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A preliminary study on dating of ancient written records from ink marks

Abstract

It is of great significance and challenge to identify the authenticity and date ancient cultural relics, such as ancient written records involving calligraphy and paintings, by using scientific instrumental analysis. In this paper, the ink marks' of five ancient written records from different ages, i.e., two in the Republican period, two in Qing dynasty and one in Ming dynasty, were analyzed by using FT-IR and Raman spectrometers. The experimental results revealed that:

a.According to FT-IR analysis, it was found that with the increase of retention time, there were regularities on the group variations of the additive gelatin in the ink marks and the changes of the amide groups could be used as a key character to estimate the relative date of the ink marks. In addition, the stretching vibration peak of C≡C in carbon black and the characteristic peak of C-H on the aromatic ring also exhibited significant changes over time, which also could be a relative criterion in estimating the cultural relic's age.

b.Raman spectra showed that the ink marks were composed of carbon black with high structural defect and with the increase of retention time, the grain size of carbon black decreased gradually, which could be a criterion for estimating the relative date (old or new) of the ink marks. However, due to the rarity and non-destructive of Chinese ancient calligraphy and paintings, the earlier samples were difficult to collect and analyze. It is expected that this preliminary study provides guidance for identification and conservation of cultural relics.

Keywords: ancient written records (calligraphy and paintings), ink marks, infrared spectroscopy, raman spectroscopy

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Introduction

The Chinese nation has a long history and rich cultural heritage including a large number of ancient calligraphy and paintings, however, in which there are a lot of fakes from a later generation. At present, there are two main methods for identifying the authenticity of ancient calligraphy and paintings, i.e., traditional archaeological method and identification using scientific instruments. In general, the archaeological method largely relies on rich experience of specialist who can make identification through appearance and configuration, called "look it up and down". The main principles include:

a. Comparison in terms of their own perceptual experience and the visual impression;

b. According to the style of art history and regarding times style and personal style as the main basis for identification;

c. Identifying from the artistic point of view, etc.

By contrast, the authenticity identification through scientific instruments mainly depends upon the comparisons of difference in chemical compositions and microstructures between authentic work and counterfeit of inks or pigments. For example, in public security criminal investigation system, authenticity identifications of calligraphy and paintings mainly rely on comparisons of the surface morphologies by using optical microscopy and logical inference, which however, are too simple to be used to complex identification and judgment. Ouyang et al.[1] used Raman and FT-IR spectra to identify the authenticity of seals, Chinese rice papers and words of calligraphy and paintings. This was attributed to the differences of chemical compositions and relative contents of each composition between the authentic calligraphies and counterfeit, which resulted in the different characteristic absorption peaks. Na et al.[2] also authenticated the Chinese calligraphies and paintings by using Raman and FT-IR spectra methods and compared with fluorescence spectrum. The results showed that inkpad, rice papers and ink marks had their own characteristic spectra due to the differences in chemical composition or the relative contents of each component, which make it easy to identify them according to the positions and relative intensities of the peaks. Obviously, these methods are of advantages, such as fast, accurate, simple and no damage, which provide an effective mean for identifying the Chinese calligraphies and paintings.

Hu et al.[3] adopted an Energy-Dispersive X-Ray Fluorescence (EDXRF) to analyzed elements and chemical compositions between modern paper and ancient paper and obtained the production process differences, which also could be used to date the papers. It was found that the peak shapes of the notebooks and letter papers were similar and however, there was a big difference with the label papers, because of the influence of the additives in the label papers and the relative fluorescence intensity decreased a lot. In addition, the maximum emission wavelength of the notebooks shifted red in comparison with letter papers, due to the oxidation in the air. Recently, with the development of imitation level of the calligraphy and painting, such as writing on the ancient Chinese rice paper using ancient ink, painting on the ancient paper using ancient pigments, etc. sometimes, it is impossible or difficult to identify the genuine and fake by means of above methods. In this paper, we are trying to explore a possibility to identify the authenticity of calligraphy and paintings by using Raman and FT-IR spectra, in terms of the variations of microstructures and components in ink marks over time,-which can also be a guide to the identification and conservation of cultural relics.

It is well-know that the main raw materials of the ink are soot and colloid and in order to improve the durability, permeability, fragrance and other properties, some precious natural herbs and other additives are often mixed into it.[4,5] In general, soot is a kind of basic black pigment. In ancient China, ink sticks were mostly made from pine tree smoke. That is, burning pine branches in the kiln and generated black ash adsorbed on the kiln wall and then separated from kiln wall to get loose smoke. Since Song dynasty of China, two raw materials (soot smoke and lampblack or oil smoke) were adopted to prepare the ink sticks. The lampblack could be obtained by burning lampblack with animal or vegetable oil in a smoke-house, in which the oil lamp was covered with porcelain bowl to absorb black ash (i.e., lampblack). Generally, the ink sticks mainly produced according to the following processes: mixing soot and melted colloid to form an ink billet and adding various additives into it, then hammering ink billet, pressing it into a mold and naturally air-dried and finally traced a design in gold. Traditionally, an important experience was so called the "slightly colloid and countless pestle", that is, the more times of hammering, the better quality of the ink sticks.[6–8] However, recently, the modern inks or ink sticks are made from industrial carbon black and chemical additives. The main raw materials are natural gas fuels, of which mostly are fossil raw materials. Some ink making factories in Shanghai city and Anhui province still follow the ancient process, which is blending lampblack or pine smoke with oxhide gelatin, then hammering nearly 10,000 times to make ink billet.

Table 1 lists the comparisons of raw materials of ancient and modern inks. It can be seen that the carbon black in the ancient ink is usually made from natural materials such as pine soot and tung oil, while that in the modern ink is the pyrolysis of natural gas. That is to say the preparation of carbon black has a big difference not only in raw materials, but also in preparation temperature (Theory group of Beijing organic chemical plant and Beijing institute of chemical technology). Therefore, the ancient and modern carbon blacks will show the significant differences in microstructure characteristics including particle size, degree of graphitization, crystallization, types of surface groups, etc. In addition, we can learn that the animal glue as adhesive are used in both methods, which indicates that both methods uses almost the same raw materials but different in preparation processes.[9] Therefore, in order to figure out the difference between the ancient and modern gelatin, the evolution of gelatin over time must be investigated by using FT-IR, which refers to the group types and the peak intensity ratio, etc. Wang et al. Wang and Shao compared the ink particle shapes and chemical compositions of the ancient inks conserved in Nanjing museum, which were from the tombs of Wang Minzhi in the Eastern Jin Dynasty (317 A.D.-420 A.D.), middle and late period of Southern Dynasty (420 A.D.-589 A.D.) and Zhang Tongzhi in Southern Song Dynasty (1127 A.D.-1279 A.D.) with two different quality modern ink spindles by scanning electron microscopy (SEM), as listed in Table 2. It was found that the ink particle shapes of the ancient inks showed more regular and grain size with relatively small and uniform. However, the size of high-quality modern ink spindles were nearly the same to the ancient ones, but the inferior modern ink spindles exhibited a very large size. In addition, ingredients of modern inks mainly contained the elements involving silicon (Si) and aluminum (Al), instead of copper (Cu). They suggested that the selected smoke during production process of the ancient inks was generally rinsed thoroughly, including less impurities and the ink grain was small and well-distributed. The degree of the ink grain in the Southern Song Dynasty (1127 A.D.-1279 A.D.) was comparable with modern high-quality ink. It is completely believable that some literatures recorded that the ancient ink smoke was hammered for "thirty thousand times ", or even "hundred thousand times". Another characteristic was that colloid in the ancient ink was generally slighter, which may be associated with degumming ancient ink and the minor ingredients in the Eastern Jin Dynasty (317 A.D.-420 A.D.) and the Southern Dynasty (420 A.D.-589 A.D.) were copper (Cu), calcium (Ca) and in the Southern Song dynasty (1127 A.D.-1279 A.D.) including not only copper (Cu) and calcium (Ca), but also silicon (Si). Copper (Cu) as an ingredient in the ancient inks might mainly because it could enhance the ink color. However, the ingredients in modern ink mainly were silicon (Si) and aluminum (Al) without copper (Cu) and the quality of the inks mainly depended on the size and uniformity of the smoke.

Table 1 Comparisons of raw materials of the ancient inks and modern inks

Varieties of ink	Carbon black	Colloid (gelatin)
Ancient ink	pine soot, tung oil soot, etc.	skin and bones of cattle, horses, sheep, deer or other animals
Modern ink	cracking natural gas, trough method (in the early modern) pine and tung oil smoke (In Anhui and Shanghai)	bones of cattle, pig or other animals

Figure 1 Dates of five ancient ink marks.

Table 2 Particle-size and minor impurity of different period inks

Period	Particle-size (μm)	Ingredient
Eastern Jin (317 A.D.-420 A.D.)	0.2-0.3	Copper (Cu), calcium
Southern Dynasty (420 A.D.-589 A.D.)	0.2-0.3	copper, calcium
Southern Song (1127 A.D.-1279 A.D.)	0.1-0.2	silicon, copper, calcium
Modern(high-quality)	0.2	silicon, aluminum
Modern(inferior)	50	silicon

Materials and methods

In the experiment, five ancient ink marks were studied, as shown in Figure 1, which are collected from the Research Center for China Civil Literature of Wuhan University. The samples include:

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I. One “Zhang zhenxiang’s deed” in twenty-five years of the Republic of China (1936 A.D.) (Sample-1936);

II. One “Guo Gensheng’s crown leases ordinance” in five years of the Republic of China (1916 A.D.) (Sample-1916);

III. One “Quan’s title deed” in the twenty-eight years of Dao Guang period in Qing Dynasty (1848 A.D.) (Sample-1848);

IV. One “Pei lianbi’s title deed” in fifteen years of Dao Guang period in Qing Dynasty (1835 A.D.) (Sample-1835);

V. One “Li ruji’s title deed” in ten years of Chong Zhen period in Ming Dynasty (1637 A.D.) (Sample-1637).

There are exact sign dates on the five samples, which are high credibility, meaning the suitability to be references for dating experiment. For comparing, a contemporary ink produced by Beijing Yidege Ink Industry Ltd. Company which is popularly and widely used in Chinese calligraphy and named as Sample-2016. The ink mark was prepared as follows, i.e., dripping the ink on an ancient paper and drying it for 48 hours in the air. The samples were characterized by using a Laser Microscopy Confocal Raman Spectroscopy (Join-Yvon LabRam, Horiba, France) with 488nm, 633nm and 785nm lasers and a Fourier Transform Infrared Spectroscopy (FT-IR) (Nicolet iS10, Thermo, USA) with the method of attenuated total reflectance (ATR). Before testing, the background was collected on the blank place near ink and then collected the spectrum of ink. The ambient temperature was 22° C and the relative humidity was 35%.

Results and discussion

FT-IR analysis

Figure 2 illustrates the FT-IR Spectra of the samples and Table 3 lists the groups and analyses of each peak. It could be seen that except in Sample 2016, all ancient samples had strong absorption peaks in the range of 3180 to 3500 cm^{-1}. The peaks of the Sample-1936 and Sample-1916 were located at 3216 cm^{-1} and 3203 cm^{-1} respectively, which were generated by the N-H stretching vibration in the secondary amide, as shown in Figure 3. However, the Sample-1848, Sample-1835 and Sample-1637 exhibited double absorption peaks with splitting tip around 3334 cm^{-1} and 3280 cm^{-1}, respectively, which were generated by two N-H bonds stretching vibrations in the primary amide groups.[10] It is well-known that in ancient time the gelatin made from animal skins and bones was always used as a binder for ink production. In general, gelatin is composed of intertwined collagen molecules chains and each collagen molecules chain is connected by peptide bond. In fact, it is amide groups by condensation reaction of carboxyl and amino of two adjacent amino acids, as shown in Figure 4 and the peptide bond is the basis of most proteins. Hence, the peaks of N-H stretching vibration appearing in the Sample-1936 and Sample-1916 were corresponding to the amide groups on the collagen chain in gelatin. In general, the dry gelatin is a stable solid, but it will be hydrolyzed slowly in humid environment and the collagen chain will absorb water and fracture to form new amino and carboxyl. Therefore, the two kinds of N-H stretching vibrations in Sample-1848, Sample-1835 and Sample-1637 should be attributed to the primary amide groups formed by the cleavage of collagen chain. In other words, the N-H stretching vibration peak in the amide group could be used as the relative standard for dating the ink marks.

That is, the collagen chain would be broken by air-slake due to the presence of water in the air over time, which resulted in generating the characteristic peaks of N-H stretching vibration in the primary amide. However, for the contemporary Sample-2016, this characteristic peak was not found in the FT-IR spectrum. These differences might be related to the different preparation methods of gelatin and within the solution state during long-term conservation. The peaks near 2920 cm^{-1} and 2850 cm^{-1} were from the methyl groups attached to the nitrogen-atom. The characteristic peak at 1635 cm^{-1} was attributed to stretching vibration of C=O in the amide group. This peak appeared in the five ancient samples, which demonstrated the presence of amide group in the ink marks. At the same time, it could be seen that the peak position of the Sample-1916 and Sample-1936 shifted to the direction of low wave number compared with the other older samples, which might be due to the influence of the adjacent substitutes different from other ancient samples. Therefore, this phenomenon could be an auxiliary judgment for dating the ink marks.[11,12] The differences of above characteristic peaks were caused by the gelatin compositions in ink marks and its changes with the time prolongation, which was related to the strong infrared activity of the main components in gelatin and the relatively poor stability of gelatin compared with black carbon.

In addition, there were some peaks that might be derived from the other components and could be analyzed as follows:

I. In the range of 2100 to 2270 cm^{-1}, there were C≡C stretching vibration peaks with different intensities in all samples, which were from the black carbon in the ink marks. The intensities showed a tendency of decline slowly with the increase of retention time, i.e., the intensity of Sample-2016 was the highest, while the Sample 1637 was almost to be disappeared, which results in the effect of the long-term exposure to the oxidizing atmosphere, that was to say, with time extension C≡C bond was oxidized slowly and transformed into other bond forms. The feature has a positive correlation with time, so it may be helpful in subdividing data and conservation of the samples.[12–14]

II. For the Sample-1637, Sample-1835 and Sample-1848, there was a strong and wide peak located around 1020cm^{-1}. It mainly came from the C-H on C=C chain and the C-H mainly came from C chain and also a small percentage among them move to low wave number, which were from aromatic ring. However, for the Sample 1916, Sample 1936 and Sample 2016, the peaks were relatively weaker, while on the contrary, there was a strong and wide peak appeared in the range of 600 to 1000 cm^{-1}, which was derived from the C-H bending vibration on benzene ring. These results revealed that in the ink marks the aromatic ring structure mainly derived from carbon black and aromatic, decreased gradually over time.[15] In general, the carbon black of the ancient samples was obtained from burning wood, animal oil or plant oil. In view of the situation of ink industry in the period of Republic of China, carbon black of Sample-1916 and Sample-1936 might also be produced from the same process. But for the contemporary sample-2016, carbon black was made from cracking petroleum gas. Generally, most of the molecules contained aromatic rings from carbon black and aromatic are more volatile. Thus, with the extension of time, the intensities of aromatic ring become weakness slowly and this phenomenon also provides an alternative evidence for identification and dating the ink marks.

Raman analysis

Three representative samples, Sample-1848, Sample-1916 and Sample-2016, were evaluated by using a Raman Spectrometer. Figure 5A illustrates the Raman spectrum of Sample-1848. Obviously, two

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strong peaks appeared in the range of 1300~1700 cm^{-1}, in which G peak was at 1596 cm^{-1} and D peak at 1372 cm^{-1}, respectively. In general, G peak occurs due to the normal vibration model (E_{2g}), which is caused by the C-C stretching vibration in the intrastratal hexagon of graphite~~ and~~ this is the characteristic vibration peak of the C-C in the fragrance structure of graphite.[11] The emergence of D peak is caused by the disordered-arrangement of carbon atoms, whose intensity increases gradually with the decrease of the crystal order degree. According to the location and shape of present two peaks, they were derived from graphite with structural defects, cluttered graphite fragment in carbon black particles. In terms of Tuinstra and Koenig's study,[16] the value $R= I_D/I_G$, where I_D is intensity of D peak, I_G is intensity of G peak, is inversely proportional to the grain size L_a that figured out from the results of X-ray diffraction (XRD). From Figure 5A, it could be observed that after storing for a long time, the residual material with Raman activity was mainly composted of graphite and amorphous carbon in the ink marks.

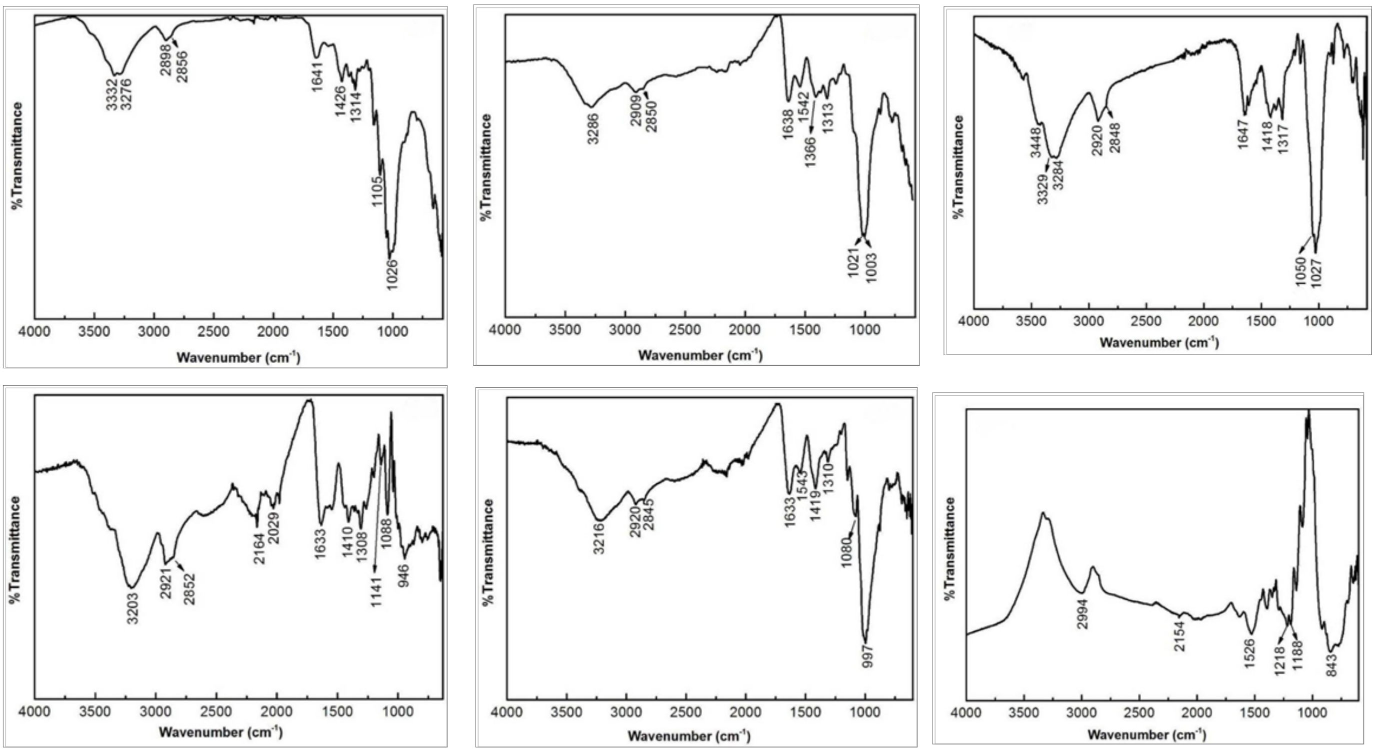


Figure 2 FT-IR spectra of the Samples. (a) Sample-1637. (b) Sample-1835. (c) Sample-1848. (d) Sample-1916. (e) Sample-1936. (f) Sample-2016.

Table 3 Results and analysis of FT-IR spectra

Spectrum peak location (cm-1)	Group	Illustration
3329-3335	N-H	primary amide, NH symmetrical stretching
3275-3290		primary amide, NH symmetrical stretching
3215-3200		secondary amide, NH symmetrical stretching
about 2920	C-H	methyl group is attached to N
about 2850		methyl group is attached to N
2100 -2140	C≡C	C≡C stretching
1633-1647	C=O	peptide bond, C=O stretching
about 1540	N-H	NH bending
1438-1454	C-N	C-N stretching
about 1410	N-H	NH deformation
about 1160	N-H	NH2 in-plane swing
about 1140	N-H	NH out-of-plane deformation
about 1056	C-H	C-H bond
about 1027	C-H	C-H bond
980-1035	C-H	CH in aromatic ring in-plane deformation
660-880	C-H	CH in aromatic ring out-of-plane deformation

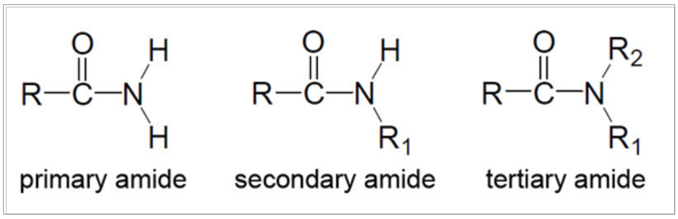


Figure 3 Sorts and structural formulas of amides.

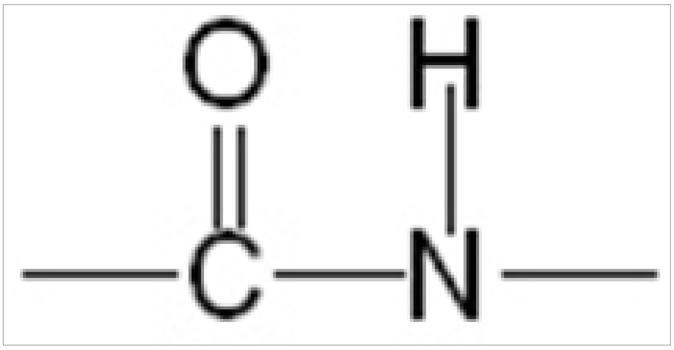


Figure 4 Structure of amide group.

Figure 5B illustrates the Raman spectrum of Sample-1916. Two peaks appeared in the range 1300~1700 cm-1, in which G peak appeared around 1593 cm-1 and D peak near 1385 cm-1, respectively. It can be judged the presence of graphite with structure defect, that is still cluttered graphite fragment in the carbon black particles, but there is a big difference between the degree of graphitization and the graphite particle size of the carbon black in Sample-1848. Figure 5C illustrates the Raman spectrum of Sample-2016. The main features of Raman spectrum are also the two strong peaks in the range of 1300-1700 cm-1, in which the higher wavenumber peak (G peak) appeared around 1602 cm-1 and the lower wavenumber peak (D peak) near 1372 cm-1. According to the reference, the main component of ink in Sample-2016 is graphite material with structural defects. Compared with ancient samples, their main difference is the intensity of the D-peak to the G-peak. When comparing the Raman spectra, it was found that all pigment compositions in three samples were carbon black.[13] In general, the internal structural differences between carbon black and the well-crystallized graphite include relative rotation, wrinkle layer and disordering of interlayer spacing appeared in adjacent layers, which exhibit a significant effect on the Raman spectra. G peak of the Sample-1848, Sample-1916 and the Sample-2016 were at 1596cm^{-1}, 1593cm^{-1} and 1602cm^{-1}, respectively. The C-C bond force in the layer is weakened since the inter-layer van der Waals force weakens and the bond length of the C-C bond in the layer is shortened and the vibration frequency becomes higher. As the degree of disorder increases, the G peak of fully crystallized graphite broadens and shifts to high wave number. The degree of disorder in Sample-2016 is greater than the Sample-1848 and the Sample-2016 is minimal. Secondly, D peak of the Sample-1848, the Sample-1916 and Sample-2016 are at 1372cm^{-1}, 1385cm^{-1} and 1372cm^{-1}, respectively. The peak gradually increases as the degree of crystal order decreases. Therefore, the degree of order in the Sample-1916 is the highest, followed by the Sample-1848 and Sample-2016. The above results show that the degree of graphitization of carbon black in the ink of the Sample-1916 is the highest, followed by Sample-1848 and Sample-2016. In addition, from the measurement of relative intensity $R=I_D/I_G$ of D peak and G peaks and the formula: La=4.4 nm/R,[14] the grain size (La) of carbon black in the three samples can be calculated, as listed Table 4. The crystal size of the graphite crystal lattice in carbon black of the Sample-2016 is approximately 7.5 nm; in the Sample-1916, it is approximately 6 nm; the Sample-1848 is the smallest, approximately 5.5 nm. That is, the crystal size of the graphite lattice in the Sample-2016 is the largest. Obviously, along with the time extension of the ink marks, the grain size of carbon black decreased gradually. Some studies suggested that during ink preparation, the grinding process would introduce the structural defects within natural graphite and with the increase of grinding time, the grain size of graphite crystal sheets would decrease gradually.[15] For the present experiment, we proposed that continuous actions of some external forces might cause a variation of the grain size within ink marks during long-term storage. Therefore, we suggest that the differences between the microstructures-can be used as a criterion for identifying the age (old or new) of calligraphy and paintings. However, in the present experiments, the data of other three old samples are not presented, duo to the following two reasons:

I. The ages of sample-1835 and sample-1936 are closer to measured sample-1848 and sample-1916 and they show almost the same results.

II. In general, Raman test needs more quantity of the sample. It can see from Figure 5 that the Raman peaks are very weak and for the sample-1628, the peak is too weak to be detected. It provides us an experience to use higher sensitive machines to do the work in future research.

Table 4 Experimental data of Raman spectra

Samples	G peak	D peak	R = ID / IG	La
sample 2016	1602cm-1	1372cm-1	0.59	7.5nm
sample 1916	1593cm-1	1385cm-1	0.73	6nm
sample 1848	1596cm-1	1372cm-1	0.8	5.5nm

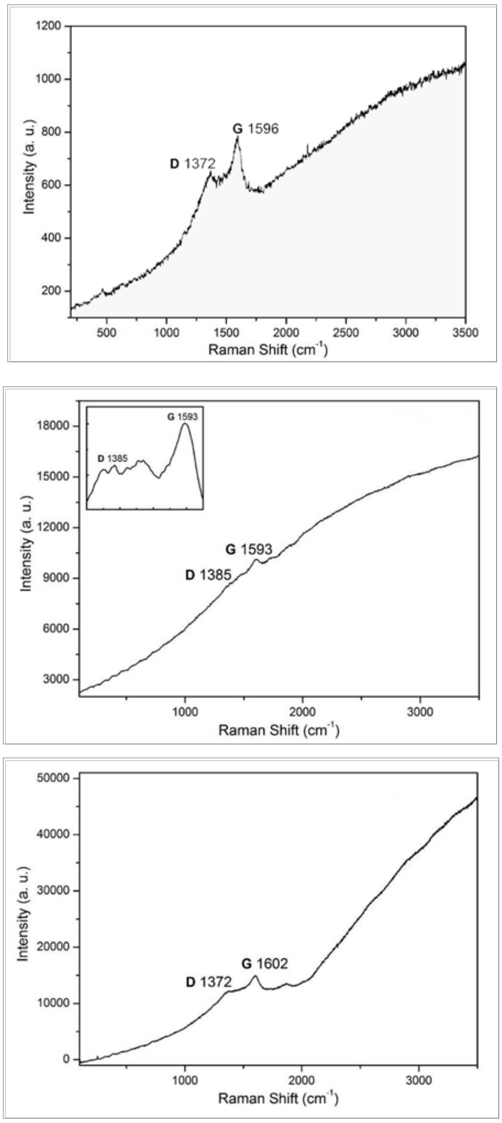
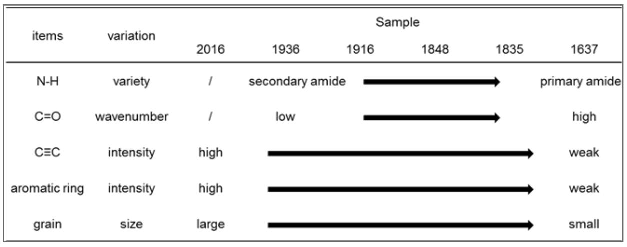


Figure 5 Raman spectra of the samples. (a) Sample-1848. (b) Sample-1916. (c) Sample-2016

Conclusion

Through FT-IR and Raman analyses, the micro-structural changes of the additives and carbon black within the ink marks can be used as a criterion for dating or estimating new or old of calligraphy and paintings. The preliminary summary of the variation trends from FT-IR spectra and Raman spectra is shown in Figure 6. According to this preliminary result from analyzing the microstructures of six ink marks involving modern times, the Republic of China, Qing Dynasty and Ming Dynasty, the main conclusions are as follows:



items	variation	Sample					
		2016	1936	1916	1848	1835	1637
N-H	variety	/	secondary amide	→			primary amide
C=O	wavenumber	/	low	→			high
C≡C	intensity	high	→				weak
aromatic ring	intensity	high	→				weak
grain	size	large	→				small

Figure 6 Variation trends of FT-IR spectra and Raman spectra.

Criteria from FT-IR measurements

i. Determine the duration of the ink marks by analyzing the microstructures of the amide group on gelatin chain. That is, for a long storage ink marks, moisture in the air will make the gelatin deliquesce and peptide bond break and form a primary amide group, which will result in a tip split double absorption peak in range of 3180~3500cm^{-1} and shows difference from the single peak of the secondary amide. In addition, the C=O stretching vibration peak around 1635 cm^{-1} provides a subsidiarity for identifying this change.

ii. Due to slow oxidation in the air, along with the time extension, the stretching vibration peak of C≡C in carbon black of the ink marks will crack slowly, which leads to peak intensity weakened, or even disappeared.

iii. Since the molecules containing aromatic ring in the ink marks are more volatile, the intensity of characteristic peak of CH on the aromatic ring will decrease with increase of time.

Criteria from raman measurements

i. In terms of position and shape of G peak and D peak in Raman spectrum, it can be inferred that the sample contains graphite material with structural defects, that is, the pigment components in the ink marks are carbon black. The degree of graphitization of carbon black in the ink of the Sample-1916 is the highest, followed by Sample-1848 and Sample-2016.

ii. The grain size (La) of carbon black can be calculated from the formula La=4.4nm / R ($R=I_D/I_G$), which decreases gradually with the increase of the storage time and can be used for identifying the authenticity of calligraphy and paintings.

Due to the rarity and non-destructive nature of the ancient Chinese calligraphy and paintings, the earlier samples are more difficult to collect and analyze. It is expected that this preliminary study provide a guiding significance in identification and conservation of cultural relics.[17,18]

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Conflict of interest

Authors declare that there is no conflict of interest.

References

1. Ouyang Q, Ouyang J. The Study of Characterization of Calligraphy and Painting by Modern Techniques. *Journal of Kunming University of Science and Technology.* 2006;31:32–35.
2. Na N, Ouyang Q, Qiao Y, et al. Rapid and Non-Destructive Identification of Calligraphies by Fourier Transform Infrared Spectroscopy and Fourier Transform Raman Spectroscopy. *Guang Pu Xue Yu Guang Pu Fen Xi.* 2004;24:1327–1330.
3. Hu L, Zeng Q, Zhang G. The Study on Papers Pigment at Different Years by Raman Spectra and Fluorescence Spectra. *The Journal of Light Scattering.* 2010;22:86–89.
4. Zhang W, Liu H, Guo S. A Study of the Manufacture and Conservation of Ancient Ink-stick. *Sciences of Conservation and Archaeology.* 1995;7:21–27.
5. Yan Y, Chen M. Trivial Talk About Ancient Ink. *Relics From South.* 2000;2:115–116.
6. Wang Z, Shao L. The Discussion of Formation of Ancient Chinese Ink and Related Problems. *Southeast Culture.* 1983;2:78–84.
7. Winter J. Preliminary Investigations on Chinese Ink in Far Eastern Paintings. *Archaeological Chemistry.* 1974;138:207–225.
8. JISC. *Animal Glue and Gelatin.* 2001.
9. Qiu J, Xu L, Xu F, et al. Study of Acrylonitrile and Butyl Acrylate-modified Gelatin Adhesives to Repair Ancient Ink-stick. *Sciences of Conservation and Archaeology.* 2010;22:33–39.
10. An Y, Li Y, Meng L. et al. The Characteristic Infrared Spectra of N-(2-Phenyl-(1,2,3-Triazoleformyl)-N-Arylthioueas. *Guang Pu Xue Yu Guang Pu Fen Xi.* 2001;21(2):177–199.
11. Yang X, Wu Q. Analysis and Application of Raman Spectroscopy. *National Defend Industry Press.* 2008.
12. Ferrari AC. Robertson J. Raman Spectroscopy in Carbons: from Nanotubes to Diamond. *The Royal Society.* 2004.
13. Chang J, Xue L. A Study on Raman Spectra of Particle Size of Graphite in Inkblot. *Journal of Wuhan University of Technology.* 2000;22:25–27.
14. Lespade P, Al-Jishi R, Dresselhaus MS. Model for Raman Scattering From Incompletely Graphitized Carbons. *Carbon.* 1982;20:427–431.
15. Nakamizo M, Honda H, Inagaki M. Raman Spectra of Ground Natural Graphite. *Carbon.* 1978;16(4):281–283.
16. Tuinstra F, Koenig JL. Raman Spectrum of Graphite. *J Chem Phys.* 1970;53:1126–1130.
17. Wang L. *The influence of Materials On The Style and Aeslhetic Characteristics of Chinese Calligraphy and Painting.* Master's thesis, Zhengzhou: Zhengzhou University. 2006.
18. Carbon Black Production and the Contributions of Legal Scientists of Ancient China. *Chemistry.* 1975;5:46–47.

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