Materials characterization

Into the deep blue: Identification of natural and synthetic indigo pigments and dyes using the Thermo Scientific RaptIR+ FTIR Microscope with NIR capability

Authors

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Industry/application

Art restoration and archeology, materials characterization

Products used

Thermo Scientific Nicolet RaptIR+ Fourier Transform Infrared (FTIR) Microscope

Goals

Demonstrate the advantages of an NIR detector to analyze samples without any preparation. (It is not possible to obtain the same results with mid-IR analysis.) Provide a non-destructive analytical workflow for heritage textiles, identifying dyes directly on silk fibers, and differentiating natural and synthetic indigo pigments.

Key analytes

Indigo pigments (reference powders and dyed silk), silk fibroin

Key benefits

- No sample preparation required to achieve best results
- Increased cost benefits due to elimination of sample preparation
- Improved capability to identify and classify unknown pigments directly on the substrate
- Multicomponent analysis for complex mixtures

Abstract

The identification of pigments and dyes in historical and contemporary textiles is essential for advancing conservation science, as these materials often hold cultural, economic, and technological significance. The study described herein demonstrates the analytical capabilities of the Thermo Scientific™ Nicolet™ RaptIR™+ FTIR Microscope, equipped with an extended near-infrared (NIR) spectral range and Thermo Scientific™ OMNIC™ Specta™ multicomponent software for the non-destructive analysis of natural and synthetic pigments and dyes, with a particular focus on indigo.

Analyses were carried out both on pigment powders and on indigo applied directly to silk fibers. The NIR range proved especially valuable for differentiating chemically similar materials and for separating pigment signatures from the fibroin matrix. The results highlight the advantages of using NIR micro-FTIR to analyze heritage textiles, and they demonstrate the technique's broad applicability for characterizing natural and synthetic colorants.

Introduction

Historical background on coloring materials

Since antiquity, humans have sought colored materials to decorate pottery, textiles, cave walls, and even themselves. Pigments and dyes, derived from diverse sources like minerals, insects, roots, lichens, berries, and plants, played central roles not only in artistic production but also as markers of social, economic, religious, and political identity.

Natural dyes were particularly versatile; they could be used for textile dyeing, for preparing inks and cosmetics, or for medicinal or ritual formulations. Although technological knowledge was limited, ancient artisans achieved remarkable sophistication in extraction, mordanting, and application techniques. Mordants such as alum and alkaline substances were commonly employed to enhance color fixation and modify hues.

Among natural colorants, indigo stands out as one of the most ancient and widely used blue dyes, with evidence of indigo-dyed textiles dating back over 6,000 years at Huaca Prieta (Peru). Indigo remains essential today, especially in the textile industry.

For millennia, only a limited palette of dyes was available. A major transformation occurred during the industrial revolution: In 1856 William Henry Perkin synthesized mauveine, the first fully synthetic dye, rapidly triggering the replacement of natural dyes across Europe between 1870 and 1880. It is now commonplace to find man-made dyes like Prussian blue, aniline red, and of course, synthetic indigo.

Analytical challenges in dye identification

Textiles dyed in antiquity often lack clear documentation regarding how they were made. Dyes may also degrade over time, particularly under light exposure, forming products that complicate analytical interpretation. The wide structural diversity of natural dyes, the many possibilities of mixtures, and the contributions of substrate fibers themselves further increase complexity.

Non-invasive and micro-invasive analytical techniques such as UV–Vis–NIR reflectance, fluorescence analysis, and Raman spectroscopy are commonly used but have limitations, particularly in distinguishing mixtures and degraded components. Chromatographic approaches offer a high level of accuracy but require sampling, which is often not permitted on materials that might be delicate or rare.

FTIR spectroscopy has been extensively applied to heritage science, yet traditional mid-IR analysis may require sample preparation and often suffers from band congestion. The integration of near-infrared (NIR) detection with micro-FTIR microscopy opens new opportunities, offering deeper penetration, minimal preparation, and improved discrimination among structurally similar compounds.

Indigo: A natural dye and pigment

Indigo is unique in being both a dye and a pigment: Although organic and plant-derived, it is insoluble in water and deposits directly onto fibers without the need for mordants. Traditionally extracted from various members of the flowering plant species Indigofera, indigo contains indigotin as its primary chromophore. This is accompanied by indirubin, isoindigo, and various inorganic and organic minor components.

In its solid state, indigo appears as a deep blue powder. It is soluble in polar aprotic solvents (e.g., DMSO, DMF), pyridine, sulfuric acid, and nitrobenzene.

For this study, three types of indigo pigments available on the market from European pigment supplier Kremer Pigmente were examined (see Figure 1).

Figure 1. From left to right: 36000 - Natural indigo powder; 360003 - Indigo made of woad; and 360005 - Indigo pale blue employed for dying the silk cocoon.

The pigments employed were Kremer products #36000 - Natural indigo powder (derived from Indigofera tinctoria); #360003 - Indigo made of woad (derived from Isatis tinctoria); and #360005 Indigo pale blue (synthetic pigment precipitated with aluminum hydroxide). The first two were commonly used in the past for painting and particularly textiles; the last is mainly employed in modern industrial applications.

Each type of indigo was applied to silk fibers, enabling evaluation of pigment–matrix interactions. Silk was selected because it is one of the most precious textiles, historically used to create dresses and tapestries for many centuries.

Materials and methods

Instrumentation

Analyses were conducted using the Thermo Scientific™ Nicolet™ RaptIR™+ FTIR Microscope (Figure 2) operating in reflectance, attenuated total reflectance (ATR), and transmittance modes. Key features include:

- Extended NIR spectral range (12,500–4,000 cm^{-1})
- High-NA objectives for precise micro-sampling
- Spatially resolved mapping for heterogeneous samples
- Compatibility with classical glass slides, which do not absorb in the NIR range
- Direct, non-destructive analysis on textile fibers without sampling

Figure 2. Thermo Scientific Nicolet RaptIR+ FTIR Microscope.

Sample types

Two sample categories were examined:

- **Powdered pigments**, used to obtain reference spectral signatures (Figure 3). Specifically, 36000 - Natural indigo powder (derived from Indigofera tinctoria), 360003 - Indigo made of woad (derived from Isatis tinctoria), and 360005 Indigo pale blue (synthetic pigment precipitated with aluminum hydroxide) were purchased from Kremer Pigmente company (Germany).
- **Pigments applied to silk**, allowing evaluation of mixture spectra and matrix effects. Different methodologies are available to fix pigments to textiles; some are quite complex and may also compromise the integrity of the fibers. In this case, a combination of calcium hydroxide and fructose was used to create a reducing water bath to fix the pigment (see Kremer Pigmente Dyeing with Indigo; https://www.kremer-pigmente.com/en/information/recipes/dyeing-with-indigo-36000/). Among others benefits, this recipe is simple, sustainable, and can be made individually.

This approach enabled direct comparison between pure pigment spectra and pigment–fiber composites.

Spectral processing with OMNIC Specta multicomponent software

The OMNIC Specta multicomponent software was used for several purposes:

- Deconvolution of overlapping spectral contributions
- Identification of pigments, fibers, and minor components
- Statistical discrimination of chemically similar materials
- Automated matching against extended IR and NIR reference libraries

This workflow enabled clear attribution of signals to indigo, silk fibroin, and accessory compounds.

Results and discussion

Advantages of the NIR region for dye and pigment analysis

Compared to the mid-IR region, the NIR region offers multiple advantages:

- **Reduced spectral congestion**, as overtone and combination bands are more widely spaced
- **Greater penetration depth**, enabling analysis of layered or embedded pigments
- **Less interference from the silk substrate**, improving pigment detectability
- **Enhanced discrimination** among natural vs. synthetic indigo variants

These advantages are particularly relevant for heritage textiles, where sampling is restricted and dye layers are thin.
Figure 3 shows the FTIR signal of the analyzed indigo in the mid-IR range (4000-400cm$_{-1}$). The three indigo samples clearly show different and peculiar spectral habits. Despite this, when the pigment is fixed on silk, the intense absorption of the fiber covered almost all the indigo signal, and only minor differences are detectable as peak shoulders or shifts (Figure 4).

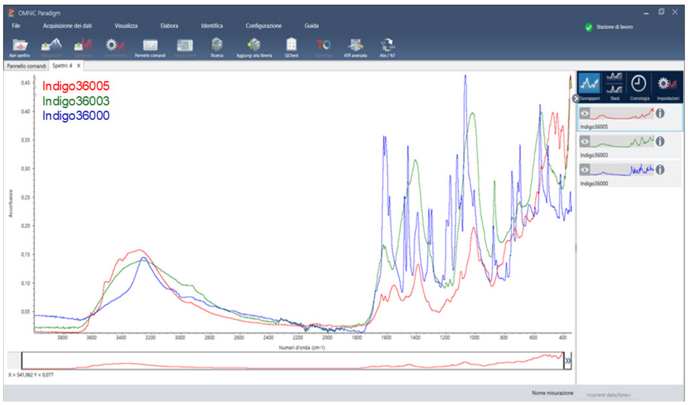

Figure 3. FTIR spectra acquired in the mid-IR region of Indigo 36000 (blue), Indigo 36003 (green), and Indigo 36005 (red).

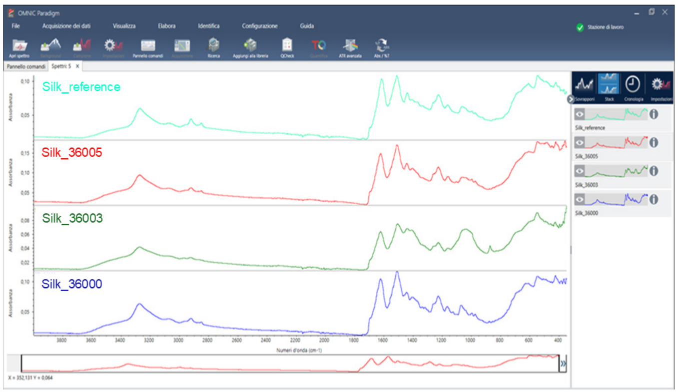

Figure 4. FTIR spectra of silk and dyed silk with the different indigos in the mid-IR range, most of the dye signals are covered by the strong absorption of silk.

Looking at the pure indigo dyes in the NIR region (Figure 5), it is possible to clearly distinguish them thanks to their overtone and combination bands.

Figure 5. FTIR spectra in the NIR range of the three indigo reference materials: 36000, 36003, 36005.

Indigo and silk: Spectral behavior

NIR spectra of the three indigo types on silk showed the following:

- Distinct overtone patterns associated with the different forms of indigotin and its derivatives
- Clear contributions from fibroin (the structural protein of silk), which OMNIC Specta software successfully separated from pigment signatures
- Subtle but diagnostically important differences between natural and synthetic indigo
- A unique spectral profile for Saxon blue, reflecting chemical alterations induced by sulfuric acid treatment

These distinctions were more detectable in the NIR region than in the mid-IR region, where bands overlap and strong fibroin absorptions limit interpretability. Figures 6, 7, and 8 display the spectra collected for the dyed silks in the NIR range.

With respect to the mid-IR-range, the NIR range, thanks to multicomponent analysis and minor bands, can identify matches with the dyes that may have been used. Moreover, the combination with the microscope allows, even on a small fiber, direct work in transmission mode without compromising the sample's integrity.

Application to broader pigment sets

Although indigo was the focus of this study, the workflow is broadly applicable. Because NIR spectra are highly sensitive to molecular structure, the RaptIR+ spectrometer can distinguish subtle differences:

- Mineral pigments with closely related crystal structures
- Organic pigments with overlapping MIR signatures
- Mixture systems where matrix and pigment contributions must be separated

This positions NIR micro-FTIR spectroscopy as an essential tool for both heritage science and modern materials research.

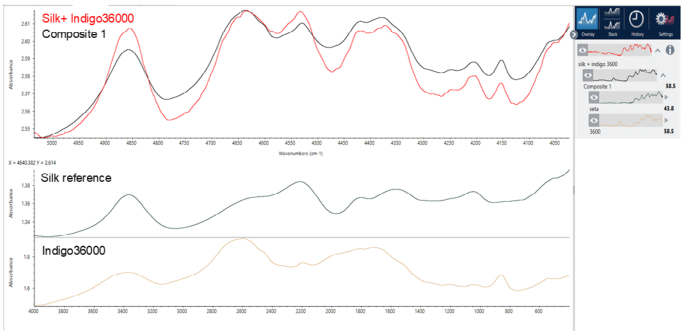

Figure 6. Multicomponent analysis of the silk dyed with Indigo 36000 in comparison with the reference materials (silk and Indigo 36000).

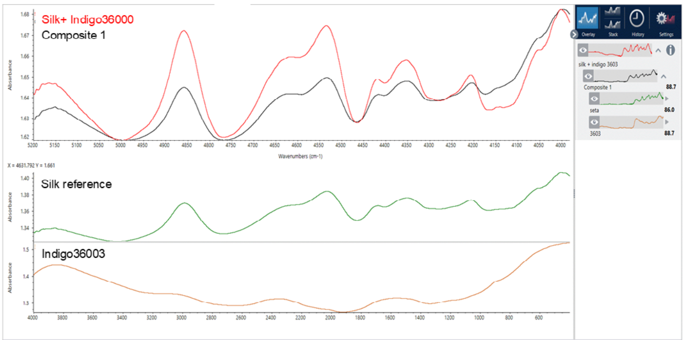

Figure 7. Multicomponent analysis of the silk dyed with Indigo 36003 in comparison with the reference materials (silk and Indigo 36003).

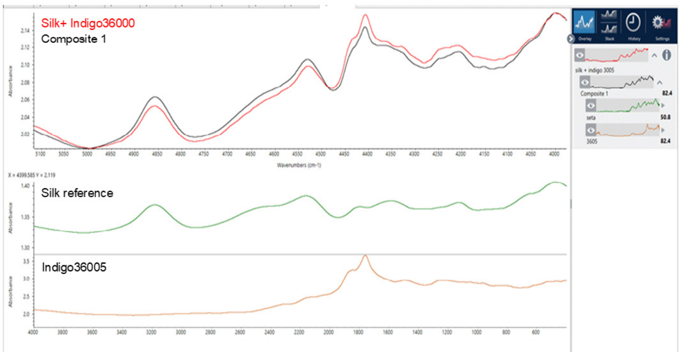

Figure 8. Multicomponent analysis of the silk dyed with Indigo 36005 in comparison with the reference materials (silk and Indigo 36005).

Conclusions

This work demonstrates the power of combining NIR spectroscopy with micro-FTIR microscopy using the Thermo Scientific Nicolet RaptIR+ system for the identification of dyes and pigments, particularly in delicate historical textiles. Key findings include:

- **Superior diagnostic capability of the NIR region** for both organic and inorganic colorants
- **Accurate, simultaneous identification of pigment and matrix** through Specta multicomponent software
- **Non-destructive, preparation-free analysis** directly on silk fibers
- **Clear differentiation among natural, synthetic, and semi-synthetic indigo varieties**
- **Broad applicability to diverse pigment systems**, extending beyond the case study presented here

Together, these results highlight the RaptIR+ FTIR Microscope as a versatile, advanced analytical solution for researchers, conservators, and material scientists working with complex, multicomponent systems.

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