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Non-destructive and in situ identification of rice paper, seals and pigments by FT-IR and XRD spectroscopy

Na Na[a], Qi-ming Ouyang[b], Hui Ma[c], Jin Ouyang[a,*], Yanping Li[d]

[a] *Department of Chemistry, Beijing Normal University, Beijing 100875, PR China*
[b] *Department of Arts, Capital Normal University, Beijing 100037, PR China*
[c] *Analytical and Testing Center, Beijing Normal University, Beijing 100875, PR China*
[d] *The National Museum of China, Beijing 100006, PR China*

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Abstract

This paper studied the chemical characteristics of rice paper, pigments and seals on Chinese calligraphies and traditional Chinese paintings. The techniques used here were Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). FT-IR allows good identification of the substances present in pigments and inkpads and differentiates each era of rice paper. This can be the base of estimating the age of rice paper. Different crystalline phases can be identified by XRD, which is further evidence to separate different kinds of pigments or inkpads. Both of these methods were non-destructive in situ analysis and can be used in the identification in calligraphies and traditional Chinese paintings. These results confirmed that the applied techniques are relatively quicker and more reliable than traditional approaches authenticated by years of experience.

Keywords: FT-IR spectroscopy; X-ray diffraction; Non-destructive analysis; Rice paper; Seals; Pigments

1. Introduction

Chemical analysis and technical examination of art works play an essential role in providing historical, artistic and technical information. It is important in furthering the understanding of our cultural heritage, notably in connection with the restoration, conservation, dating and authentication of artifacts.

In the past 25 years, and especially in the last decade, the techniques have been increasingly applied in the identification of the archaeology. Among these, non-destructive methods, which leave the sample viable and undisturbed and allow monitoring over a long period of time, are of great interest [1]. A variety of non-contact, applicable spectroscopic techniques have been experimentally used over the last decade. Established spectroscopic techniques such as Fourier transform infrared (FT-IR) [2–10], X-ray diffraction (XRD) [3–9,11] have been extensively applied and evaluated in the scientific analysis and documentation of artistic and historical objects. In previous work, Mazzocchin used FT-IR and XRD to investigate the physico-chemical characteristics of pigments found on pottery fragments from an excavation in Vicenza [3]. And Edreira used FT-IR and XRD in the spectroscopic analysis of Roman wall paintings and Egyptian Blue mixed with other pigments [4–6]. Daniilia et al. [7] examined Panselinos' Byzanitine wall paintings by XRD. Dom é nech-Carbó and coworkers [8] made the identification of inorganic pigments from paintings and polychromede sculptures immobilized into polymer film electrodes by stripping differential pulse voltammetry in agreement with XRD and FT-IR analysis. Casellato and Vigato [9] used FT-IR and XRD to identify the iron-containing pigments of historical wall paintings. Cheng et al. [11] reported the experimental results of the identification of some Chinese stamps of different editions by the proton induced X-ray emission (PIXE) and the change of the structure measured by XRD. Langkilde and Svantesson [12] studied five different celluloses with FT-IR spectroscopy. However, the works reported are the identification of the debris from the arts, and the in situ identification of pigments or seals on

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* Corresponding author. Tel.: +86 10 62795561; fax: +86 10 62799838.
E-mail address: jinoyang@bnu.edu.cn (J. Ouyang).

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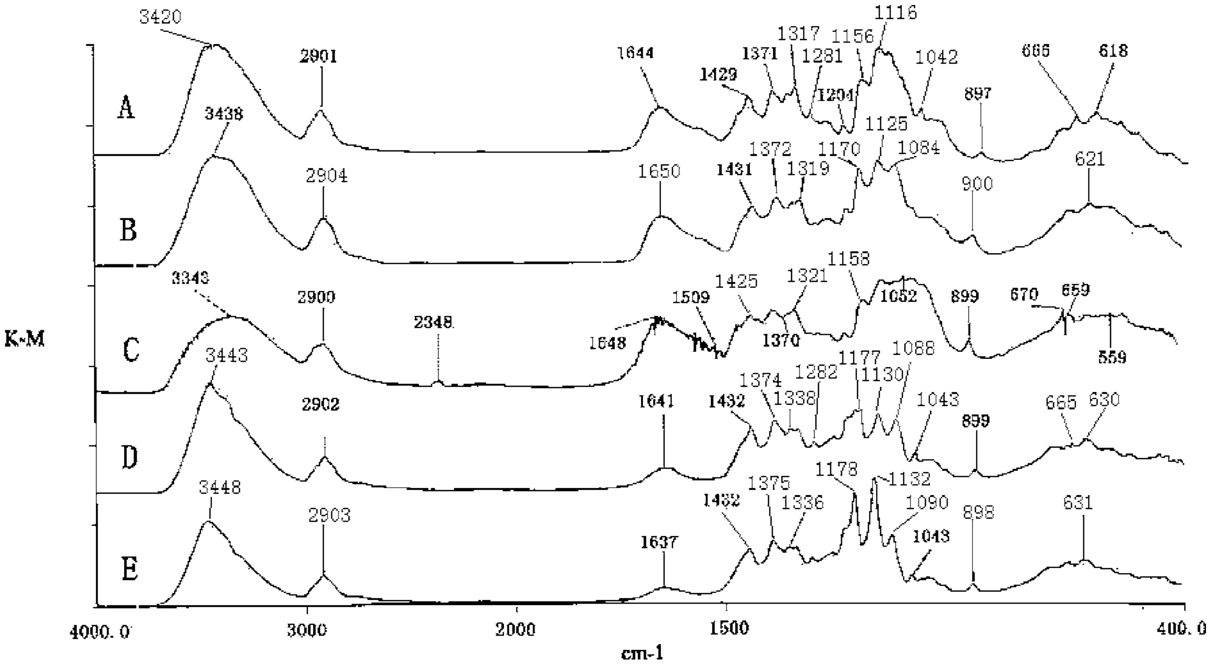

Fig. 1. FT-IR spectra of the rice paper of five different eras. (A) The rice paper of Tang Dynasty; (B) the rice paper of Song Dynasty; (C) the rice paper of Xi Xia Dynasty; (D) the rice paper of the Late Qing Dynasty; (E) the rice paper of modern times.

works of arts by these techniques have not been reported. The identification of rice paper of different eras has not been reported, either.

The techniques, which will be discussed in this paper in detail, are FT-IR and XRD. Photometric and wavelength accuracy, spectral quality and reproducibility of modern instruments in combination with new emerging techniques of chemometrics open a wide area for new applications. The first work in this paper was the identification of rice paper, which gave the evidence to differentiate rice paper of different eras.

Another work was to study the pigments and seals on the arts in situ. The study of a mural painting sample involves the characterization of the pictorial surface, which is

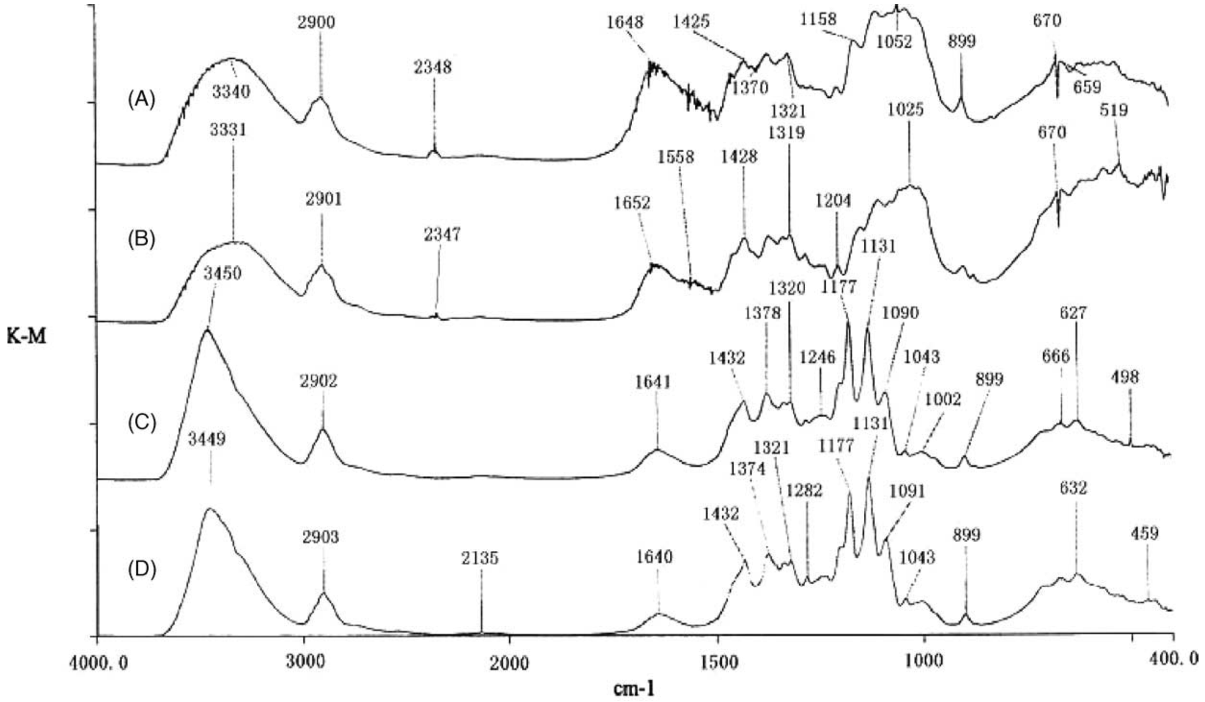

Fig. 2. FT-IR spectra of the rice paper of the same eras. (A, B) The rice paper of Xi Xia Dynasty; (C, D) the rice paper of modern times.

constituted of the pigment and the substrate that immersed. The chemical composition of both pigment and substrate is responsible for the final color and it can offer substantial information about the techniques that were used in the artwork manufacture [4]. IR spectra can provide useful information on the reflectivity of pigments at specific wavelengths. More important, the specificity is sufficient to enable the differentiation of pigments based on their infrared spectra. IR spectroscopy is commonly used in conservation science to identify pigments and other materials [10]. The different manufacture of artworks and the different content of some kinds of volatile due to their belonging to different eras lead to different characters in vibration frequency of IR functional groups, which are the base to the determination of the age of artworks non-destructively. Similarly, we can use differences in the IR and XRD spectral properties of substances to try to differentiate different kinds of pigments or inkpads of the time. In addition, the famous Chinese calligraphers always use a certain kind of inkpad. And because of their special requirements and tastes, they are used to adding some additives into the inkpad before using it. It is the base of authenticating the arts of the time.

FT-IR and XRD can give the required structural information to authenticate. The unique and characteristic IR spectra of different kinds of pigments, inkpads and rice paper of different eras can be obtained in situ and without damage to the analyzed material. In addition, we used XRD spectroscopy to identify the crystalline phase present in the pigments and inkpads. These can be achieved practically without any sample preparation and any sample destruction, which have increased the potential types of samples irrespective of their form or nature. Because of the wide use of rice paper, pigments and inkpads in the arts of painting and calligraphy in China, the identification is of great significance.

2. Materials and methods

2.1. FT-IR measurements

All FT-IR spectra were recorded by using a Perkin-Elmer Spectrum GX FT-IR system operating in diffuse reflectance (DR) mode and averaged over 32 scans with a resolution of 4 cm^{-1}. Measurements were made by using the diffuse reflectance integrating sphere, equipped with a denterated triglycine sulphate (DTGS) detector. The samples were placed on the reflectance accessory for direct measurement. The reflector contained integral spacers that allow two passes of the beam through the sample. The absorbance spectrum was obtained by ratioing the single-beam spectrum against that of the background from 4000 to 400 cm^{-1} at intervals of 1 cm^{-1}. The total number of data points was 3601 for each spectrum. Interferograms were co-added followed by strong Beer–Norton apodization. And the spectra were replotted using the Kubelka–Munk function supplied with the spectrum for windows (ver. 3.0) software.

2.2. Equipment for XRD

X-ray diffraction analyses were performed by a PANalitical X’pert Pro MPD diffractometer (PANalitical, Holland), using Cu Kα radiation (40 kV, 40 mA), a flat sample holder and an X’celerator detector. Measurements were carried out in the range $5^\circ < 2\theta < 80^\circ$ with a step of 0.033°. The scan

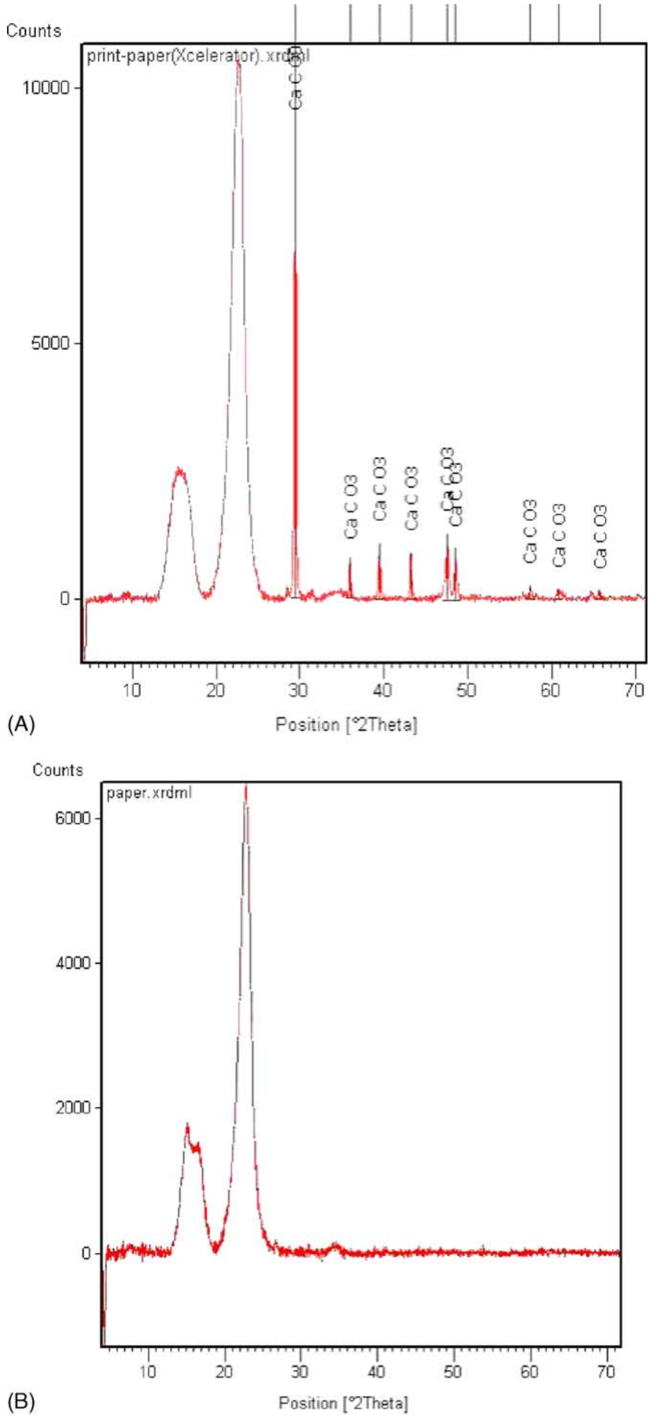

Fig. 3. XRD response of paper. (A) The print paper with calcite crystalline phase; (B) the rice paper without crystalline phase.

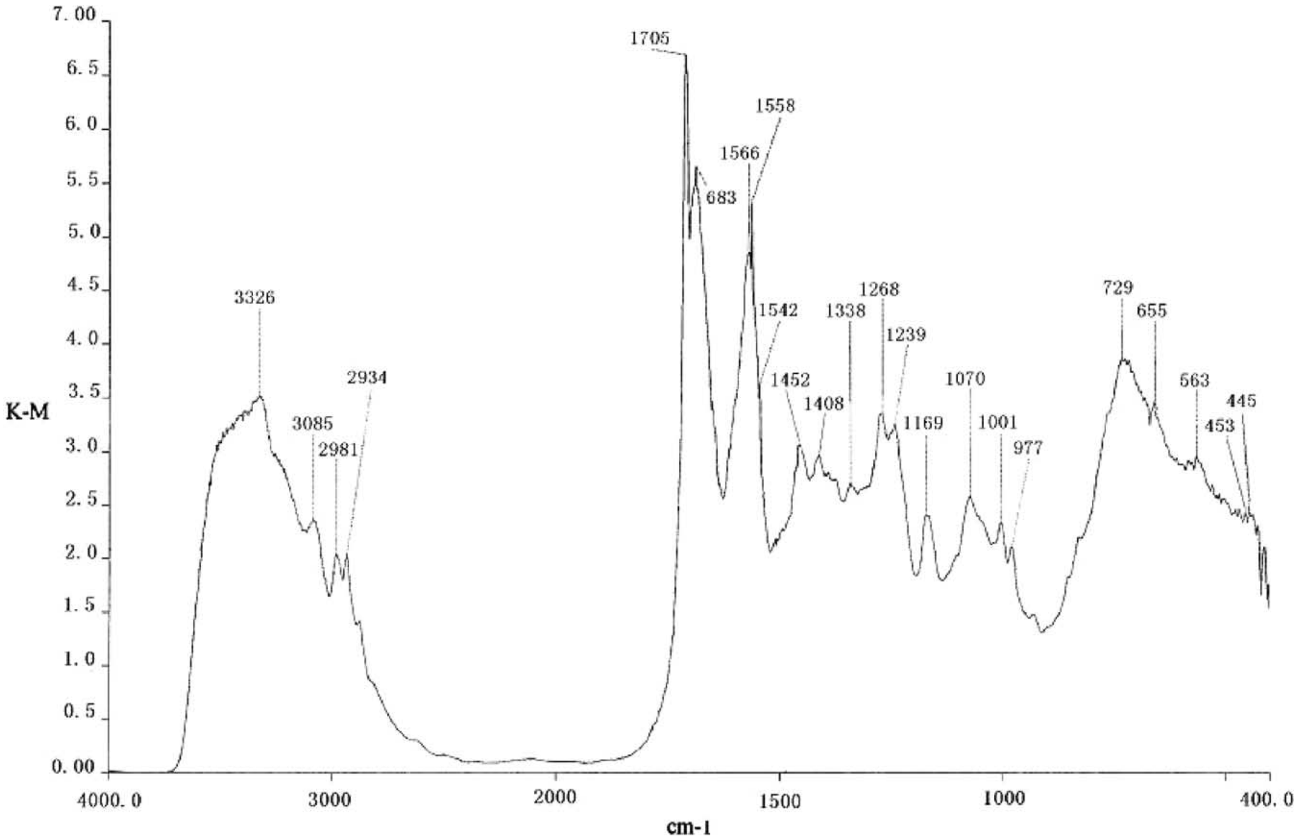

Fig. 4. FT-IR spectrum of the cover of the Yongle Canon of Ming Dynasty.

step time was 15 s. The JCPDS data bank of standard X-ray powder spectra was used for phase identification [JCPDS (2002)].

2.3. Samples

In this paper, pieces of rice paper of the time and several patches of rice paper from the National Library of China were studied. They are the literature of Xi Xia Dynasty, the Yongle Canon of Ming Dynasty and the Rare Book of Tang Dynasty. Pieces of calligraphies of one famous contemporary Chinese calligrapher of the time and the counterfeits were studied, too. In addition, the identification of a piece of traditional Chinese painting coming from Capital Normal University was reported.

3. Results and discussion

3.1. Identification of the rice paper

3.1.1. Comparison of rice paper of five different eras by FT-IR

In Fig. 1 the spectra of the rice paper of five different eras are shown. The rice paper came down from the eras of Tang Dynasty (A), Song Dynasty (B), Xi Xia Dynasty (C), the Late Qing Dynasty (D) as well as modern times (E). We can differentiate them after examining the spectra. In spectrum A, the band at 1116 cm^{-1} can be explained by the presence of C–OH strength vibration, which can be used in separating from other spectra. Examining spectrum B, the ratios of the peak height of three peaks from 1200 to 1084 cm^{-1} are different from D and E. And the band at about 1043 cm^{-1} cannot be observed, but the band can be found in spectra A, D and E. The band of 1043 cm^{-1} is attributed to the stretching vibration of –S=O. In spectrum C, some bands are different from others. They are at 2348 cm^{-1}, which can be attributed to the presence of CO_2, between 1200 and 1000 cm^{-1}, which can be related to some kinds of glucide, and below 700 cm^{-1}, which shows containing some inorganic materials. Because the samples of D and E belong to two eras near to each other, the spectra of them are similar. But the difference of the ratio of three peaks from 1200 to 1088 cm^{-1} can still be observed.

In the IR spectra of the rice paper of five different eras, the quantity and distribution of the different functional groups varied. These were significative in the identification of eras. As for the IR spectra of D and E, most structural and functional groups gave similar signals. We speculated that the chemical components of the rice paper of the same era might be consilient and show the similar IR spectrum. Thus, two different eras of rice paper were tested and reported as follows.

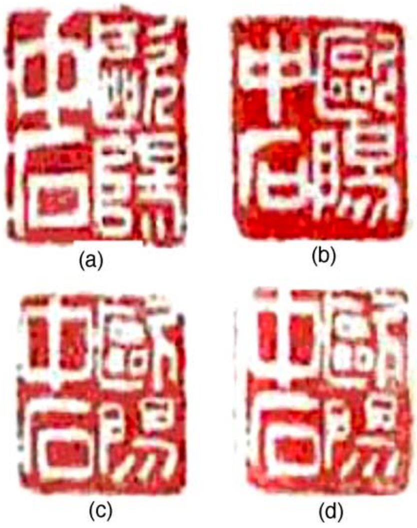

Fig. 5. The picture of the seals on the calligraphies. (a, b) The seals of real calligraphies; (c, d) the seals of counterfeits.

3.1.2. *Comparison of rice paper of the same era by FT-IR*

The spectra of the nature of the rice paper are shown in Fig. 2, which includes two patches of the rice paper of Xi Xia Dynasty (A, B) and two patches of the rice paper from modern times (C, D). From Fig. 2, we can see that the spectra of the same era are similar and show the same peak pattern, but there is much difference between the rice paper of two eras.

The spectra of A–D clearly show the presence of the cellulose of the animal, as one can infer from the bands present at about 3300 cm^{-1} (N–H strength vibration and O–H strength vibration), about 2900 cm^{-1} (C–H strength vibration) and from 1655 to 1640 cm^{-1} (the characteristic peaks of acylamide). The cellulose of the plant can be seen from the bands 3450 to 3300 cm^{-1} (ν_{OH}), 1370 to 1340 cm^{-1} ($\delta_{CH} + \delta_{OH}$), 1430 cm^{-1} ($\delta_{CH}$) and from 1100 to 1000 cm^{-1} ($\nu_{R\text{-}O\text{-}R}$). Examining the spectra of A and B, the broad intense band at about 3340 cm^{-1} is due to the stretching vibration of bound and unbound hydroxyl groups. But the corresponding bands in the spectra of C and D are at about 3450 cm^{-1}, and the peaks are much sharper than the peaks of A and B. The bands at 2348 cm^{-1} (A) and 2347 cm^{-1} (B) can be assigned to CO_2, but cannot be seen in the spectra of C and D. The broad bands from 1150 to 900 cm^{-1} in the spectra of A and B can be attributed to some kinds of glucide, which are different from the spectra of C and D. In the same bands, the spectra of C and D take another look. In each spectrum, there are three sharp peaks related to C–O stretch of esters (C: 1177, 1131, 1090 cm^{-1}; D: 1177, 1131, 1091 cm^{-1}). From the bands, one can conclude the presence of ethyl cellulose (EC), assisting by the bands around 3450, 1378 cm^{-1} (C), 3449 and 1374 cm^{-1} (D). The peaks from 800 to 500 cm^{-1} are attributable to inorganic materials. The band of 670 cm^{-1}can be observed in A and B, but cannot be observed in C and D.

Through examining the IR spectra of two eras, we make a primary conclusion that the paper of the same era has the similar IR spectrum. Another seven pieces of the rice paper of the time were studied, which showed the similar IR spectrum. As the unquestionable value of historical objects, we had not gotten the adequate samples of the antiquity. So more work will be done if we got more patches of antique rice paper in our future works. With plenty of the samples, it can be expected to set up a rice paper collection of IR standard spectra, made up of IR spectra of different eras of rice paper. Then not only can we distinguish real antique arts from counterfeit ones quickly, but also judge the age of the rice paper.

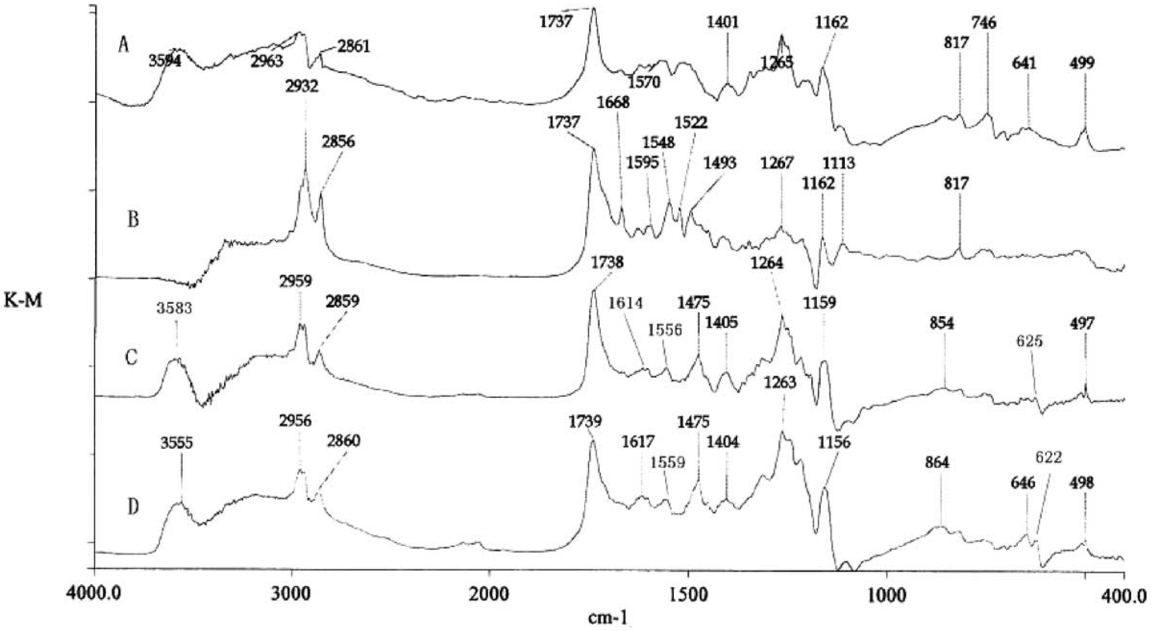

Fig. 6. FT-IR spectra of the seals. (A, B) The seals came from two real calligraphies; (C, D) the seals came from two counterfeits.

3.1.3. *Identification by XRD*

We tried to identify the crystalline forms of the components in rice paper of different eras and print paper by XRD. There is no difference between each era of rice paper, because XRD is used to identify the different crystalline phases present in the samples and the rice paper in China is mainly made up of cellulose. But the difference between the print paper and the rice paper was found. In Fig. 3, the XRD spectra of the print paper (A) and the rice paper (B) are shown. A clearly confirms the presence of calcite ($CaCO_3$), but B confirms nothing at all. It is irradiative in the identification of different kinds of paper.

3.2. *Identification of the cover of Yongle Canon of Ming Dynasty*

The cover of Yongle Canon of Ming Dynasty was examined by FT-IR due to its main component of cellulose. Fig. 4 shows the FT-IR spectrum of the cover of Yongle Canon. One can judge the characteristic peaks of some kinds of the cellulose of the plant by some bands. The corresponding bands are at about 3326 cm^{-1} (ν_{OH}), 1452 cm^{-1} (δ_{CH}) and 1338 cm^{-1} ($\delta_{CH} + \delta_{OH}$). In addition, one can observe the characteristic peaks of chrysotiles at 1070, 1001 and 977 cm^{-1}. So the chemical information of this sample can be shown by FT-IR to assist the identification.

3.3. *Identification of the seals*

A similar spectral analysis was applied to the seals on some pieces of real and counterfeit calligraphies. This work leads to good results. The inkpad we discussed here is called Babao Inkpad, only used in calligraphies and paintings of China. There are two kinds of Babao Inkpad in China. They are rosiness and crimson.

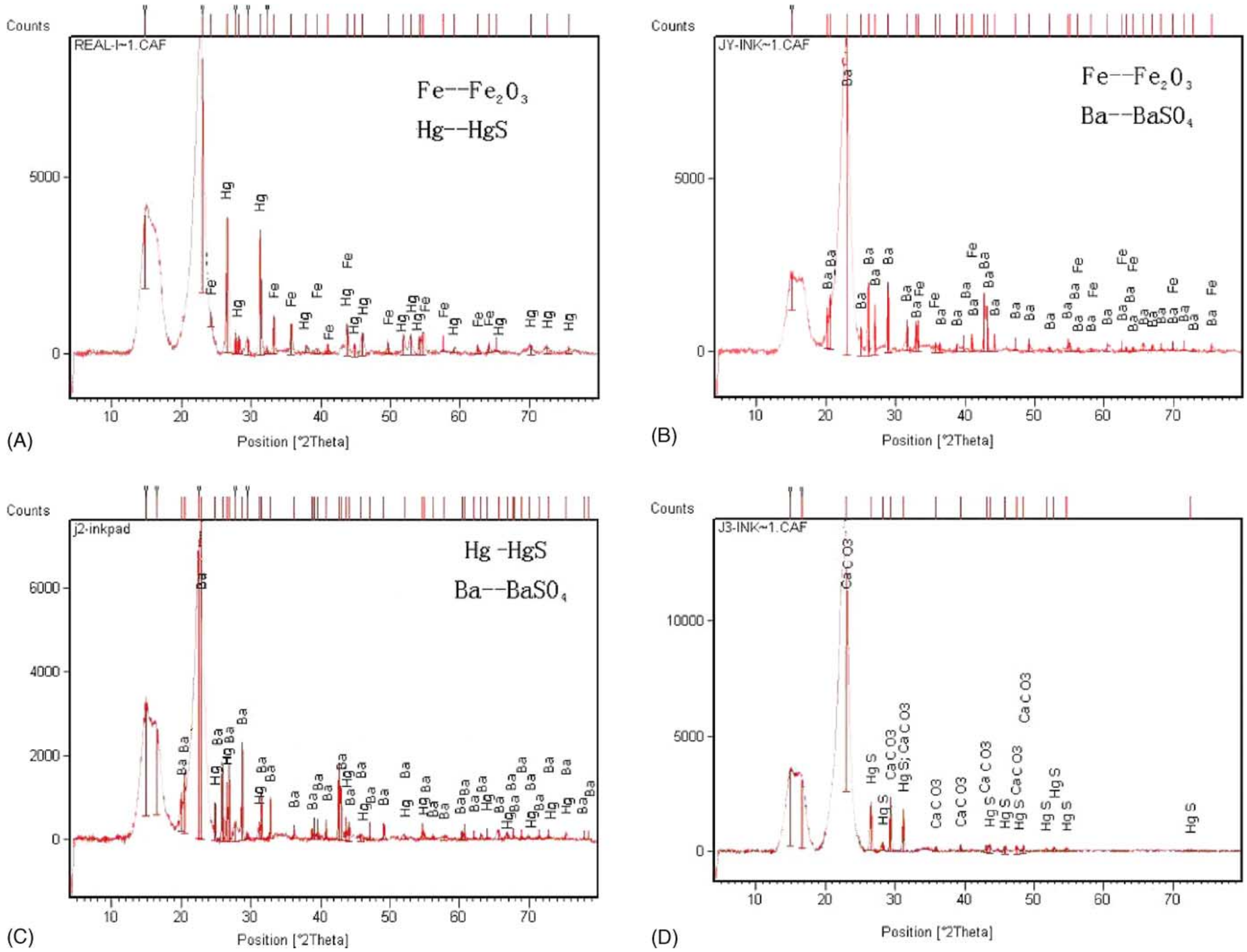

Fig. 7. XRD response of the seals. (A) The seal of the real calligraphy with the following crystalline phase: iron oxide (Fe_2O_3) and cinnabar (HgS); (B) the seal of the counterfeit named sample 1 with the following crystalline phase: barite ($BaSO_4$) and iron oxide (Fe_2O_3); (C) the seal of the counterfeit named sample 2 with the following crystalline phase: barite ($BaSO_4$) and cinnabar (HgS); (D) the seal of the counterfeit named sample 3 with the following crystalline phase: calcite ($CaCO_3$) and cinnabar (HgS).

Fig. 8. Photograph of the traditional Chinese painting.

3.3.1. Identification by FT-IR

Fig. 5 shows four pictures of seals on the calligraphies. A and B are the pictures of the seals from the real calligraphies. C and D are from the counterfeits. Fig. 6 shows the IR spectra of those four different seals. All the spectra were subtracted by the paper spectra of themselves. A and B are the spectra of the real ones, whose inkpads belong to different kinds of compounds. C and D are the spectra of the counterfeits. In the spectrum of A, Ar-COOK appears with bands at 2963, 2861, 1737, 1265 and 1162 cm^{-1}, which are similar to the other three spectra. We can conclude that this is the main component of the inkpads. Spectrum B is different from A. At about 3594 cm^{-1}, there is no peak, which can be due to O–H stretching vibration. The band at 1668 cm^{-1} can be attributed to Ar–O–Ar. Dye of acetyl–arylamide appears with bands at 1595, 1548, 1522 and 1493 cm^{-1}, which shows orange or yellow. The spectra of C and D are very similar and show the same peak pattern. The spectra also clearly show the presence of carbonate, as one can infer from the bands present at 1614, 1556, 1475 and 854 cm^{-1} (C), 1617, 1559, 1475 and 864 cm^{-1} (D). One can observe the characteristic of anatase concave bands between 700 and 500 cm^{-1} on the C and D spectra.

So the IR spectrum is a perfect method to describe the chemical information of the inkpads. By this non-destructive method, different kinds of inkpads were distinguished, which was also the base of the authentication of the arts.

3.3.2. Identification by XRD

In Fig. 7, the XRD spectra of the seals are shown. A is the spectrum of the seal on the real calligraphy; B, C and D are the spectra of seals on the counterfeits. A clearly shows the presence of iron oxide (Fe_2O_3) and cinnabar (HgS). Barite ($BaSO_4$) and iron oxide (Fe_2O_3) have been detected in sample B. C confirms the presence of barite ($BaSO_4$) and cinnabar (HgS). XRD investigation of D confirms the presence of calcite ($CaCO_3$) and cinnabar (HgS).

The XRD response confirms the required structural information since those elements constitute the crystalline phases present in the inkpads. From the analysis, one can know

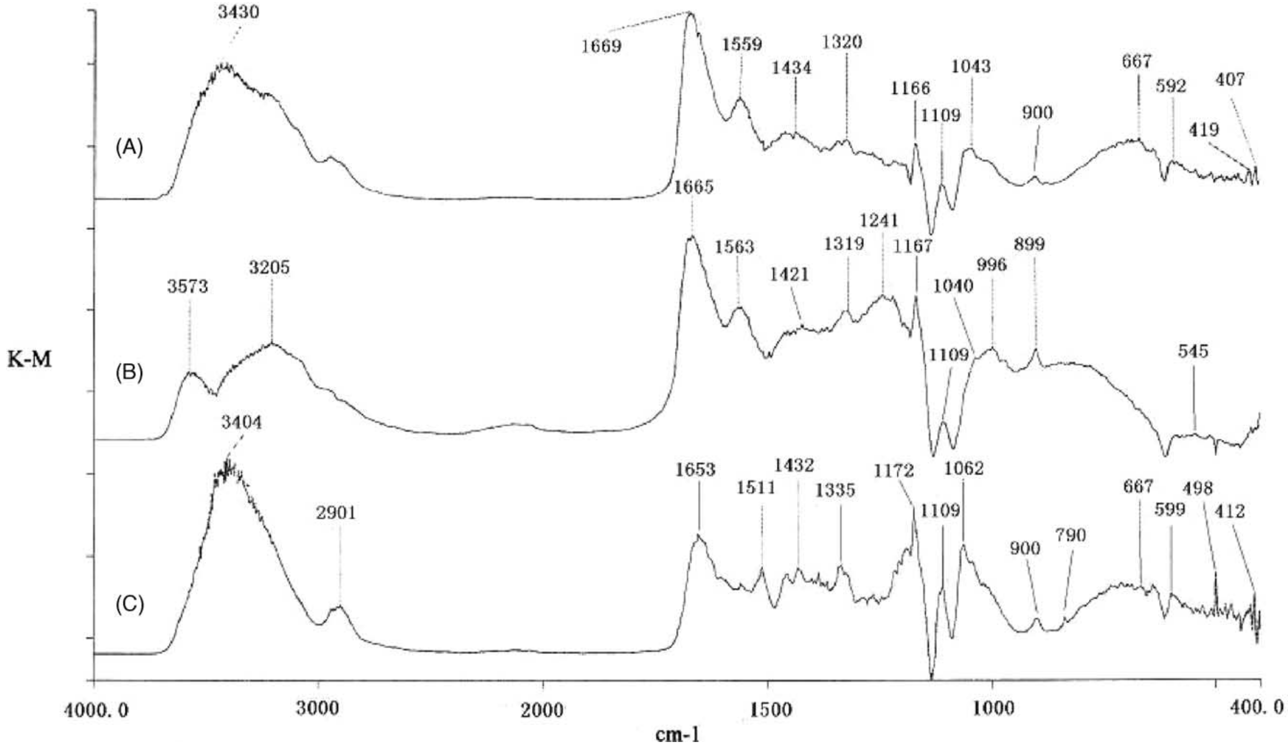

Fig. 9. The FT-IR spectra of the pigments on a piece of traditional Chinese painting. (A) green color; (B) white color; (C) pink color.

more about the knowledge of the materials used in different kinds of inkpads, which makes the authentication more credible.

3.4. Identification of three kinds of pigments on the traditional Chinese painting

IR and XRD spectral analysis was also applied to a piece of traditional Chinese painting. In order to make the non-destructive detection, only three kinds of pigments on the painting were performed. Fig. 8 shows the photograph of this piece of traditional Chinese painting.

3.4.1. Identification by FT-IR

Fig. 9 shows the IR spectra of three pigments on a piece of traditional Chinese painting of modern times. They are the spectra of green (A), white (B) and pink (C). Each of them was subtracted by the paper spectrum of themselves. The pigments contain some kinds of ketone shown by bands 1669 cm^{-1} (A), 1665 cm^{-1} (B) and 1653 cm^{-1}(C). Some kinds of nitro compounds can be concluded at 1559 and 1320 cm^{-1} (A), 1563 and 1319 cm^{-1} (B), 1511 and 1335 cm^{-1} (C). The spectra can also clearly show the presence of carbonate, as one can infer from the bands at 1434 and 900 cm^{-1} (A), 1421 and 899 cm^{-1} (B), 1432 and

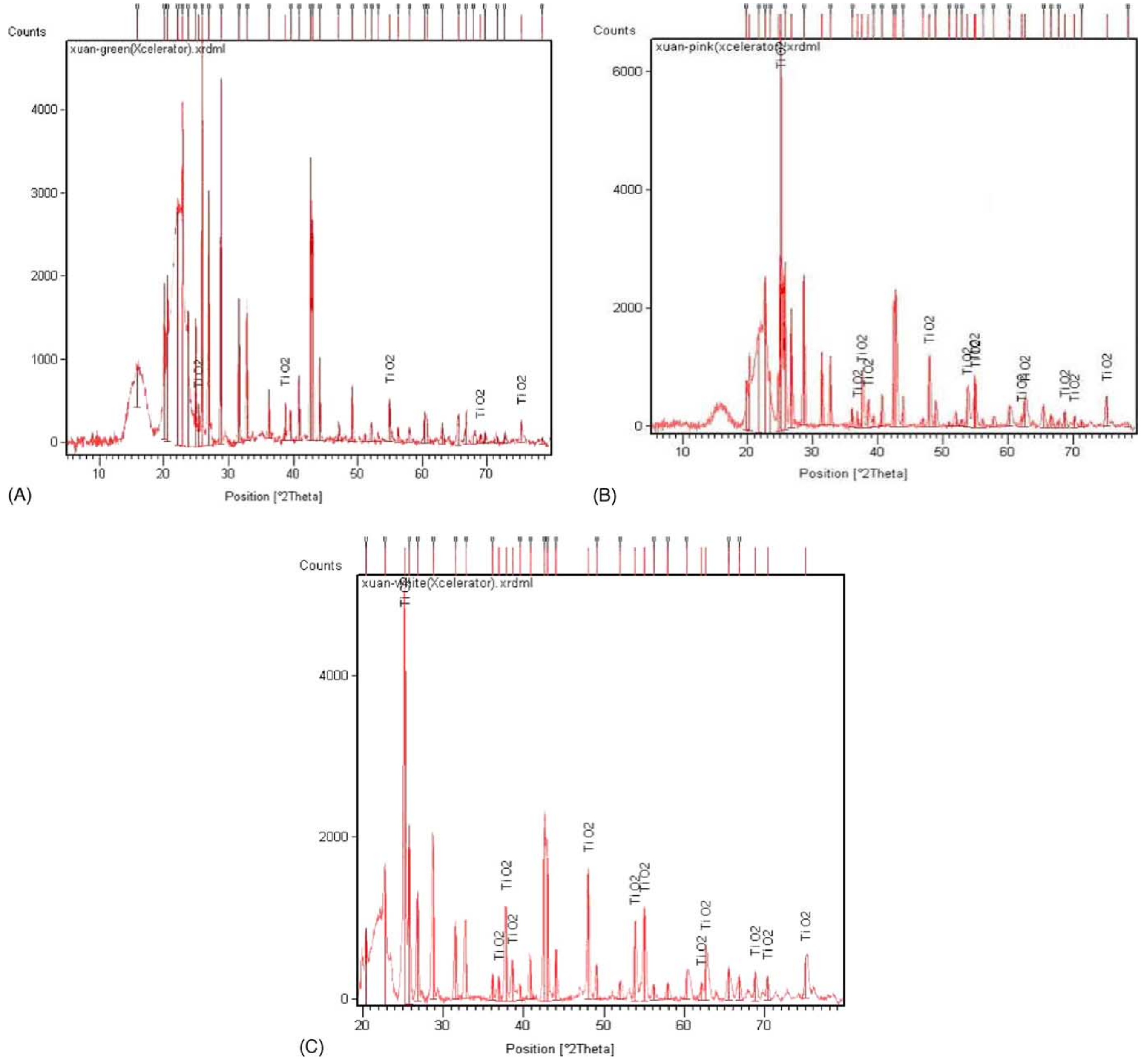

Fig. 10. XRD response of three kinds of pigments. (A) green color; (B) pink color; (C) white color (the peaks that have not been marked are the peaks of barite).

900 cm^{-1} (C). One can see the frequencies (cm^{-1}) of some kinds of sulphate by the bands at 1166 and 1043 cm^{-1} (A), 1167 and 1040 cm^{-1} (B), 1172 and 1062 cm^{-1} (C). So the presence of acid color in the pigments can be concluded. There are other kinds of inorganic compounds such as TiO_2 in the pigments judged by the concave bands between 700 and 500 cm^{-1}.

There are some differences among themselves. In the B spectrum, the bands at 1241 and 996 cm^{-1} can be attributed to P–O strength vibrations. So the presence of phosphate can be concluded. In spectrum C, the characteristic ferric oxide red bands at 2901, 900 and 790 cm^{-1} can be observed.

Through IR spectrum, one can make out the chemical information of the pigments in situ without any destruction. These can be used in the authentication of the antique paintings because the chemical components of the counterfeits cannot be completely tallied with the real ones.

3.4.2. Identification by XRD

In Fig. 10, the XRD spectra of three kinds of pigments are shown. Some kinds of inorganic material can be made out by XRD. Examining the spectra of A (green), B (pink) and C (white), the presence of barite ($BaSO_4$) and anatase (TiO_2) is detected as the basic constituent of the pigments. In the spectra, the peaks we had not marked are the peaks of barite ($BaSO_4$).

The crystallographic analysis by diffractometric method applied to each chromatic group allows a correct identification of pigments. It is more effective in the identification of paintings and wall paintings.

4. Conclusions

The techniques used for the chemical characterizations of rice paper, pigments and inkpads were satisfactory for obtaining the required results. FT-IR spectroscopy was quick and simple in identifying the organic groups of rice paper. In addition, it can be used for the identification of the anionic groups in inorganic pigments and inkpads. XRD gave the required structural information even using a small angular width, 5–80° range, and rather short measurement time. It was proved to be effectual in the identification of the different crystalline phases present in pigments and inkpads. From the information received from the test, we can authenticate the antique arts due to the material difference between modern times and antiquity. We can also distinguish contemporary art works from the counterfeit ones. This gave a contribution to the knowledge of the materials used in the arts without any destruction.

Acknowledgements

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