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Chapter 9: Multi-instrumental Analysis of Pigments and Dyes

Abstract: This chapter presents the results of various instrumental analyses applied to study the wide range of different colourants found in the *tsakali*. These are paints based on mineral pigments, dyes derived from plants or mixtures of both. The results of the multispectral data prepared by Ivan Shevchuk and Kyle Ann Huskin (see Chapter 4) served as a starting point for further non-invasive analysis using XRF scanning, Raman spectroscopy, FTIR spectroscopy and FORS. Measurements taken from six different *tsakali* are compared to each other, aiming at the identification of their colourants.

1 Introduction

As mentioned above, the *tsakali* contain a wide range of different colourants, such as paints based on mineral pigments, dyes derived from plants or mixtures of both. The uniqueness of the area of Tibet and Central Asia originates from the extreme climatic conditions and range of altitudes in the region, characterised by both the highest Himalayan ranges, with their deep valleys, and the deserted regions of Central Asia. It is probably why, besides the common materials composing these books, some local materials are also found. These rarer local materials are good references for further comparative studies.

The multi-instrumental analysis of the colourants was conducted after the MSI investigation described in Chapter 4. This was useful not only because it provided us with good-quality digital images of the *tsakali* to document the analysis, but also because the post-processing analysis already hinted at features of interest, such as different colourants used for red backgrounds. We focused our analysis on six cards (0, 1, 3, 25, A and D), which appear representative of the different colours (yellow, red, blue, green, orange, gold, black, white and pink) observed. To be able to analyse and identify both organic dyes and inorganic pigments, we used a combination of four non-destructive and non-invasive techniques: X-ray fluo-

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rescence (XRF) scanning, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and fibre optic reflectance spectroscopy (FORS).[1]

2 Methods

2.1 X-ray fluorescence scanning

X-ray fluorescence (XRF) spectroscopy has become one of the most commonly used analytical techniques for non-destructive material analysis of cultural artefacts, including miniatures on manuscripts, usually in combination with other non-invasive techniques.[2] There is now a wide range of XRF devices available, ranging from handheld portable spectrometers for quick on-site analysis to bulkier but more precise scanning devices, some of which are transportable. Since the *tsakali* were brought to our laboratory, we were able to use a large scanning device without the effort of transporting it. The analysis was performed using an M6 Jetstream (Bruker Nano GmbH) large-area µ-XRF scanner. This device has an adjustable measuring spot ranging from 50 to 650 µm and is equipped with a low-power Rh X-ray tube, polycapillary X-ray focussing optics, a 50 mm^2 Xflash SDD detector and two microscopes for positioning. Since scanning is conducted in air atmosphere, only elements heavier than magnesium (Mg) can be securely identified. All the measurements were performed at 50 kV and 600 µA, with a spot size of 50 µm, an acquisition time of 15 ms / pixel and a pixel (step) size of 150 µm. The concentration of an element within the volume sampled is related to the counts detected for that element, making the method suitable for quantitative analysis in theory (at least for bulk materials, with the use of correcting algorithms and standards).[3] However, a number of other factors, such as the fluorescence yield (different for each element) and matrix effects (absorbance and fluorescence of the matrix in the X-ray region of the electromagnetic spectrum), also affect the counts detected. Furthermore, the nature of the objects to be analysed, such as the unknown thickness of the inks and colourants applied to the heterogeneous paper support, makes straightforward analysis difficult, so that in practice, only semi-

1 The complete dataset is available in Bosch et al. 2025.

2 See, for example, Moura et al. 2007; Deneckere et al. 2011; Aceto et al. 2012; Guerra et al. 2013; Mosca et al. 2016; Ricciardi et al. 2016; Bosch and Janke 2021; Brocchieri et al. 2021; Biolcati et al. 2023; Koochakzaei, Mobasher Maghsoud and Jelodarian Bidgoli 2023; Jembrih-Simbürger et al. 2024.

3 Mantler et al. 2006.

quantitative results (e.g. comparing element intensities in different areas of the paper) can be achieved.

2.2 Raman spectroscopy

Raman spectroscopy is widely used in archaeometry, in particular for the non-destructive identification of pigments.[4] As with XRF devices, mobile Raman spectrometers allow on-site analysis, but at the expense of larger spot sizes and lower spectral resolution. Since the *tsakali* were brought to our laboratory, we were able to use a more powerful benchtop instrument. The analysis was performed with a Renishaw inVia spectrometer, fit with optic fibres to be able to accommodate larger objects. All the measurements were performed using a long focal 100× magnifying lens, allowing for the investigation of small details (spot size of about 10 μm diameter), and with the following parameters: integration time of 1 to 5 s, 10 to 50 scans, 2 to 6.3 per cent laser power (< 3 mW), 785 nm (near infrared) and 532 nm (green) lasers.[5]

2.3 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is another popular technique in the field of cultural heritage, and is usually used to complement Raman spectroscopy when analysing colourants. FTIR spectroscopy employs several modes for analysing different types of samples and objects. In the field of non-destructive and non-invasive analysis, either external reflectance (ER) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used depending on the nature of the object. While the DRIFTS mode is particularly suitable for larger object areas (in the centimetre range) and rough surfaces such as paper,[6] the ER mode enables the analysis of very small (in the millimetre range), non-rough surface structures and provides a non-destructive way for the characterisation of both the

4 See, for example, Burgio, Ciomartan and Clark 1997; Clark 1999; Bicchieri, Nardone and Sodo 2000; Deneckere et al. 2011; Aceto et al. 2012; Guerra et al. 2013; Mosca et al. 2016; Marucci et al. 2018; Biolcati et al. 2023; Koochakzaei, Mobasher Maghsoud and Jelodarian Bidgoli 2023.

5 The main shortcoming of this technique is the competition of the Raman scattering with fluorescence when enough energy is provided to the molecule analysed for electronic transitions to occur. As fluorescence can sometimes mask the Raman signal completely, it is important to try to minimise it. Using a different laser is one of the main strategies to achieve that.

6 See Chapter 8.

writing supports and the inks and colourants used.[7] However, the spectra acquired with the ER mode are often affected by distortions that sometimes lead to inverted peaks and peak shifts when compared to spectra acquired with other modes. This can complicate the interpretation of the results. The device we used to investigate the colourants of the *tsakali* is the compact Alpha II (Bruker Optics GmbH) FTIR spectrometer, which was placed perpendicularly to the object with slight contact to the surface. The spectrometer is equipped with an ER module and an integrated video camera for the positioning of the exact measuring spot. This setup allows for the rapid investigation of the object with an interaction spot size of 4 mm. The spectrometer is further equipped with a thermoelectrically cooled DLaTGS (Deuterated Lanthanum α Alanine doped TriGlycine Sulphate) detector allowing for measurements in a spectral range of 4000 to 400 cm^{-1} and a spectral resolution of 2 cm^{-1}. A gold reference cap was used for background calibration, and sixteen scans were collected per measurement.

2.4 Fibre optic reflectance spectroscopy

Fibre optic reflectance spectroscopy (FORS) is another common technique for the non-destructive identification of pigments and dyes, as it is very easy to use and devices are usually very compact and easily portable. This, however, comes at the expense of lower accuracy and spatial resolution. Therefore, the method is mostly employed as a rapid tool for preliminary analysis.[8] The device we used to investigate the colourants of the *tsakali* is the compact Labspec 4 HR (Malvern Panalytical) equipped with an integrated halogen light source. The spectrometer is coupled with one VNIR detector and two thermoelectrically cooled short-wavelength (SWIR) detectors with an InGaAs photodiode. The interaction spot dimension is *c.* 2 mm. The reflectance spectra were collected in the spectral range 350 to 2500 nm with a spectral resolution of 3 and 6 nm at 700 and 1400/2100 nm, respectively; a sample count of 50; and a scanning time of 34 to 136 ms. The raw reflectance spectra were further transformed into first derivative spectra in order to extract inflection points.[9]

7 Nodari and Ricciardi 2019.

8 Aceto et al. 2012; Aceto et al. 2014; Pronti et al. 2018; Brocchieri et al. 2021; Koochakzaei, Mobasher Maghsoud and Jelodarian Bidgoli 2023; Jembrih-Simbürger et al. 2024.

9 Aceto et al. 2014.

3 Results

This section summarises the results of the study of the colour palette of the *tsakali* based on the evaluation of the multi-instrumental analysis with non-destructive XRF scanning, FORS, Raman and FTIR spectroscopy. The analysis was carried out on six cards (Tsakalis 0, 1, 3, 25, A and D) and led to similar results in the identification of the colourants and inks for all the cards examined. Table 1 summarises the results and shows the broad palette of different materials used to create these cards.

Table 1: Summary of the materials identified used in the *tsakali* from the Zhangzhung Nyengyü collection.

Colour	XRF	Raman	FTIR	FORS	Assignment
red	Hg, S, Zn	cinnabar	-	cinnabar	cinnabar
orange	As, S	orpiment, cinnabar, pararealgar (Tsakali 3)	-	-	orpiment (mixed with cinnabar)
yellow	As, S	orpiment	-	orpiment	orpiment
green	Cu, Fe, Mn	malachite, azurite, indigo, orpiment, carbon	malachite, azurite, indigo	malachite azurite, indigo	malachite or indigo/azurite + orpiment (mixed with carbon)
blue	Fe, As	indigo, carbon	indigo	indigo	indigo (dark blue mixed with carbon)
pink	Fe, As, Zn	-	-	-	-
gold	Au, Zn	carbon, orpiment	-	-	gold (on top of other colourants)
white	-	-	kaolinite	-	kaolinite
black	-	carbon	-	-	carbon
black ink (Tsakalis 25 and A)	-	aniline	-	-	aniline

The final assignment of all the applied pigments, dyes and inks used was only possible by combining the above-mentioned techniques. In a first step, the cards were subjected to XRF scanning that enables the analysis of large areas, which ultimately provides a representative characterisation of the heterogeneous objects and minimises errors due to material inhomogeneity. The evaluated data is

presented in the form of element maps that display the elemental distribution across the surface of the cards with high spatial resolution. Fig. 1 shows the results of Tsakali D, which already allow for the assignment of some colourants, such as real gold (Au) used to paint the jewellery, crowns and other highlights, and cinnabar (mercury sulphide (HgS) with zinc (Zn) as an impurity) used for the red areas. Other materials used cannot be clearly determined due to the limitations of the XRF method. Since no light elements such as carbon can be detected with the applied XRF instrument, the method does not allow for the determination of organic dyes or inks. Furthermore, the detection of certain elements can indicate a variety of different materials or their mixture.

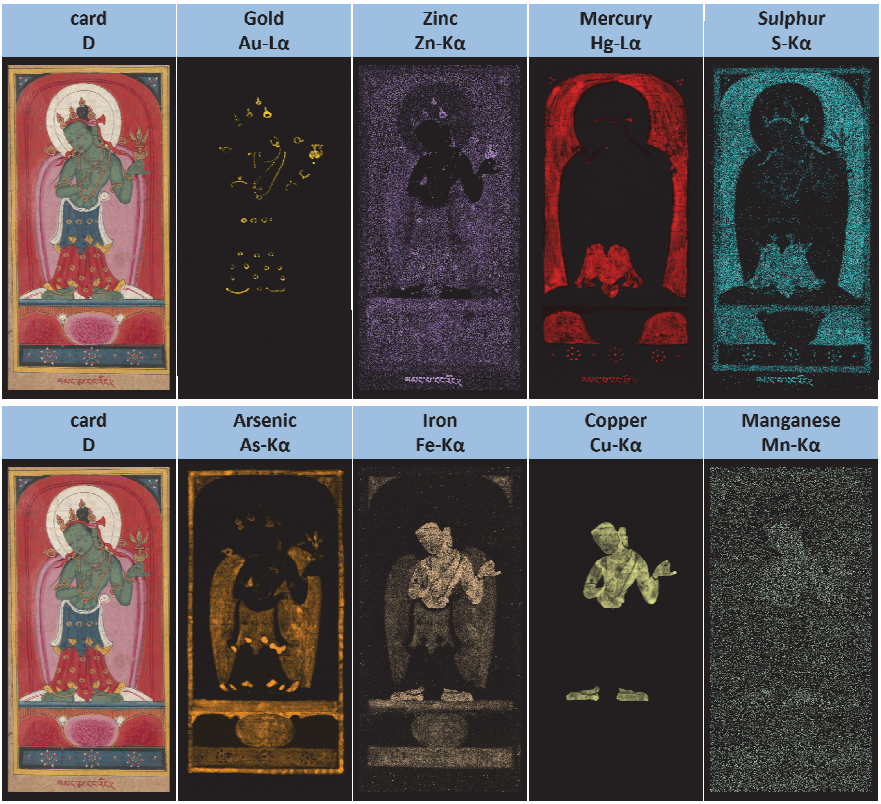
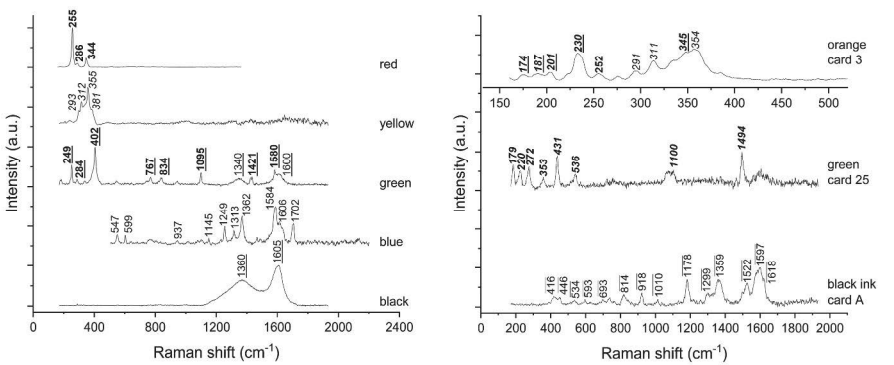


Fig. 1: XRF element maps for Tsakali D showing the distribution of the detected elements.

The XRF results can be further specified with the aid of Raman spectroscopy. This method allows the unambiguous determination of many inorganic pigments, organic dyes and black inks based on characteristic signals in the Raman spectra. Based on the XRF results, it was possible to select certain locations that required further spectroscopic measurements. The Raman results are summarised for Tsakali D in Fig. 2a. The other cards showed identical results; however, in some areas we found additional materials, which are presented in Fig. 2b. For the red areas, the Raman measurements clearly identified cinnabar and thus confirm the XRF results. Orpiment was evidenced for the yellow and orange areas. These results are also consistent with the XRF results, as here mainly arsenic (As) and sulphur (S) were detected. Some pararealgar, mixed with orpiment and cinnabar, was also found at an orange spot on Tsakali 3. In the case of the green areas, the Raman measurements detected a variety of colourants. A rich variety of hues were obtained by mixing blue indigo and azurite, yellow orpiment and green malachite with carbon. The identification of azurite and malachite is consistent with the XRF results, which show a high content of copper (Cu) in these areas. Indigo and carbon could not be evidenced by XRF, as the detection of light elements is limited. The Raman results were further verified by FTIR measurements (Fig. 3), which confirmed malachite, azurite and indigo in the green areas. Indigo was also detected in the blue areas. Carbon black was found in several spots, mixed with other pigments and dyes in order to obtain darker hues.



Figs 2a–b: Raman spectra obtained for spots of different colours, after baseline subtraction, with the observed main peak positions marked. (a) From Tsakali D; (b) other pigments and dyes not detected on Tsakali D, but identified on other cards. Normal: indigo; underlined: carbon black; bold underlined: azurite; bold italic: malachite; italic: orpiment; bold: cinnabar; bold italic underlined: pararealgar; overlined: black dye (closest match aniline).

On two of the cards investigated, Tsakalis 25 and A, there is a line written in black ink below the image. For both cards, the Raman spectra obtained for this ink do not match the expected carbon or iron-gall inks. Instead, the spectrum fits closely with that of aniline black, a synthetic pigment that was mainly used between the end of the nineteenth century and the 1930s.[10] Since such ink was not available at the alleged time of making of the *tsakali*, these lines must be a later addition, possibly related to their use in rituals.

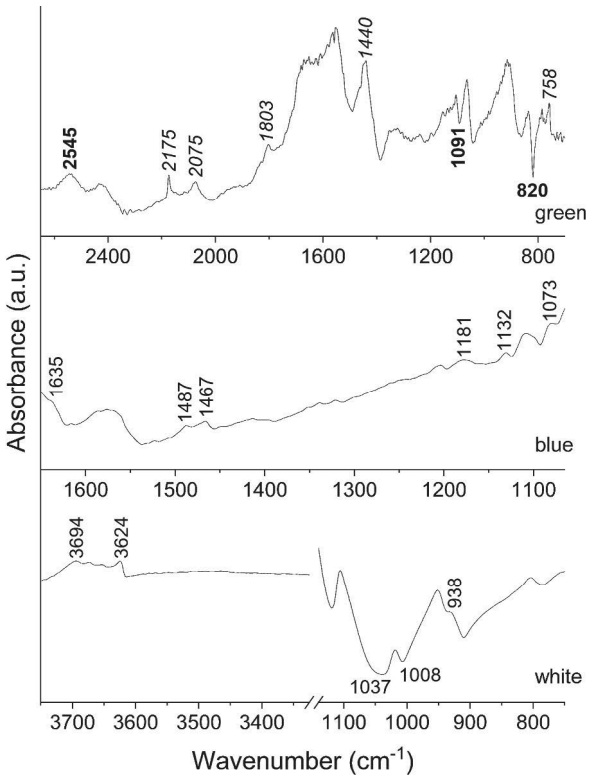


Fig. 3: FTIR spectra obtained for spots of different colours from Tsakali D, with the observed main peak positions marked. Top, bold: malachite; top, italic: azurite; middle: indigo; bottom: kaolinite.

10 Travis 1994.

For the white and pink areas, unfortunately the Raman signal was completely masked by fluorescence, even when using a laser with lower energy (785 nm), a well-known issue of this technique.[11] This again shows the importance of multi-instrumental analyses, as the white pigment kaolinite could only be detected with FTIR (Fig. 3). Only the pink pigment could not be identified despite extensive analyses. Interestingly, the XRF scans of both the pink and blue areas show the elements arsenic (As) and iron (Fe). As already mentioned in Chapter 7, it has been determined that these areas were painted with a mixture of indigo and a previously undiscovered pigment, designated as the Tibet phase.[12]

4 Conclusion

This chapter demonstrates the power of multi-instrumental analysis using non-invasive equipment for the identification of a wide range of artists' materials. The pigments and dyes used for the production of the *tsakali* are consistent with the supposed date of their production (fifteenth century). Furthermore, the palette is very similar to that identified by Jessica Brocchieri, Laurence Viguerie, Carlo Sabbarese and Marion Boyer for Buddhist thangka paintings, with the exception of minium and calcite, which we did not detect in the *tsakali*.[13] Interesting findings of this study are, on the one hand, the detection of real gold, which was used as a very precious material for some highlights on the cards, as well as the use of quite a modern black ink, which was most certainly added at a later phase. Finally, the results are consistent with those in Chapter 7 and served as the basis for an in-depth study to investigate a previously unidentified pigment.[14]

11 Edwards, Vandenabeele and Colomban 2023, 23–24.
12 Haas et al. forthcoming.
13 Brocchieri et al. 2021.
14 Haas et al. forthcoming.