ANALYTICAL IMAGING OF CULTURAL HERITAGE BY SYNCHROTRON RADIATION AND VISIBLE LIGHT- NEAR INFRARED SPECTROSCOPY

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Abstract: Imaging is an important tool for analyzing cultural heritage. Due to its delicate nature, the analysis presents numerous technical challenges, probably the most important of which is its requirement for non-destructive and non-invasive investigation. In this study, two techniques used in the analysis of cultural heritage are presented. The first one, synchrotron radiation x-ray fluorescence, is an advanced analytical technique with high accuracy and good spatial resolution. On the other hand, spectroscopic technique based on visible light-near infrared spectrum is becoming popular due to some information that it can provide, which are not available even in advanced analytical techniques. These two techniques were used to analyze real cultural heritage such as an ancient Mongolian textile, traditional Korean painting and commonly used pigments in Japanese paintings. The results revealed that using synchrotron radiation-based techniques is sometimes not enough in providing critical information (e.g. spectral reflectance, color, etc.) necessary for understanding of cultural heritage. This can be complemented using visible light-near infrared technique.

1 INTRODUCTION

Cultural heritage refers to artifacts and intangible features inherited from previous generations, which are preserved or maintained for the benefit of future generations. The cultural heritage which we inherited, show the techniques, the way of life, the social values and the way people were thinking in old days. In the past, interests in cultural heritage are mainly based on its artistic and historic values. However during the recent years, it has been attracting the attention of scientists and engineers because of the technical challenges it presents during analysis, restoration and preservation. Its delicate nature requires that the investigation should be non-destructive and non-invasive (Faubel, et al., 2007; Toque, et al., 2008).

Among the available analytical techniques, synchrotron radiation-based analysis offers high precision and high accuracy in addition to being non-destructive. Synchrotron radiation (SR) is emitted in the tangential direction when electrons and positrons are accelerated at relativistic speed subjected to a magnetic field (Margaritondo, 1988). The energy of SR covers a broad spectrum. X-ray fluorescence analysis using synchrotron radiation is a powerful technique in terms of detecting ultra trace elements and studying them in detail. Its unique features include local area analysis by using micro beam; capability of doing measurement in air or water; non-contact and non-destructive assay; rapid measurements; and precise assay of trace elements (Ide-Ektessabi, 2007). However, even though SR-based techniques are powerful, there are information they cannot provide, such as spectral reflectance, color information and others. These are important in analyzing cultural heritage.

To compensate for some inadequacies of SR-based techniques, imaging at the visible light-near infrared (VL-NI) spectrum is employed. The basic idea is to use polychromatic images (with RGB tristimulus values) or multispectral images to extract spectroscopic data. It has been reported that materials emit specific spectral features within a

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certain range (Balas, et al., 2003). In other wavelength range, this is more pronounced. However, at the VL-NI range the interaction is more complex. Nonetheless, there are some unique features that are only observable within this range. This makes it valuable in cultural heritage analysis.

2 EXPERIMENT

2.1 Imaging and Spectroscopic Synchrotron Radiation Analysis

Synchrotron radiation X-ray fluorescence (SRXRF) was performed on a 13th century Mongolian textile and dislodged fragments collected from an old Korean painting. Measurements were done at beam line 4A of Photon Factory. The electron beam energy in the storage ring was 2.5 GeV, with a maximum current of 400 mA. Incident X-ray energy was 15 keV. The cross-section of the beam was approximately 1(v) x 1(h) mm^2 on the sample. The synchrotron radiation was monochromated by a multilayered reflecting mirror. Precise beam size of monochromated X-rays was adjusted using slits. The incident and transmitted X-rays were monitored by ionization chambers that were set in front of and behind the sample. The fluorescent X-rays were collected by a solid-state detector at 90 degrees to the incident beam. Measurements were performed in air. Point spectra were measured for obtaining consistent elements of the samples. The spectra were obtained by using a multi-channel analyzer. The measurement time was 100 seconds for each spectrum. XRF imaging technique was applied in order to investigate the distributions of main elements. X-Y step pulse motors moved the sample stage. The measurement areas were divided into matrices of 20 x 20 pixels. At each pixel, the XRF yields for each element were integrated by single channel analyzers. The measurement time was three seconds for each pixel.

Synchrotron radiation was also used to investigate the relationship between fine structural change and color fading in natural mineral, specifically azurite and malachite. Heating of natural pigments is well practiced among traditional Japanese painters to modify the shade and color of the pigments. It is of great interest to understand the factors involved in this process. Ten samples of each pigment were heated at 260°C with holding time from 10 minutes up to 90 minutes at 10-minute increments. The spectral reflectance of the heated and unheated pigments was measured to track the changes in color. X-ray fluorescence and X-ray absorption fine structure (XAFS) were used to characterize the pigments. The incident X-ray was 15 keV for XRF analysis while the energy was scanned at the Cu K absorption edge from 8.90 to 9.09 keV for XAFS.

2.2 Imaging at the Visible-Near Infrared Range

In order to use VL-NIS for the analytical imaging of cultural heritage, a technique for image analysis was developed. Figure 1 illustrates the basic scheme of the analysis. It begins by capturing an image of the object to capture spectral and color information. The picture can be an RGB or a multispectral image. An RGB image refers to an image captured using tristimulus values corresponding to red, green and blue colors. A multispectral image, on the other hand, is an image captured by using 6-7 bands of color and infrared filters. The images are captured within a certain wavelength band. The color information is then used to simulate the geometrical and light flux conditions. The simulation enables the estimation of the spectral reflectance, which is used for comparison with a database to provide useful information about the image. The database includes more than 1000 mineral pigments and is continuously being updated. The database also includes additional data such as SRXRF spectra, XRD spectra as well as information about the artwork's history.

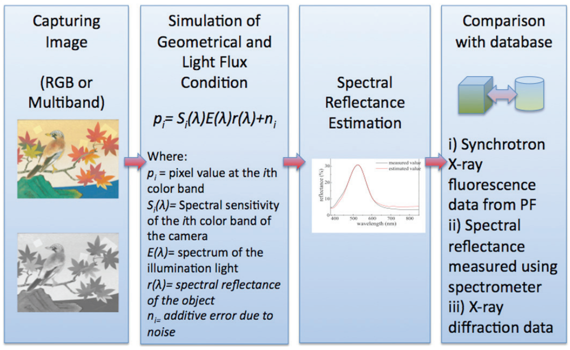

Figure 1: Image analysis scheme using VL-NIS.

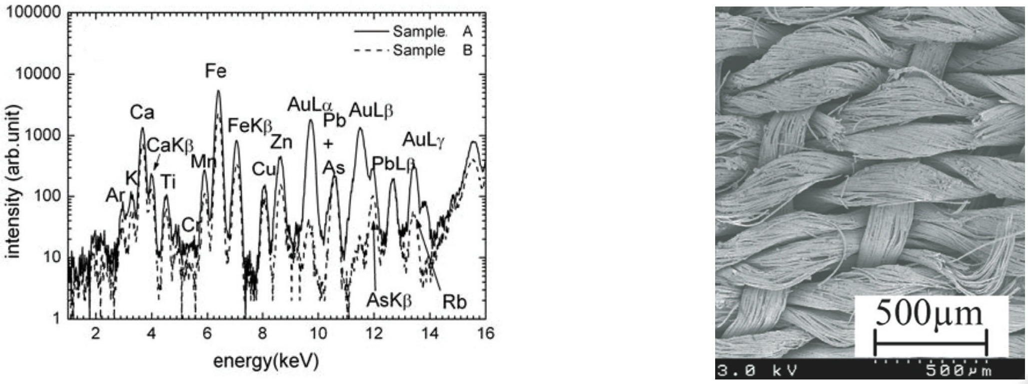

Figure 2: (a) SRXRF spectra of an ancient Mongolian textile. Sample A refers to the gold thread while Sample B refers to the textile; (b) Field-emission SEM showing textile structure.

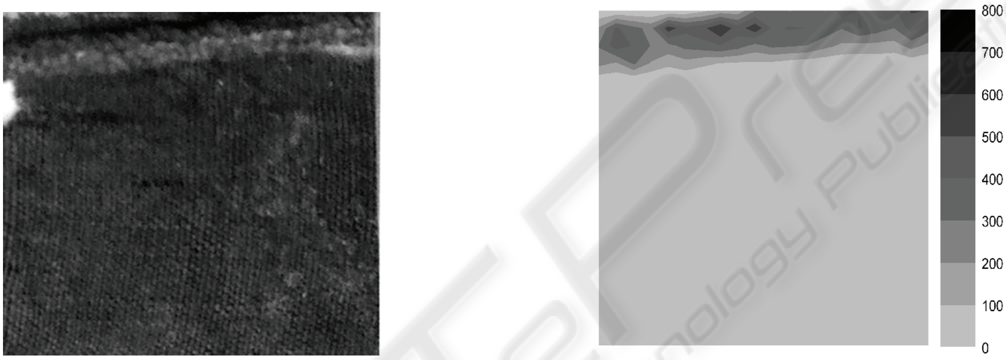

Figure 3: (a) Optical image of an ancient Mongolian textile laced with gold thread; (b) Elemental distribution image of gold derived from the SRXRF spectra.

3 RESULTS AND DISCUSSION

3.1 Synchrotron Radiation of Actual Cultural Heritage

3.1.1 Ancient Mongolian Textile

SRXRF was used to detect the constituent elements used for the manufacturing of the ancient textile as well as obtaining elemental distribution images. Figure 2a shows the XRF spectra of the Mongolian textile. The spectra revealed the presence of significant amount of gold and iron. The textile was dated to be about 700-800 years old. It is believed that the textile was produced during the 13th century at the height of power of the Mongolian empire under Genghis Khan and Kublai Khan. This may explain why gold was detected from the XRF spectra. Lacing and decorating the textile with gold was a symbol of wealth and prosperity in the old days. The spectra also show traces of Cu and Ti. These elements are well-known metallic mordant and are believe to be widely used during that period. Fig. 2b shows a field-emission SEM image of the Mongolian textile sample. It depicts textile structure and weaving condition. In addition, Figure 3a shows an optical image of a textile laced with gold thread. An elemental image distribution of gold (Figure 3b) is derived from the XRF spectra.

3.1.2 Old Korean Painting

SRXRF was used to investigate a traditional Korean painting. Figure 4 shows the spectra of several natural pigments used (white, blue, green and red). The main elements detected were Pb, Cu, Hg and Fe. It is interesting to note that the spectra of the blue and green pigments are very similar to popular pigments used in traditional Japanese painting known as *gunjo* (azurite) and *ryokusho* (malachite). These pigments are copper-based pigments [$2CuCO_3 \bullet Cu(OH)_2$ and $CuCO_3 \bullet Cu(OH)$ respectively]. The difference lies with the significant trace of Pb found in the Korean painting. It is

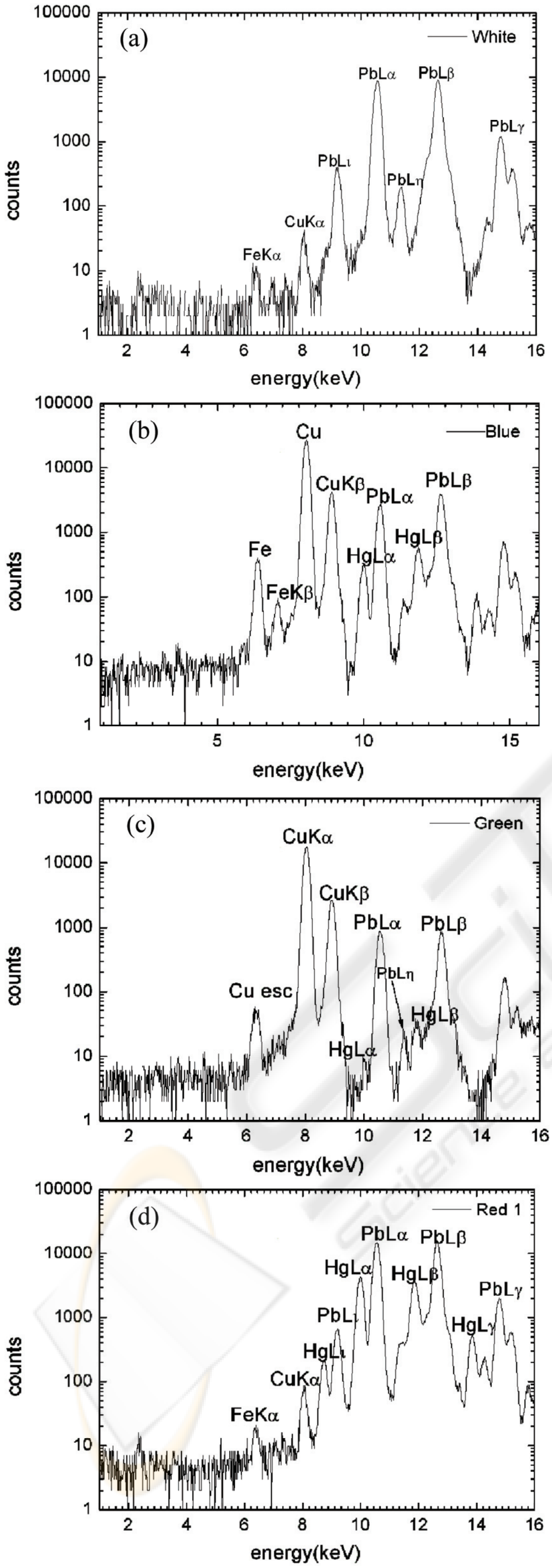

Figure 4: SRXRF of different pigments used in a traditional Korean painting. Note: (a) white pigment; (b) blue pigment; (c) green pigment; (d) red pigment.

Figure 5: Optical images of the pigments used on a traditional Korean painting: (a) white pigment; (b) blue pigment; (c) green pigment; (d) red pigment.

attributed to the white pigment used in the painting. It is believed that the white pigment was used as a base medium. This may explain why all the pigments studied contain significant traces of Pb. Figure 5 shows the optical images of the pigments used on the Korean painting investigated. It also shows that the pigments used are granulated.

3.1.3 Effect of Heating on Pigment Discoloration

Figure 6 shows the spectral reflectance of azurite and malachite pigments as a function of heating time. These two pigments were selected as test samples because they are the most commonly used blue and green pigments in traditional Japanese paintings. The pigments predictably changed its color upon heating. It is interesting to note however that the discoloration did not change the position of the spectral peak. This implies that the color wavelength did not change, only the luminosity (Toque, et al., 2008). The samples got darker with the increase in heating time. In addition, abrupt change in color was observed between 40-60 minutes of exposure to elevated temperature.

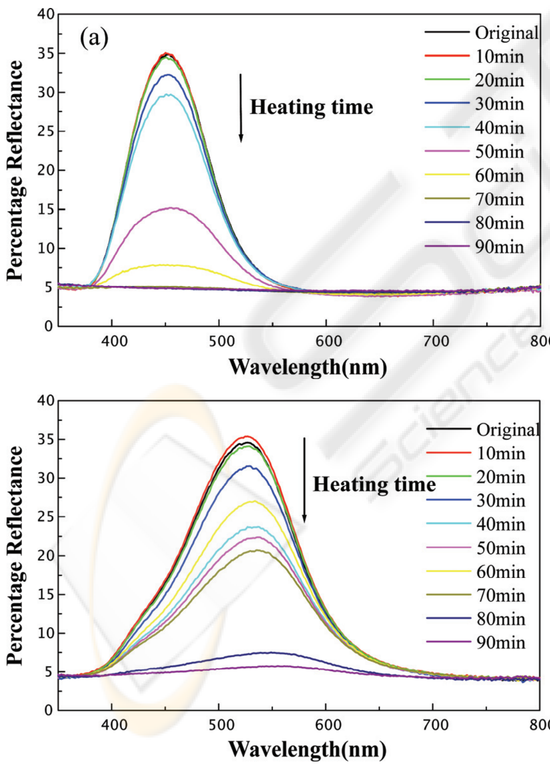

Figure 6: Spectral reflectance of (a) azurite and (b) malachite as a function of heating time. Prolonged exposure to elevated temperature lowers the reflectance of the pigments.

In order to understand the mechanism of discoloration of the pigments when subjected to elevated temperature, they were subjected to synchrotron XRF and XAFS analysis. Figure 7 shows the XRF spectra of azurite and malachite. It shows minimal change in the spectra. This implies that the color change was not due to the trace elements of the pigments. The trace elements of both the pigments are similar but their colors are quite different. The spectral reflectance of azurite leans toward the short-wavelength range giving it a shade of blue while malachite is around the mid-wavelength range giving at a shade of green.

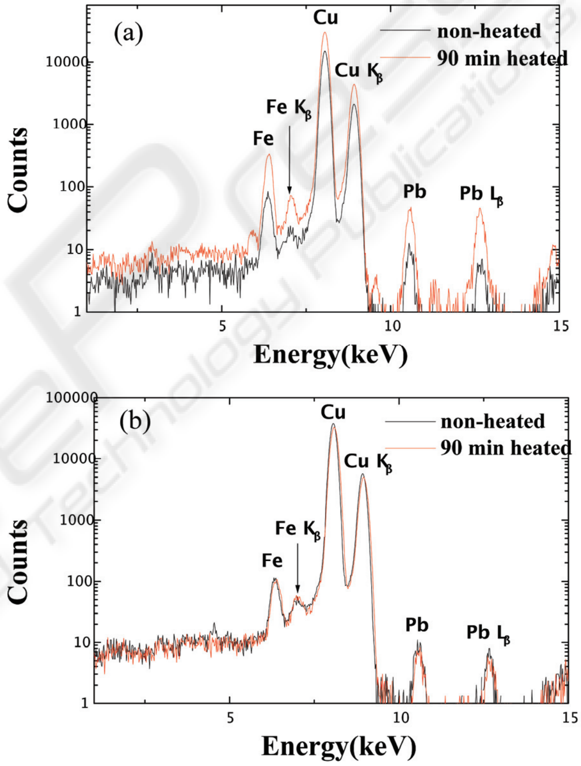

Figure 7: XRF spectra of the heated and non-heated: (a) azurite and (b) malachite. Both the pigments have similar spectra. In addition, minimal change is observable between the burnt and unburned pigments.

The changes in color of both the pigments may be more attributed to the change in chemical bonding state of the main element Cu. Figure 8 shows the XAFS spectra of the pigments. It was found that the absorption edge of the samples heated for 80 and 90 minutes shifted to lower energy level. This may also explain the abrupt change in color as the pigments were heated for a long time.

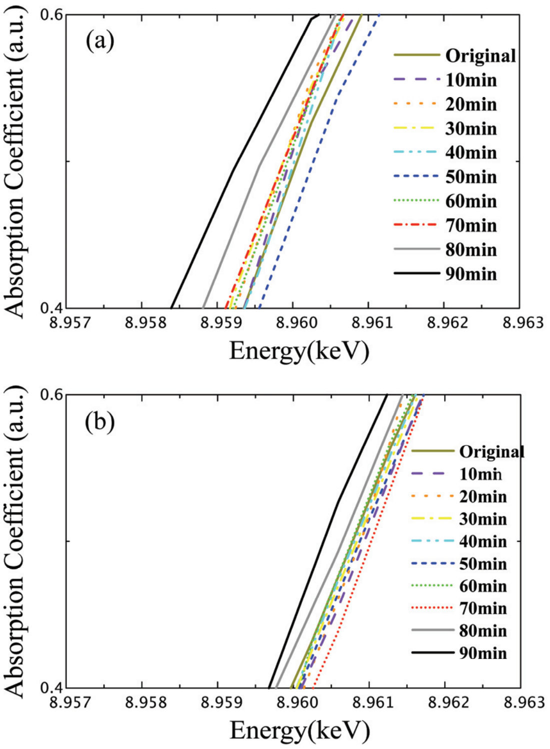

Figure 8: Position of Cu K absorption edge of heat-discolored (a) azurite and (b) malachite. Unlike the XRF spectra, XAFS provide more insights about the discoloration of the pigments.

3.2 Visible Light-Near Infrared Spectroscopy of Cultural Heritage

Visible light- near infrared spectroscopy (VL-NIS) gives information about an image, which can provide better understanding of the mechanism of degradation and useful insights for the restoration and preservation of cultural heritage. Some information about a material can be extracted by analyzing the interaction between matter and light at the visible to near infrared radiation spectrum, which are not noticeable in other range.

The analysis covers the electromagnetic radiation wavelength from 380-850 nm. This range includes the visible to near infrared range. IR is included since recent investigations have shown that unique spectral characteristics are observable, especially from 650-800nm wavelengths. Figure 9 shows the spectral characteristics of different azurite pigments. They are grouped into natural and artificial mineral pigments. It is noticeable that all the pigments have similar peak positions around 430-480 nm, which gives them bluish hue. However, starting from about 650 nm, the percentage reflectance of the artificial pigments starts to increase drastically while the natural pigments did not show significant change. These spectral signatures may be used to identify the nature of the pigments used in an artwork.

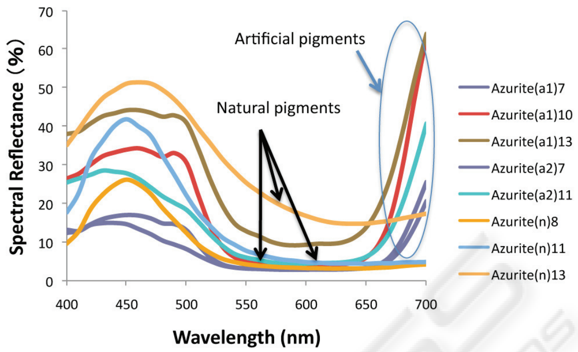

Figure 9: Spectral reflectance of natural and artificial azurite mineral pigments. The alphanumeric symbol enclosed in parentheses indicates whether the pigment is natural or artificial while the other indicates relative particle size: the higher the number, the smaller the particle size.

3.3 Analysis of Cultural Heritage

The analysis of cultural heritage presents several technical challenges. First, its delicate nature requires non-destructive and non-invasive analysis. The techniques presented in this paper satisfy the requirement. However, there are some issues that cannot be fully covered by a single technique. For example, SRXRF method offers high accuracy and precision but it can only give information about the chemical composition of the pigments used in the artwork. When it is used in the study of discoloration of heated pigments, it cannot give sufficient information. VL-NIS can give more information in this case; the changes in color due to heating can be tracked by the changes in spectral reflectance. XAFS can also provide insight on the discoloration by analyzing the chemical state of copper absorption edge. However, neither SRXRF nor XAFS can distinguish between the differences in pigment size. It was observed that pigment particle size affects the hue. Small pigments have lighter hue than large pigments even though they have the same chemical composition. This is illustrated by Figure 10 and confirmed by the SRXRF spectra given by Figure 11.

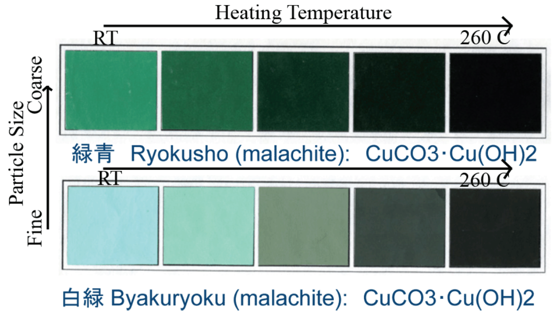

Figure 10: Pigment hues as a function of relative particle size and heating temperature.

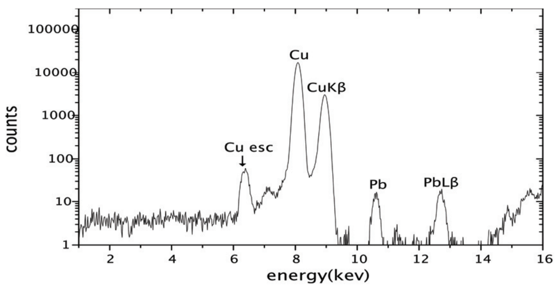

Figure 11: Corresponding SRXRF spectra.

Another concern that poses technical challenge on the analysis of cultural heritage is the preparation of sample. In advance analytical techniques such as synchrotron radiation, the size of the sample is quite small. In order to satisfy this, preparing a small fraction of the sample is necessary. In this regard, this can be considered destructive. In most cases, this is unacceptable since a cultural heritage is irreplaceable. On the other hand, VL-NIS can address this concern. The size of the sample is basically irrelevant. In VL-NIS, the major concern is the accuracy. It is worth mentioning that the limitation in sample size in X-ray techniques can be addressed by using portable devices, such as portable XRF. This is widely practice in analyzing artworks. However, its accuracy is inferior compared with large-scale X-ray devices. Therefore, in the analysis of cultural heritage, the techniques presented should be used in conjunction with one another and not independently. This ensures that the information extracted from the images can be maximized.

4 CONCLUSIONS

Analysis of cultural heritage using analytical imaging is a burgeoning field. This is attributed to the numerous technical challenges it presents (i.e. non-destructive and non-invasive). In this study, synchrotron radiation and visible light-near infrared techniques were used to analyze real cultural heritage. It is considered that detailed analysis of such historic objects (in this case, an ancient Mongolian textile and old Korean painting) is of prime importance. In addition, the mechanism of color discoloration as a result of heating was investigated. Synchrotron radiation analysis revealed that it was due to the change in chemical bonding state. VI-NI analysis also revealed some results. It was shown that the change in chemical bonding state results in increase or decrease in magnitude of the spectral reflectance but does not affect the position of the peaks. Having a clearer understanding of pigment degradation can help in cultural heritage preservation and restoration efforts. The results have also shown that no single technique is capable of providing all the necessary analytical information. The available techniques should be used to complement one another. It was also shown in this study that analysis using visible light- near infrared radiation could be an indispensable tool for investigating cultural heritage. This is due to some unique spectral features of materials that are only observable in this range. Since VL-NIS does not require complex instrumentation, robust and flexible systems are achievable.

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