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Analytical characterization of East Asian handmade papers: A combined approach using Py-GCxGC/MS and multivariate analysis

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ABSTRACT

An analytical method based on the combination of on-line pyrolysis-comprehensive two-dimensional gas chromatography/mass spectrometry and multivariate analysis for a direct characterization of traditional East Asian handmade papers is presented here. The method was applied to three kinds of widely used handmade papers in East Asia followed by an attempt of identification of ancient lining papers belonging to museum samples of unknown origin. The results indicated that Py-GCxGC/MS, together with multivariate data analysis, was more efficient and reliable compared to the compound presence/absence analysis to meet the challenging search for organic markers in rare cultural heritage materials. The established method showed promises as an efficient analytical tool for the characterization of artwork and culture heritage materials and in filling the lacuna for papermaking fiber analysis which is currently almost entirely relied on microscopy analysis. Results also revealed that two-dimensional techniques could constitute an efficient approach for the analysis of complex artwork samples to circumvent the limitation of materials at disposal in cultural heritage studies.

1. Introduction

Paper, one of the Fourth Great Inventions of ancient China, originates approximately from 2,000 years. Historical reports agreed that paper was invented by a Chinese political official, Cai Lun (ca. 60-121 AD) in the year 105 AD. Nevertheless, new archaeological findings have demonstrated that papermaking may date back to approximately 200 BC [1]. Papermaking technology firstly spread from China throughout Asia and propagated to Islamic world and Europe through the Silk Road. Since then, paper became the prime medium for the mass transition of idea and memory into notation and later paved way for the typographical revolution spurred by printing press [2].

Until nowadays, microscopic observation of the fibrous materials used during the handcraft making process was the main technique allowing the identification, authentication and determination of provenance for historical and archaeological East Asian handmade papers. In microscopic analysis, fiber identification relies on the careful observation of the fiber morphology to identify the material origins and the pulping processes. Nevertheless, microscopy observation is sometimes insufficient to assess precisely the nature of the fibers: in particular, the use and consultation of reference materials reveals themselves as a necessity for a proper identification of the raw material [3,4]. Moreover, the identification of fibers by optical microscopy necessitates a good experience in fiber analysis for the experimentalist. A main drawback of this technique concerns the possibility for some plants to produce more than one type of fibers, which requires further investigation to characterize the differences shown by varieties of the same species [5,6]. Even in that cases, however, the omission of certain plants in the analysis may induce misleading interpretations of the analyzed samples [5,7,8]. Consequently, we consider that the development of an experimental method based on the chemical analysis of fiber constituents deserves further investigation for the identification of traditional, historical and archaeological East Asian handmade papers.

It is commonly admitted that the application of on-line pyrolysis as a routine analytical method date back from the second half of the 20th century [9]. Since then, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has been widely used for the characterization of organic materials used in artworks and archaeological samples: e.g. resins and gums [10,11], Asian lacquer [12,13], or varnishes [14,15]. Although analytical pyrolysis profiles on cellulosic materials have been established previously [16,17], studies concerning East Asian handmade papers have not been reported except for the Py-GC

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characterization of the likely mucilaginous compounds present in traditional East Asian handmade paper [18] and our recent investigation on the characterization of kozo, mitusmata and gampi handmade papers by Py-GC/MS [19].

If, in the past, the introduction of on-line pyrolysis permitted to enlarge the scope of analysis of polymers and natural materials [9,20], the identification of molecular constituents within complex organic mixtures or with low quantity samples at disposal may typically not be achieved after a one dimension chromatographic separation. The introduction and development of comprehensive two-dimensional gas chromatography (GCxGC) offered greatly enhanced resolution for identification of organic analytes in complex mixtures compared to one-dimensional separation techniques [21–23]. As a consequence, the enhanced separation power and ability to gather information of GCxGC/MS system has rapidly attracted the attention of analysts from different scientific fields [24,25]. However, few application was reported in cultural heritage studies where two-dimensional techniques could constitute an efficient approach for the analysis of complex artwork samples to circumvent the limitation of materials at disposal in cultural heritage studies.

The specificity in the art of traditional East Asian papermaking resides in the rational choice of fiber plants adequate to obtain the required quality for the final paper sheets. This specificity constitutes an opportunity to chronologically and geographically locate the origin of samples if a thorough identification of plant components is available. Noteworthy, phytochemistry studies have demonstrated that different plant species may present specificities in their bio-synthesis pathways for certain low molecular weight metabolites, which provides the foundation to establish new criteria for their characterization [19]. However, similarities in the structure of these potential markers render tedious identification, especially for species having close botanical relations. The coupling of pyrolysis with GCxGC/MS (Py-GCxGC/MS) was recently demonstrated to enlarge potentialities for the analysis of fibrous materials like cellulosic materials, increasing sensitivity and resolution for the analysis of samples at disposal in minute amounts, a current situation in cultural heritage studies [26]. Compared to conventional Py-GC/MS, the information contained in a two-dimensional chromatogram is significantly larger, consequently, this increased amount of information favorably benefits the use of multivariate analysis for the interpretation of data. As such, multivariate analysis facilitated the comparison of complex chromatograms, and principal components analysis (PCA) is currently a widely used multivariate approach in combination with comprehensive two-dimensional analysis [27,28]. As an example, application for the investigation of materials from different plant origins had been illustrated in food chemistry [29–31].

In the aim of gaining a thorough knowledge on the provenance and the making technique of East Asian handmade papers, the present study explored the benefits of using Py-GC × GC/MS combined with multivariate analysis for their characterization. Three traditional Japanese handmade papers widely used in East Asia were investigated and their characterization was refined through the identification of their triterpene and phytosterol plant markers. The improved analytical fingerprints of these papers were then employed for the identification of three lining papers of unknown origin in the course of the restoration of three paper paintings belonging to the Musée national des arts asiatiques–Guimet (Paris). Such approach based on the application of Py-GC × GC/MS associated to multivariate analysis is for the first time explored and proposed in cultural heritage studies and is a continuation of our previous study initiated on the Py-GC × GC/MS characterization of traditional handmade kozo paper [26].

2. Materials and methods

2.1. Materials

Materials used in the present study consisted of three types of handmade papers made from kozo (*Broussonetia kazinoki* Sieb.), mitsumata (*Edgeworthia papyrifera* Sieb. et Zucc.) and gampi (*Wikstroemia sikokiana* Franch. et Sav.). These modern reference papers were prepared following the Japanese traditional processes. Three ancient samples of lining papers were employed in this study. All these lining papers were taken from paintings belonging to the Musée national des arts asiatiques–Guimet (Paris). These original artworks are dated from the first half of the Five Dynasties (907-960 AD) and are originating from the library cave in Mogao-ku, Dunhuang, China. Sampling on these original artworks has been conducted in the course of their restoration. A first sample of a lining paper was removed from a paper painting showing “Two Bouddha and a Bodhisattva” (reference No. EO3642, refer to sample A in the present work). The second sample of a lining paper was removed from a painting showing a “Bodhisattva Ksitigarbha” (sample EO17656, refer to sample B). A third sample of lining paper was removed from a “mandala of Vajrasattva” (sample EO1167, refer to sample C). All these samples are of unknown origin and may date from the collection of the paper paintings in the Musée national des arts asiatiques–Guimet at the beginning of the twentieth century. One set of kozo (*Broussonetia kazinoki* Sieb.) reference paper was artificially aged by thermal aging for 3 weeks at 80 °C and 60% relative humidity and gamma irradiation at 390 kGy using the methods described elsewhere [32,33].

2.2. Py-GCxGC/MS analysis

Analysis was conducted with a Shimadzu QP 2010-Ultra gas chromatograph mass spectrometer (Shimadzu, Champs-sur-Marne, France) equipped with a two-stage thermal modulator ZX 2 (Zoex, Houston, USA). Pyrolysis was performed using a vertical micro-furnace-type pyrolyzer PY-3030iD (Frontier Lab, Fukushima, Japan) directly connected to the injection port of the gas chromatograph. The sample was placed in a stainless steel sample cup. Typical quantities of sample paper used in this work were ca. 40–50 µg weighted with an XP2U Ultra Micro Balance (Mettler Toledo, Viroflay, France). The pyrolysis temperature was defined to be 500 °C. The pyrolyzer interface was held at 320 °C. An OPTIMA-5HT column (30m × 0.25 mm I.D., 0.25 µm film thickness, Macherey-Nagel, Hoerdt, France) was used as first dimension column and a Zebron ZB-50 (2.8m × 0.1 mm I.D., 0.1 µm film thickness, Phenomenex, Le Pecq, France) was used as a second-dimension column and for the loop modulator system. The separation was carried out at a constant pressure of 300 kPa using Helium Alphagaz 1 as carrier gas (Air Liquide, Bagneux, France). The ZX 2 two-stage thermal modulator was utilized with a modulation period of 10 s with a programmed hot pulse of 0.350 s. A two-step temperature program was used for the hot jet set at 200 °C for 30 min and subsequently raised to 280 °C. The oven temperature was initially held 1 min at 100 °C, and then ramped at 2 °C min^{-1} to 325 °C, where it was held for 25 min. The injector was held at 280 °C and used in split mode (1:30 of the total flow). The mass spectrometer was operated at 20,000 u s^{-1}, with a scan range from 50 to 500 u, using electron ionization at 70 eV. The interface was kept at 280 °C and the ion source at 200 °C. All analysis have been conducted in triplicate except for the ancient lining papers from the Musée national des arts asiatiques–Guimet (Paris) which were sampled once due to the limitation of quantity of samples. Data processing of the Py-GCxGC/MS raw data was achieved using GC Image software, version 2.4 (Lincoln, NE, USA). Identification of pyrolysis products was performed by comparing the mass spectra of unknown components with the NIST mass spectra library (2011 edition) and by interpretation of the main fragmentations.