [18–20]. Briefly, contact mode SPME was used to collect the volatile compounds emitted from the papers. The holder needle was placed between two pieces of the same paper in a controlled environment (23 °C, 50% RH). The fibers were in direct contact with the sample paper for 240 minutes. After extraction, the fibers were withdrawn into the holder needle and immediately introduced into the GC-MS injector port for 10 min at 240° C for thermal desorption. Fibers, procedural blanks and furfural standard (Sigma Aldrich) were extracted using the same conditions. The reproducibility of analyses were evaluated by extracting in triplicates each sample and the peak areas showed a variability of 20–30%, depending on the compound considered. A fiber blank chromatogram was acquired after each analysis to confirm the fiber cleanness prior the subsequent extraction. GC-MS analysis was performed with a 6890-N GC system coupled to a quadrupole mass spectrometer 5973 (Agilent Technologies, Santa Clara CA, USA). The chromatographic analysis was carried out using a capillary column (DB-WAX, 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness). Helium

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