Application of FTIR Microscopy to Identify Some Glass Plates of Golestan Palace Photo Archive

Sahar Noohi*, Helen Asadian

Research Center for Conservation of Cultural Relic (RCCCR), Tehran, Iran

Article Info

Received: 2017/05/07;

Accepted: 2017/07/21;

Published Online 2017/10/29

Ir Cons Sci J
2017; 1(1):48-53

ABSTRACT

A great percentage of photographic documents are usually assessed through visual analysis or optical microscopic investigations. Yet, since many related analysis (e.g. dating, identification of materials, knowing ancient techniques, and conservation and restoration) could not be performed through these methods, application of analytical instruments, specially nondestructive or micro-destructive ones which could reveal detailed information, become of great concern of researchers.

The main result of the study is to prove that μ -FTIR is one of the most, rapid, and economic technique which could be explored as a routine diagnostic tool to identify the type of photographic glass plates. We identified some photographic glass plate emulsions of Golestan palace photo archive, by μ -FTIR technique; and the result approved the efficacy of the technique to study such cases.

Keywords: μ -FTIR, Collodion, Glass plate, Golestan Palace

Corresponding Information: Sahar Noohi, Research Center for Conservation of Cultural Relic (RCCCR), Tehran, Iran.

Email: Saharnoo1980@gmail.com

Copyright © 2017, Ir Cons Sci J. This is an open-access article distributed under the terms of the Creative Commons Attribution-noncommercial 4.0 International License which permits copy and redistribute the material just in noncommercial usages, provided the original work is properly cited.

1. Introduction

The nineteenth and early twentieth century glass plate photographic products, have a multi-layer structure, composed of a support (made of glass), emulsion layer containing silver particles and a binder (of albumen, collodion, or gelatin) that formed the image layer, and a varnish overcoat in some cases (Valverde, 2005: 4). Identifying the binder layer and bearing in mind the visual characteristics of each type of glass plate negatives the type of the glass plate could be identified; in consequence, most of related deterioration belong to that specific type could be predicted and controlled. Therefore, it is important to identify the composition of the emulsion layer.

Fourier transform infrared spectroscopy (FTIR) and Fourier transform infrared microscopy (μ -FTIR) techniques are most effective methods, which can be used to identify the emulsion layers that used in the glass based photographic productions. This method makes it possible to identify the emulsions used in photography with a minimal amount of sample. (Christensen, 2007: 1; Leyshon, 1984: 45; Cattaneo et al., 2008: 279; Ricci, 2007: 337).

In this regard, some examples of glass plate photographs related to different historical periods, different appearance, deterioration and damage, from the Golestan Palace photo archive, were studied in order to identify the emulsion layer by using (μ -FTIR) technique.

2. Material and Methods

FTIR Microscopy Technique

Generally FTIR is a spectroscopy based on measurement of vibration of a molecule excited by IR radiation at a specific wavelength range. An FTIR microscopy combines a light microscope with an FTIR spectrometer to provide versatility for rapid analysis and visualization of samples. FTIR microscopy has become an essential analytical tool available to scientists to study various materials due to many advantages:

1. Relatively fast and simple to use: Little or no sample preparation required for spectral acquisition.
2. Sensitive method that requires very little sample: μ g.
3. Nondestructive: The sample remains intact during analysis.

4. Universal method: The instrument and software are readily available and can be used for routine analysis.

5. Sample manipulation under magnification

- Isolate areas of interest for interrogation
- Work with very small samples, down to 10 micrometers or smaller

6. Multiple sample environments: Samples in the form of liquid, gas, powder, solid, or film can be tested.

FTIR microscopy analysis became one of the main used techniques when specific analytical topics have to be addressed, mainly when non-destructive analysis is needed.

Samples

The studied samples were three glass plates belong to Golestan Palace photo archive. All of them were related to the Qajar era.

Sample No.1, a stereoscopic type glass plate negative, with 10.5 x 4.5 centimeters dimension, and No. GP 7978 (Fig 1), which suffered from damage and deterioration such as breakage, emulsion layer detachment, yellowing at the edges of the image, mirroring and fingerprint smudges. Glass (support layer) thickness is low in it. This plate is kept in a greaseproof paper cover. Further information about the precise historical period, nature, people and places related to the image is not available. Glass cutting is probably to be carried out with machine. The emulsion color is almost black.

Samples No. 2, is a positive type of glass plate, with a length of 7.7 centimeters and maximum width of 5.1 centimeters, and no number is allocated to it, probably because of some technical difficulties; since despite a clean cutting in the left corner of the image (probably cutting to be carried out with machine), the image is incomplete and it has some deficiencies as could be seen in Fig 2. It also seems the two pictures in the sample are belonging to two different locations. Sample damage include the lack of pieces and scratches. The emulsion color is more black and white and the emulsion layer is too thin.

This glass plate has been kept as a case study sample. Further information is not available about the precise historical period, nature, people and places that were in the picture.

Sample No. 3, a negative type with 21.5 x 16.6 centimeters dimensions, and No. GP 5178 (Fig 3),

fortunately, only small part of the picture faced with briefly emulsion detachment. There is no else serious damage or degradation in this picture. Glass in comparison with other samples has relatively higher thickness. Rough glass edges and loss of emulsion in the corners of the picture could be seen. The emulsion color is milky.

In the below of printed photograph from this negative, which is available in Golestan Palace photo archive, in album No.130, page 68, is written: "Saaed aldoleh". Of course, no information is available about the type of the glass plate.

Fig. 1. Sample No. 1, (GP 7978: Belonging to the Golestan Palace photo archive): On light table

Fig 2. Sample Number 2, (Belonging to the Golestan Palace photo archive with no number): On the light table

Fig 3. Sample No. 3; (GP 5187: Belonging to the Golestan Palace photo archive); Negative on the light table (left), printed image (right)

2.1. Experimental

Working with such precious samples and thus access to the minimal amounts of samples, the μ -FTIR technique was used to analyze the emulsion of these photographic products.

For this purpose, after sampling, the samples (500 μ g) were mixed with KBr, pulverized, and formed into a disk-shaped transparent pellet.

A Nicolet 510P spectrometer is used coupled to a Nicolet Nic-Plan IR Microscope fitted with an MCT-A detector cooled by liquid nitrogen. All spectra were recorded in the frequency region 650 – 4000 cm^{-1} , in transmission mode, under a resolution of 4 cm^{-1} and 64 scans per sample.

In order to μ -FTIR test a small part of the emulsion layer was scratched by a tungsten fine-point needle, from part of the image that causes minimal damage.

3. Results and discussion

The FTIR spectrum of sample No.1 and No.2 have much in common and are essentially similar to each other (Fig 4).

These two samples showed three bands in the band area, at about 1645 cm^{-1} , 1545 cm^{-1} , and 1450 cm^{-1} (Fig 4); which could indicate the presence of a proteinaceous material, respectively assigned to the vibration of C=O bond in Amide I, C-N-H bond in Amide II, and C-H bond (Fig 5).

In addition to the three fingerprint bands of proteins, two absorption bands in the region of 2800 - 3000 cm^{-1} are related to the C-H bonds that are present in all organic compounds.

Fig 4. (a) Comparison of FTIR spectra related to sample No. 1 (Gray) and sample No.2 (Black) (b) Reference FTIR spectrum of Gelatin

Considering the protein detection in samples 1 and 2 as well as their visual characteristic, and deterioration arising out of the gelatin dry plate type, certainly could be said that the applied emulsion is not albumen but gelatin. For the sample No. 1 it can be safely considered that the Sample is a gelatin dry plate negative.

Fig 5. The vibrations responsible for the Amide I and Amide II bands in the infrared spectrum of proteins. The Amide I band is due to carbonyl stretching vibrations while the Amide II is due primarily to NH bending vibrations.

The absence of any absorption band in the range of 1700 to 1750 cm^{-1} , indicates the lack of any kind of oil or natural resin as plasticizer. This can be as gelatin emulsion layer causes more damage like flaking and detachment from the surface to be considered.

Considering the appearance of sample No. 2, it is possible that the sample be a collodion direct or an inter-positive or slide. In collodion direct, collodion is used as the emulsion (Rahimi, 1391: 711). But the emulsion used in Inter-positives can be collodion or gelatin; and be named based on the emulsion used in their structure. The same goes for slides (Michael, 2007: 31; Maurice, 1993: 59). Revealing the gelatin emulsion in the structure of sample No. 2 can be determined that the sample is an inter-positive or slide. Considering the very thin layer of emulsion, and completely transparent appearance of the sample it probably is a slide.

Standard sample of cellulose nitrate has characteristic bands at 1632 cm^{-1} , 1272 cm^{-1} , and 824 cm^{-1} ; respectively attributed to asymmetric and symmetric stretching of NO_2 , and stretching vibrations of N-O bond (Fig 6 & 7).

Taking into account the bands observed in the FTIR spectrum of sample No. 3 (Fig. 7), by the peaks at 1641 cm^{-1} , 1278 cm^{-1} and another one at 839 cm^{-1} , and its comparison with reference spectrum, it is speculated that the analyzed sample is collodion or cellulose nitrate.

The analyzed sample featured another peak at 1714 cm^{-1} , that could be attributed to a carbonyl C=O bond stretch. The presence of a carbonyl containing plasticizer, such as camphor, was ruled out according to references, as it was shown the other characteristic bands for camphor (sharp peaks at 2922 and 2852 cm^{-1}) (Cattaneo et al., 2008: 280).

Fig 6. The vibrations responsible for N-O bands in the infrared spectra of cellulose nitrate.

Fig 7. (a) FTIR spectra related to sample No. 3; (b) Reference FTIR spectrum of cellulose nitrate

Adding camphor, glycerol or castor oil to the emulsion has made the emulsion resistant against condensation and shrinkage and made it more flexible in the solid state. More over the resulting solution under these conditions was more uniform solution (McCabe, 2005: 239) Soft emulsion, no cracks and micro-cracks in it also confirms this entry.

Presence of C-H bond in all organic compounds that results in appearance of bands at 2922 cm^{-1} and 2859 cm^{-1} is seen in related spectrum of sample No. 3. Not to mention that if varnish layer is used in the glass plate structure, absorption bands in this range would be intensified; which is happened in the spectra of sample No. 3.

The FTIR test result, and appearance of the sample No. 3, certainly has allowed the attribution to a collodion as emulsion in the studied glass plate. Considering the information in the below of printed photograph from this negative which reveals that the image is belong to the year about 1286; as well as the presence of another organic material except collodion, it could be concluded that most probably the negative is a dry collodion glass plate which belongs to Naseri era (about 1870s). Since wet collodion glass plate method were used frequently during 1851 ca. to 1885 whereas, dry collodion method is used from 1850 ca. to 1930 (Hentschel, 2002: 184; Valverde, 2005: 9).

4. Conclusions

Looking deeper into the material science and the importance of identification of materials used in relics, it could be realized that using analytical instruments and techniques, in addition to historical and visual characteristic, in order to better clarify the identification of these things, is one of the needs of enterprises in the field of conservation and restoration of cultural heritage. Identification of used emulsion in three glass plates of

Golestan palace photo archive, belonging to the Qajar era, by μ -FTIR technique can be a good evidence of this claim.

This study highlights the possibility of performing μ -FTIR as a powerful, non/micro-destructive and efficient technique to identify the emulsion of photographic products. However, in cases with the possibility of using materials with the same chemical nature (such as gelatin and albumen), historical information can be very helpful for more accurate result.

This technique can also be used to investigate other photographic layers like coatings, different degradation types of photographic products, their side-products, chemical changes resulting from them and other similar items.

This first promising result open up future applications, also dealing with the other conservation issues such as mentioned above which will be considered in future.

5. Conflict of Interest

Authors declared no conflict of interest.

6. References

- Allen, E., & Triantaphillidou, S. (2010). *The Manual of Photography* (10th ed.). Oxford: Focal Press / Elsevier.
- Carretti, E., Milano, M., Luigi, D., & Baglioni, P. (2009). Noninvasive physicochemical characterization of two 19th century English ferrotypes. *Journal of Cultural Heritage, Vol, 10*, 501–508.
- Cattaneo, B., Chelazzi, D., Giorgi, R., Serena, T., Merlo, C., & Baglioni, P. (2008). Physico-chemical characterization and conservation issues of photographs dated between 1890 and 1910. *Journal of Cultural Heritage, 9*(3), 277-284.
- Christensen, M. C. (2007). *FT-IR Techniques for Studying the Composition and Degradation of Photographic Materials*. Denmark: Department of Conservation.
- Clarke, S., & Frey, F. (2003). *Care of photographs*. Amsterdam: European Commission on Preservation and Access.
- Valverde, M. F. (2005). Photographic negatives: nature and evolution of processes.
- Flowers, J. K. (2009). *19th Century Photograph Preservation a Study of Daguerreotype and Collodion Processes*. University of Oklahoma Preservation of Information Materials.
- Gilberto, A. (2010). *Scientific Methods and Cultural Heritage: An Introduction to the Application of Materials Science to Archaeometry and Conservation Science*. Oxford: University Press.
- Lavédrine, B., Gandolfo, J. P., & Monod, S. (2003). *A guide to the preventive conservation of photograph collections*. Getty Publications.
- Leyshon, W. E. (2001). Photographs from the 19th Century: a Process Identification Guide.
- McCormick-Goodhart, M. (1989). Research on collodion glass plate negatives: Coating thickness and FTIR identification of varnishes. *Topics in photographic preservation, 3*(s 139).
- Maurice, P. (1993). Ambrotypes: Positively Capturing the Past. *Material History Review Vol, 3*, 50–64.

- Mazurek, J. (2010). Antibodies and art: Characterization of albumen and gelatin on paper. *International Preservation*, 6.
- McCabe, C. (Ed.). (2005). *Coatings on photographs: materials, techniques, and conservation*. Washington, DC: American Institute for Conservation.
- Michael, R. P. (2007). *The Focal Encyclopedia of Photography Digital Imaging, Theory and Applications, History, and Science* (4th ed.). Amsterdam: Elsevier.
- Perron, J. (1989). The use of FTIR in the study of photographic materials. In *Topics in Photographic Preservation: Volume 3* (Vol. 3, pp. 112-122). Photographic Materials Group (PMG) of the American Institute for Conservation of Historic and Artistic Works (AIC).
- Ricci, C., Bloxham, S., & Kazarian, S. G. (2007). ATR-FTIR imaging of albumen photographic prints. *Journal of Cultural Heritage*, Vol, 8, 387–395.
- Stulik, D. C. (2013). *The Atlas of Analytical Signatures of Photographic Processes* (p. 16). Los Angeles: The Getty Conservation Institute.

How to Cite This Article:

Noohi S, Asadian H. Application of FTIR Microscopy to Identify Some Glass Plates of Golestan Palace Photo Archive . *Ir Cons Sci J*. 2017; 1 (1) :48-53

URL: <http://journal.richt.ir/ics/article-1-27-en.html>