Multi-analytical techniques in characterization and identification of Chinese historical rubbings

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Research article

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Abstract

For authenticity and conservation purposes, the precious historical rubbings preserved in Wuyuan Museum were studied by multi-analytical techniques including Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), SEM-EDS and Herzberg staining method. Through Py-GC/MS analyses, five types of constituents could be detected: (1) polycyclic aromatic hydrocarbons from soot; (2) retene and methyl dehydroabietate from tar of conifer wood; (3) marker compounds of egg; (4) additives of menthol and curcumene compounds; (5) biochemical compounds of bark paper. Based on this analytical results, the ink type, binding media and additives in the ink, as well as the fiber origin source of the rubbing paper could be concluded. The materials information of the rubbings obtained through this study could not only provide evidence for its authenticity, but also supply scientific support for its conservation and restoration.

Introduction

Rubbing is an ancient traditional Chinese skill to copy the characters and patterns on the stone carving or bronzes with handmade paper and ink [[i]]. The precious historical rubbings in Wuyuan Museum of Jiangxi Province were reproduced from the stone carved the preface of Sanzang holy religion, which was written by Li Shi Min (Tai Zong emperor of Tang Dynasty) and carved with Wang Xizhi's (famous calligraphers in the Eastern Jin Dynasty) calligraphy style in the third year of Tang Xianheng (A.D 672). For authenticity and conservation purposes, it is particularly important to character and identify the materials of paper and ink in the historical rubbings, mainly including the type of paper fiber, ink, binding media and additives in ink, etc.

China is the birthplace of traditional handmade paper. The commonly used traditional handmade paper includes ramie paper, bamboo paper, mulberry paper and kozo paper, etc. Kaolin was often used as fillers in ancient papermaking process to improve the whiteness, smoothness and opacity of paper, as well as improve the ink moistening property in the paper [[ii]]. The traditional method for identifying the raw materials of a paper is microscopy as Herzberg staining method [[iii], [iv], [v]], through observing the fiber morphology characteristic. In recent years, Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) and Pyrolysis gas two-dimentional chromatography-mass spectrometry (Py-GCxGC/MS) have been introduced for the differentiating East Asian handmade paper (kozo paper, mitsumata paper, and gampi paper) according to the chemical markers of origin of the plant fibers, since each paper has characteristic pyrolysis fingerprints[[vi], [vii], [viii], [ix]].

Chinese ink has a long history and a special importance in the Chinese culture, which was made by mixing soot with pre-dissolved glue and additives, followed by kneading, pounding, molding and drying process[[x]]. The early Chinese ink was the pine wood soot ink, which was obtained by the incomplete combustion of cedar, fir, hemlock, larch, pine and spruce, etc. The preparation process of pine wood soot ink had been basically completed by the Han Dynasty (202 BC- AD 220) and developed in the later dynasties [[xi]]. After 11th century, the lamp soot ink was more widely in use than the pine wood soot ink.

The lamp soot was mainly obtained from the incomplete combustion of vegetable oil and animal oil [[xii]]. The commonly used additives in ink mainly are camphor, borneol, musk and lacquer, etc [[xiii]]. In the past, soot used in ink was characterized through the morphology and size of the soot particles by using Scanning Electron Microscopy (SEM) [[xiv]] and Transmission Electron Microscope (TEM) [[xv]]. Py-GC/MS was applied to characterize Chinese ink by Wei et al in 2011, through the detection of main chemical compounds in soot including phenanthrene, fluoranthene, pyrene, triphenylene and benzofluoranthene and their relative amount, pine wood ink and lamp oil ink can be differentiated[[xvi]]. Later on, this method and the criteria were used for the identification of the archaeological ink stick in Eastern Jin Dynasty (317 - 420 AD), which was identified as pine wood soot ink. Meanwhile, animal glue was found as binding media; borneol and cedar oil were detected as additives in the ink stick [[xvii]]. Recently, pine wood soot was also identified in the ink as early as Han Dynasty (202 BC- AD 220) by Py-GC/MS[[xviii]].

In summary, from the literature it can be seen that Py-GC/MS was successfully used for the identification of paper fibers, soot and additives in Chinese ink, respectively. The rubbings are made of handmade paper covered with Chinese ink, so thus Py-GC/MS was applied to characterize both the paper and the ink of the rubbings simultaneously, hopefully the fiber origin of the paper, the soot and additives, as well as the binding media used in ink could be identified in one analysis. In addition, SEM-EDS and Herzberg staining method were also applied for complementary information. This paper demonstrates the methodology chosen could obtain maximum information with a small amount of sample, which is in accordance with the special requirement of a precious sample, such as the historical rubbings. Furthermore, the results obtained through this study could not only provide evidence for its authenticity, but also supply scientific support for its conservation and restoration.

[i]. Jiang M. The making and preservation of rubbing. Archaeology of Luoyang. 2018; (3):79-82.

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[x]. Guan L. Hai hun hou mu chu tu gu mo kao [□□□□□□□□□]. Cultural relics world. 2020; (10):69-71.

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Experimental

Materials

Rubbing sample: a sample was taken from the page fringe of one historical rubbing (Fig. 1) of the Sanzang Holy Preface for analyses, which were written by Tang Dynasty Emperor Li Shimin in recognition of Xuan Zang Masters' the study of the Buddhist scriptures of the Western countries. The rubbings were preserved in Wuyuan Museum of Jiangxi Province, China.

Modern reference paper sample: typical Chinese traditional handmade bark papers made from mulberry bark (*Morus alba* L.)

Techniques and Methods

SEM-EDS: TESCAN VEGA 3 XMU scanning microscope linked to a Bruker Nano Gmbh XFlash Detector 610M (Czech Rep, SEM-EDS).

Py-GC/MS: It was performed using a vertical micro furnace-type pyrolyzer PY-3030D (Frontier Lab, Japan) directly connected to the injection port of a Shimadzu QP2010Ultra gas chromatograph mass spectrometer (Shimadzu, Japan). The sample was placed in a stainless steel sample cup. Reference paper used in this work for the development of the analytical method was 2.5mm times 2.5mm size. The sample cup was placed on top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace at 600 °C, and then the temperature program of the gas chromatograph oven was started. The Py-GC interface was held at 320 °C. Chromatographic separation was carried out on an UA+-5 Frontier Lab 5 %- dimethyl diphenyl polysiloxane column (30 m length, 0.25 mm inner diameter and coated with a 0.25-μm film thickness). The oven temperature was initially held 3 min at 40 °C, and then ramped at 5 °C min^{-1} to 325 °C, where it was held for 5 min. The total duration of GC analysis was 65 min. The helium carrier gas, was used in the linear velocity mode (1 mL min^{-1}). The injector was held at 280 °C and used in split mode (1:10 of the total flow). A scan range from 50 to 750 was used in mass spectrometer, using electron ionization at 70 eV. The interface was kept at 280 °C and the MS source at 200 °C. Identifications were achieved on the basis of EI mass spectra by interpretation of the main fragmentations and using the NIST14 and NIST14s MS library. The same amount of sample was pyrolysed in three replicates, and the variability between replicate pyrograms was minimal. A blank run (sometimes two or three) was inserted between each pair of actual analyses to be able to rule out such influences.

Herzberg staining method: XWY-VI paper fiber analyzer (China) was used to observe the morphological characteristic of the sample fibers after the iodine - zinc chloride reagents. The preparation method of the iodine - zinc chloride reagents refers to Li's literature [[i]].

[i]. Li T. Indigo and Madder Dyed 11th to 13th Century Chinese Papers Unearthed at Khara Khoto in Northwestern China. Tangut Research. 2017; (3):3-14.

Results And Discussion

Characterization of the rubbing sample by using SEM-EDS

The morphology characteristics of ink on the historical rubbing sample were observed by scanning electron microscopy (SEM) at a magnification of 20000 times. The results are shown in Fig. 2. As can be seen, the ink particles were closed to circle. The ink particles were not uniform in size, the large particles were about hundreds of nanometers, and the small particles were dozens of nanometers. This feature is consistent with the characteristics of pine wood soot ink, which give a clue that the ink used for the rubbings is probably pine wood soot ink [15]. Due to the limit of this method, further investigation by Py-GC/MS was carried on, which is stated in the following subsection.

The mapping analysis of scanning electron microscope and energy dispersive spectrometer (SEM-EDS) was used to analyze the particulate in the paper in the historical rubbing sample. The results are shown in Fig. 3. It can be clearly seen that the particles primarily contain Al, Si and Ca elements, which confirmed that kaolin (a kind of clay, molecular: $Al_20_3 \cdot 2Si0_2 \cdot 2H_20$) is present in the rubbing sample, which is used as fillers in papermaking process to improve the whiteness, smoothness and opacity of paper according to the literature [2].

Characterization of the historical rubbings by using Py-GC/MS

Py-GC/MS was utilized to analyze the historical rubbing sample, the chromatogram obtained is presented in Fig. 4, while the primarily compounds identified are listed in Table 1. Five types of substances were detected in the historical rubbing sample by using Py-GC/MS analysis. (1) a series of polycyclic aromatic hydrocarbons (PAHs) could be identified as the follow compounds: anthracene, fluoranthene, pyrene, triphenylene, benzo[k]fluoranthene and benzo[ghi]perylene, labeled as S1, S2, S3, S4, S5, and S6 in Fig. 4 respectively. The PAHs were from soot, in which the relative high content of S5 and S6 could be used as an indication of the presence of certain soot ink [16]; (2) a small number of compounds including retene (as show in Fig. 4, labeled as T1) and methyl dehydroabietate (as shown in Fig. 4, labeled as T2) were detected, which were from conifer tar according to the literature [17], the chemical structure of the two compounds were shown in figure 5. (3) In Fig. 4, G1, G2 and G3 represent 3-methyl-1H-pyrrole, indole, and 3-methyl-indole respectively, which were the pyrolysis marker compounds of egg white [[i], [ii]]. In addition, 3-ethoxy-, (3beta)-Cholest-5-ene (labeled as G4) was also detected, which is the main component of egg yolk; (4) Compounds of menthol and curcumene were detected in the rubbings (labeled as E1 and E2 in the chromatogram). Menthol is the main chemical component of peppermint oil, which is obtained from the roots, stems and leaves of peppermint by steam distillation. It is an important flavor additive [[iii]]. Curcumene is the main chemical component of the essential oil of turmeric herbs, which has antibacterial, antitumor and antioxidant effects [[iv], [v]]. (5) furthermore, furan structure (as shown in Fig. 4, labeled as 3), ketones (as shown in Fig. 4, labeled as 2 and 5), carbohydrate (as shown in Fig. 4, labeled as 10) and a series of compounds characterized by a base peak at 218 m/z, corresponding to the beta-amyrin (as shown in Fig. 4, labeled as 13) and alpha-amyrin (as shown in Fig. 4, labeled as 14) were noticed, which were the pyrolysis marker compounds of bark fiber [9], representing the paper probably made from mulberry bark (*Morus alba* L.). In order for the unambiguous identity of the fiber, Herzberg staining method will be carried out in following.

[i]. Giuseppe C, Guido CG, Lanterna G, et al. The potential of pyrolysis-gas chromatography/mass spectrometry in the recognition of ancient painting media. Journal of Analytical and Applied Pyrolysis. 1993;(24):227-242.

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Table 1. List of compounds of the rubbing paper with retention time (RT), expected main fragment ions, most likely attribution of the products, and relative content.

No	RT(min)	Main Ions	Identified compounds	Area (%)
G1	3.35	53, (80)	1H-Pyrrole, 3-methyl-	0.84
1	5.32	51, 78, (104)	Styrene	1.15
2	5.85	53, (67), 96	2-Cyclopenten-1-one, 2-methyl-	1.6
3	8.57	53, 67, (96)	2,4-Dimethylfuran	2.49
4	9.51	66, (94)	Phenol	1.8
5	11.61	(67), 95, 110	2-Cyclopenten-1-one, 2,3-dimethyl-	1.26
E1	12.61	69, (109), 119, 134	cis-p-mentha-1(7),8-dien-2-ol	0.82
6	13.35	79, (108)	3-methyl-Phenol	2.73
E2	16.98	71, (81), 95, 123, 138	Menthol	0.61
7	18.86	(91), 131	Benzenepropanenitrile	1.54
G2	20.57	63, 90, (117)	Indole	2.38
G3	23.29	77, 103, (130)	3-methyl-Indole	1.8
E3	25.58	105, (119), 132, 202	Curcumene	0.4
8	26.2	(55), 69, 83, 97, 111	1-Pentadecene	1.01
9	28.73	(55), 69, 83, 97, 111	1-Heptadecene	0.89
10	30.29	(60), 73	1,6-anhydro-bete-D-Glucopyranose	26.5
S1	33.2	76, 152, (178)	Anthracene	0.38
11	36.2	(74), 87, 143, 270	Hexadecanoic acid, methyl ester	4.09
S2	39.01	101, (202)	Fluoranthene	0.24
S3	40.05	101, (202)	Pyrene	0.26
12	40.18	(74), 199, 255,298	Methyl stearate	4.96
T1	41.9	189, 204, (219), 234	Retene	0.22
T2	44.02	(239), 299, 314	Methyl dehydroabietate	0.12
S4	46.07	101, 113, (228)	Triphenylene	0.15
S5	52.33	113, 125, (252)	Benzo[k]fluoranthene	0.19
G4	52.77	(57), 95, 147, 353, 368	3-ethoxy-, (3.beta.)-Cholest-5-ene	0.21
13	54.66	95, 135,189, 203,(218)	.beta.-Amyrin	0.18
14	55.3	95, 135,189, 203,(218)	.alpha.-Amyrin	1.06

S6	57.87	138, (276)	Benzo[ghi]perylene	0.29

In order to see the relative contents of the PAHs, analyses by Py-GC/MS with select ion mode (SIM) for S1-S6 were conducted. The chromatogram obtained is depicted in Fig. 6. For comparison, the relative content of the PAHs of the reference materials of the pine wood soot ink (PM), lamp soot ink (LM) and carbon black (CB), which were published earlier [16], as well as the PAHs results of the historical rubbings (RM) are listed in table 2. The relative content of benzo[k]fluoranthene and benzo[ghi]perylene in the historical rubbing sample is 31.78% (peak area), and the triphenylene is 9.93% (peak area), which is in accordance with that of pine wood soot ink. Combining the detection of marker compounds of retene and methyl dehydroabietate, pine wood soot ink used for the rubbings can be concluded.

Table 2. The relative contents of the main PAHs in the modern pine wood ink (PM), lamp soot ink (LM), carbon black (CB) and the ink used in the historical rubbings (RM) by Py-GC/MS analysis in SIM mode

Sample **PAHs**	**PM**	**LM**	**CB**	**RM**
S1 area(%) (m/z 178)	13.9	14.5	71.4	25.2
S2 area(%) (m/z 202)	27	34.3	9.8	15.89
S3 area(%) (m/z 202)	28.9	34.7	9.1	17.22
S4 area(%) (m/z 228)	10	3.8	0.0	9.93
S5/S6 area(%) (m/z 252)	20.2	12.5	9.5	31.78

In summary, the ink used for the rubbings is pine wood soot ink, with egg (egg white and egg yolk) as binding media, while peppermint oil and turmeric herbs oil are probably used as additives in the ink. No surprise, the finding of pine wood soot ink in the rubbings, since its use can date back as early as Han Dynasty (202 BC- AD 220) [11], which was continuously in use in the following Dynasties. Only after 11th century, lamp soot ink was gradually in place of pine wood soot ink. Animal glue is the common binding media used in the Chinese ink [12], However, in this case whole egg were found as binding media. Interestingly, peppermint oil and turmeric herbs oil are found as additives in the ink.

Fiber identification using Herzberg staining method

The morphological characteristics of a modern handmade mulberry bark paper are shown in Fig. 7(a) after Herzberg staining method, which was used as a reference sample. The fibers taken from the historical rubbing sample were examined under the paper fiber analyzer after Herzberg staining method. The results are shown in Fig. 7 (b). Although the fiber morphology characteristics were not obvious due to the presence of ink, however similar characteristics as the reference mulberry bark could be observed, including yellow amorphous waxy substance attached to the fiber and cell cavity, as well as the reddish brown color of the fibers. In addition, most of the fiber width is between 10-15μm, and the fiber length was about 6mm. These characteristics were identical as the morphological characteristics of the mulberry bark paper fiber [[i]]. Combining with the Py-GC/MS results about the detection of bark marker compounds, it could be determined that historical rubbings paper is mulberry bark paper.

[i]. Wang, J.H. 1999. Papermaking Raw Materials of China an Atlas of Micrographs and the Characteristics of Fibers, Beijing: China Light Industry Press P 129.

According to the *Book of the Later Han* (Cai Lun's biography), the raw materials for papermaking included ramie rags, fishing nets, and paper mulberry during the Eastern Han Dynasty. During the Tang Dynasty, kozo, mulberry bark, and rattan bark were the primary sources for papermaking. The use of bamboo to make paper was primarily developed in Song Dynasty [[i]]. The identification of mulberry bark as the origin source of the historical rubbings paper, could provide another positive evidence for its authenticity, since the rubbings was recorded made from Tang Dynasty.

[i]. Wang J, Li Y. Cong ji zhong han zhi de fen xi jian ding shi lun wo guo zao zhi shu de fa ming [a]. Cultural Relics. 1980; 26(1): 80-84.

Conclusions

In this study, multi-analytical techniques including Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), Scanning electron microscope linked to energy dispersive spectrometer (SEM-EDS) as well as Herzberg staining method were utilized for the characterization and identification of the precious historical rubbings collected in Wuyuan Museum of Jiangxi Province, China. Through Py-GC/MS analyses, five types of constituents could be detected: (1) polycyclic aromatic hydrocarbons from soot; (2) retene and methyl dehydroabietate from tar of conifer wood; (3) marker compounds of egg; (4) additives of menthol and curcumene compounds; (5) pyrolysis marker compounds of the paper fiber origin - bark. Combining with the fiber morphological characteristics by Herzberg staining analysis, the rubbing fiber origin source could be identified as mulberry bark. The ink used on the historical rubbings was determined as pine wood soot ink, egg as binding media, peppermint oil and turmeric oil as additives in the ink. In addition, Kaolin was found as fillers in the rubbing paper to improve the property of paper.

Through this study, the methodology chosen could obtain maximum information with a small amount of sample, which is important for a precious unknown sample, like historical rubbings. The materials information of the rubbings obtained could not only provide evidence for its authenticity, but also provide scientific support for its conservation and restoration.

Declarations

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

Na Yao, Professor Shuya Wei, and Professor Qinglin Ma conducted the experiments and analyzed the results. Xiangsheng Zhan supplied the precious historical rubbing sample, and provided the picture of the rubbings shown in Fig. 1. All authors reviewed the submitted article. All authors read and approved the final manuscript.

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Figures

Figure 1

The historical rubbings in Wuyun Musum of Jiangxi Province

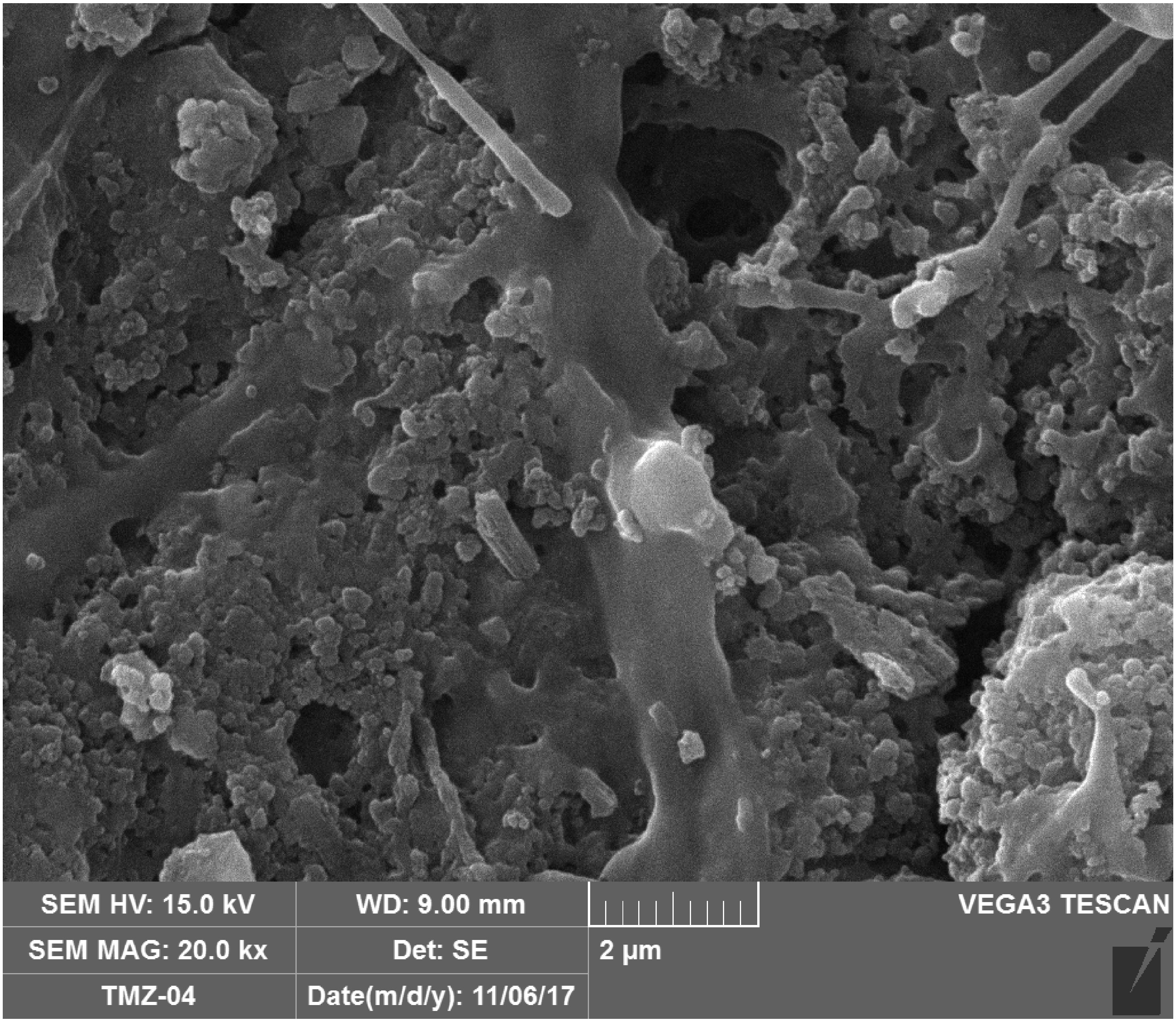

Figure 2

The ink morphology graph of SEM in rubbing sample ×20000

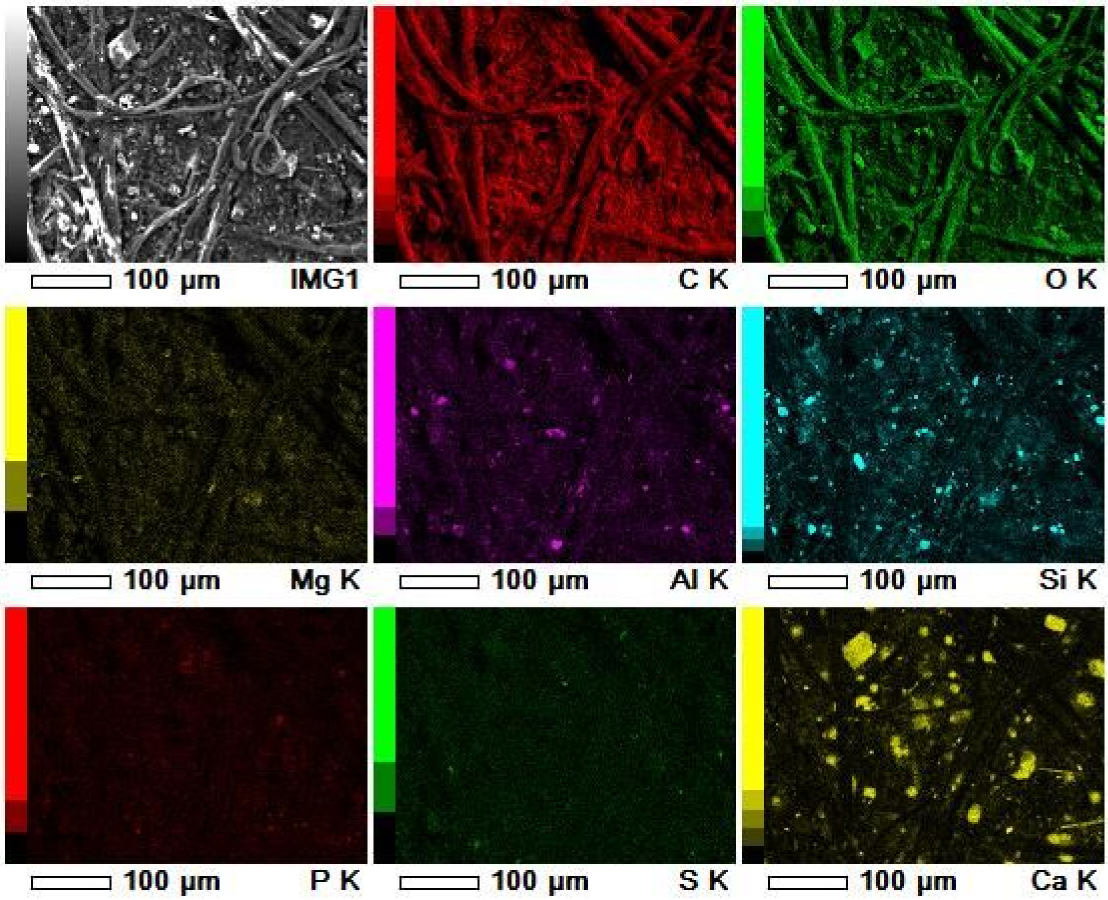

Figure 3

The mapping of paper by SEM-EDS in rubbing sample ×500

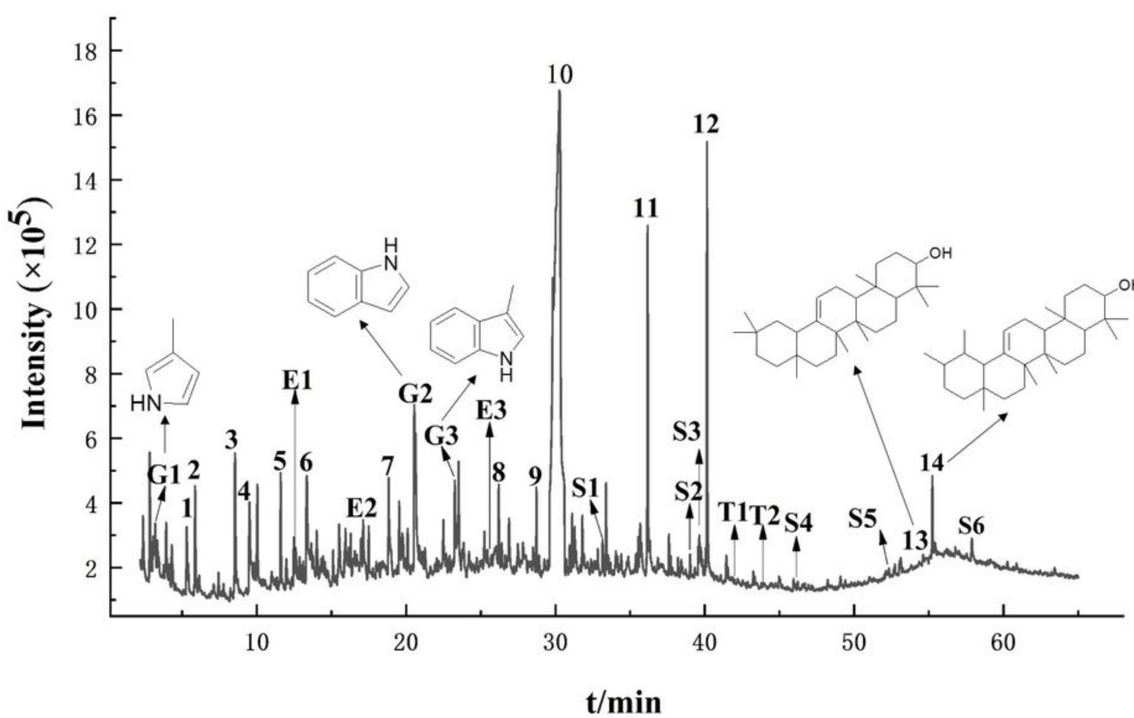

Figure 4

Total ion current chromatogram obtained from the pyrolysis of the historical rubbing sample, the peak numbers correspond to the numbers in Table 1

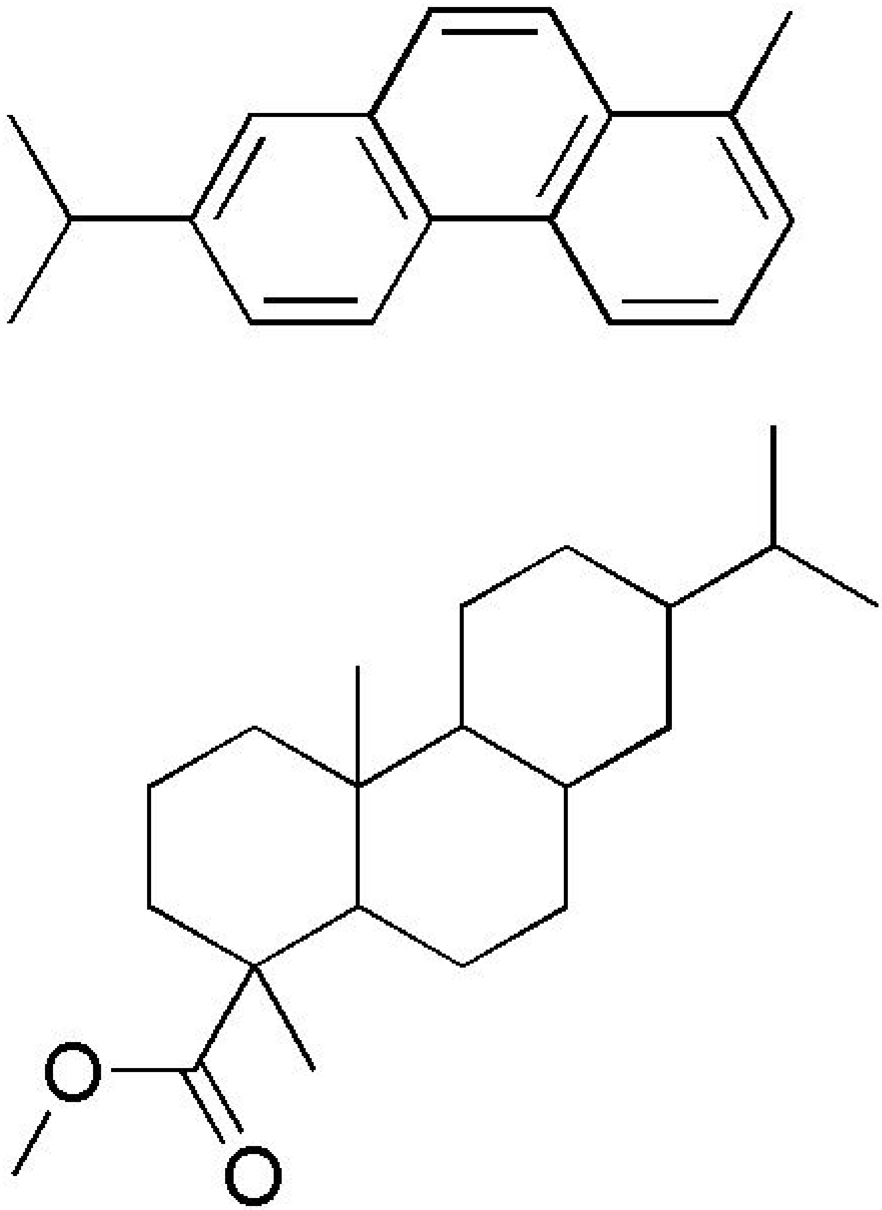

Figure 5

The figure of chemical structure of retene (T1) and Methyl dehydroabietate (T2) detected in the his-torical rubbing sample

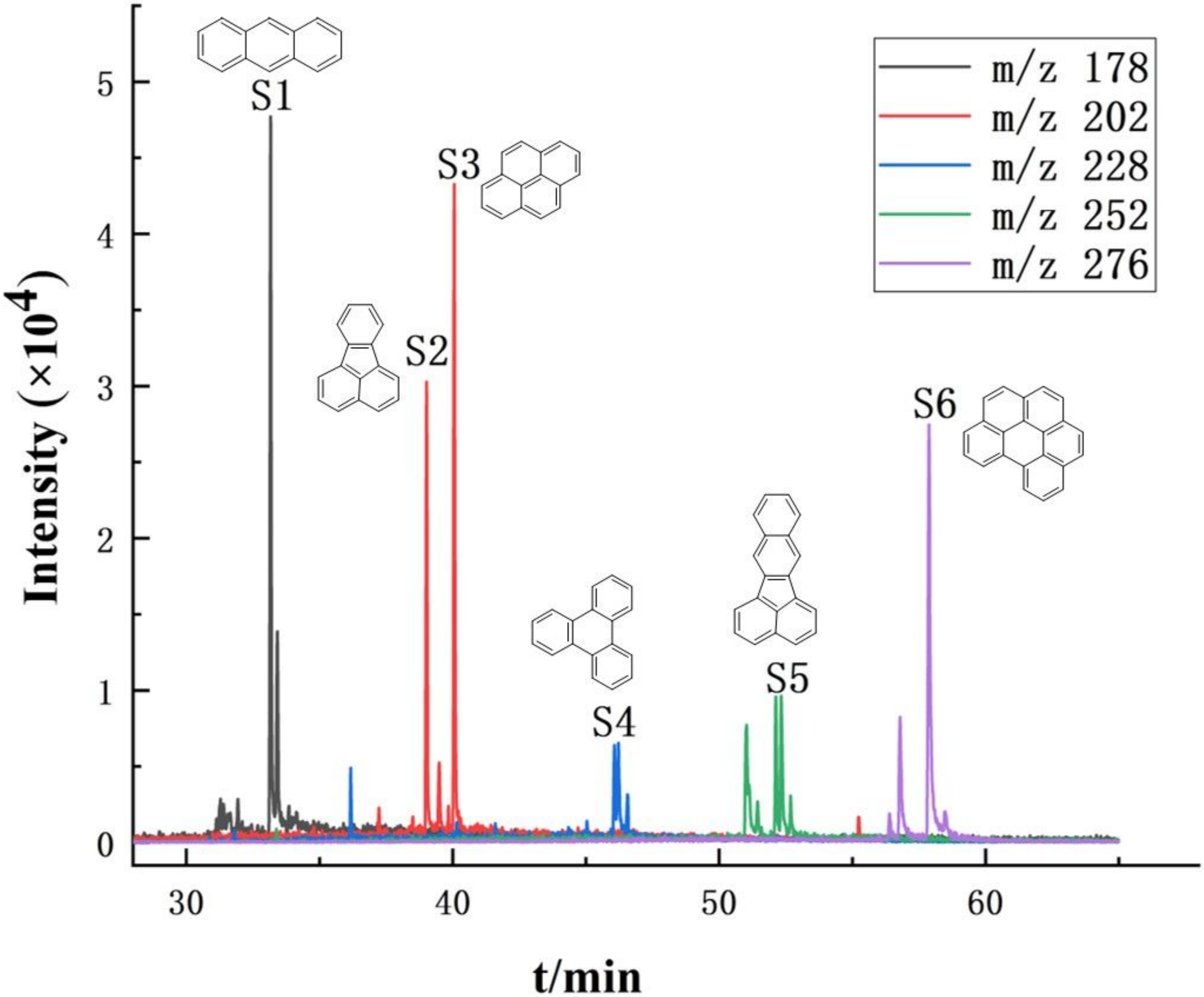

Figure 6

The select ions chromatograms (SIM) of ink in historical rubbing sample by using Py-GC/MS

Figure 7

The fiber morphology of (a) a modern handmade mulberry paper and (b) historical rubbings