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Review

Research progress in cultural relic material analysis based on portable hyperspectral instrument

Cong Wang[1,2], **Mara Camaiti**[3], **Daiyun Liu**[4], **Fude Tie**[2,5], **Yijian Cao**[5,6*]

[1] China-Central Asia Belt and Road Joint Laboratory on Human and Environment Research, Northwest University, Xi'an 710127, China
[2] Key Laboratory of Cultural Heritage Conservation and Research, Ministry of Education, Northwest University, Xi'an 710127, China
[3] CNR-Institute of Geosciences and Earth Resources, Florence 50121, Italy
[4] Shaanxi Academy of Archaeology, Xi'an 710043, China
[5] Key Laboratory of Archaeological Exploration and Cultural Heritage Conservation Technology, Ministry of Education, Northwestern Polytechnical University, Xi'an 710072, China
[6] NPU Institute of Culture and Heritage, Northwestern Polytechnical University, Xi'an 710072, China
*** Corresponding author:** Yijian Cao, yijian.cao@unwpu.edu.cn

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Abstract: Cultural relics carry splendid civilizations, inherit historical culture, and are precious heritage of all mankind. Due to the preciousness of cultural relics, which are non-renewable, and the basic principle of cultural relic protection with minimal intervention, non-destructive analysis technology has always been the most important technical means of material analysis in the research of cultural relic production technology, deterioration mechanism, and protection and restoration. Therefore, the research and development and application of new non-destructive analysis technology is an important research direction for the protection and utilization of cultural relics. In recent years, portable hyperspectral spectrometers originated from the field of remote sensing have shown great application potential in the analysis of cultural relic materials, and have been successfully applied in the restoration of cultural relics such as stone ancient buildings and paintings. As a non-invasive spectral technology that does not require sampling, the portable hyperspectral instrument can obtain a full-band, high-resolution reflectance spectrum covering the visible light-near infrared-shortwave infrared band (350–2500 nm) in a very short time. At the same time, it is highly portable and has no special requirements for the working environment, light source, etc. It can be used in situ at the site of field cultural relics or ruins. In addition, while collecting spectral data, remote sensing technology can also be used to achieve remote transmission and analysis of data. The above technical characteristics give it unique application advantages in the analysis of cultural relics materials. Based on the basic principles of spectral technology, this paper first introduces the equipment models and performance indicators of portable ground feature hyperspectral instruments commonly used in the analysis of cultural relics materials. Secondly, it carefully sorts out its application status in the qualitative and quantitative analysis of organic/inorganic cultural relics materials, analysis of cultural relics protection materials, and in-situ and real-time monitoring of cultural relics restoration in the past decade. After that, it discusses in depth the two key issues that affect the application effect of this technology, namely the specification of spectral preprocessing and the establishment of a standard spectral library. Finally, it looks forward to the development trend of this technology, and it is expected to have broad prospects in the analysis of fragile organic cultural relics, the combined application of multiple analysis techniques and quantitative analysis research.

Keywords: ground feature hyperspectral instrument; cultural relics; material analysis; nondestructive analysis

1. Introduction

Cultural heritage has extremely high historical, artistic and scientific value. It is a physical witness of the brilliant civilization of mankind and a valuable and non-renewable cultural resource. In order to understand the production process and preservation status of cultural relics, or to explore their deterioration mechanism and put forward scientific protection and restoration suggestions, it is an important prerequisite to clarify the cultural relics themselves and their deteriorated materials. Due to the precious value of cultural relics themselves and the special environment in which most immovable cultural relics are located, the development of non-destructive analysis technology that is easy to operate, fast to test, and can be applied in situ on the cultural relics or ruins has always been one of the important contents of cultural relic material analysis research [1].

In recent years, with the cross-integration of multidisciplinary theories and methods in the field of cultural relics and archaeology, portable field-portable hyperspectral radiometers (field-portable hyperspectral radiometers), which are commonly used in remote sensing geophysical exploration for the detection of surface vegetation, soil, minerals, hydrology, etc., have also been studied for the characterization of cultural relics of different materials [2–4], and have achieved good application results. Hyperspectral technology is a combination of remote sensing technology and spectral technology [5], mainly including non-imaging portable field-portable spectrometers and imaging spectrometers.

Portable hyperspectral instruments can obtain a continuous narrow-band reflectance spectrum covering the visible light-near infrared-short-wave infrared bands in a very short time (~0.1 s). It can not only be used to distinguish the surface color of cultural relics materials, but also provide strong support for the non-destructive identification of the chemical composition of organic and inorganic materials. Usually, portable hyperspectral instruments are small in size, light in weight, and come with rechargeable batteries, which are convenient to use in the field environment; at the same time, they are simple to operate and have fast testing speed. When used for cultural relic analysis, there is no need to take samples (non-invasive), and the surface materials of cultural relics can be analyzed directly using its probe (with built-in light source or natural light), and the entire analysis process does not damage the cultural relics. In 2010, Camaiti et al. first used the hyperspectral instrument to analyze the surface materials of ancient stone buildings [6], and innovatively developed a non-destructive, in-situ analysis technology for cultural relics. At present, the application scope of hyperspectral instruments in the analysis of cultural relics is constantly expanding, and it has been proven to be a convenient, safe and efficient non-destructive analysis technology.

This paper explains the basic principles of using portable ground hyperspectral instruments for cultural relic material analysis, introduces the main equipment models and their performance indicators, summarizes its current application status in cultural relic body material analysis, cultural relic protection material analysis, and in-situ and real-time monitoring of cultural relic restoration, and looks forward to the future development trend of this technology field.

2. Working principle and performance advantages of portable ground hyperspectral instrument

2.1. Working principle

The portable hyperspectral instrument combines remote sensing technology with spectroscopy technology. When used for material analysis, it is mainly realized through spectroscopy. Spectroscopy technology studies the generation of spectra of various substances and their interactions with substances. It identifies the chemical composition and relative content of substances by measuring the wavelength and intensity of emission, absorption or scattered radiation generated by specific energy level transitions of atoms or molecules inside the substance.

When the radiation wavelength used in spectroscopy is in the ultraviolet-far infrared (0.1–100 μm) range, the molecular effects produced by its interaction with matter are electronic transitions and vibration excitations [7,8]. This is the theoretical basis for the use of ultraviolet-visible spectroscopy and infrared spectroscopy for material identification. When the radiation wavelength is in the ultraviolet-visible region (0.2–1.0 μm), the electronic energy levels of the chemical bonds within the molecule will transition from the ground state to the excited state. When the radiation wavelength is in the infrared region (1.0–1000 μm), it interacts with matter to change the dipole moment of the molecule, which manifests as vibration excitation or absorption, laying the foundation for identifying molecular functional groups. For a molecule containing N atoms, a linear molecule has 3N-5 normal vibration modes (or fundamental frequency vibrations), while a nonlinear molecule has 3N-6 vibration modes [9]. At the same time, other vibrations may also occur, such as multiples of the fundamental vibration mode (overtone vibration) or the synthesis of different vibration modes (combined frequency vibration). The fundamental vibration mainly appears in the mid-infrared region (2.5–25 μm), while the overtone and combined frequency vibrations mainly appear in the short-wave infrared region (1.0–2.5 μm). Although the intensity of the characteristic peaks generated by the overtone and combined frequency vibrations is significantly weaker than that of the fundamental frequency peak, the analysis of the characteristic peaks can simultaneously achieve rapid identification of a large number of inorganic and organic materials [10].

The full-band portable ground feature hyperspectral instrument can obtain continuous, high-quality spectral data in the range of 0.35 to 2.5 μm in a short time. Its working band is complete, covering the visible light, near infrared and short-wave infrared regions, and the output spectral data types are diverse, including spectral reflectance, spectral transmittance, spectral absorption, spectral radiation and spectral irradiance [6]. The curve shape of the spectrum in the visible light band provides effective information for distinguishing the color of materials, while the characteristic peaks of the near-infrared and short-wave infrared band spectra reflect the molecular lattice vibration information (fundamental frequency, harmonic frequency and sum frequency vibration), providing a basis for the analysis and identification of complex organic and inorganic materials and their mixtures.

2.2. Performance parameters and their advantages

At present, the commercial products of portable ground hyperspectral instruments are relatively mature. Instruments of brands such as ASD of the United States, Spectral Evolution of the United States, and Avantes of the Netherlands have been successfully applied in the analysis of cultural relics. Among them, the ASD brand FieldSpec® series equipment (**Figure 1**) was the first to be applied and involved in the most types of cultural relics. Using natural light or its own contact reflection probe, this series of equipment can collect a continuous reflection spectrum covering the visible light-near infrared (VNIR: 350–1000 nm) and shortwave infrared (SWIR: 1001–2500 nm) bands within 0.1 s, with the spectral bandwidths of the two bands being 1.4 and 1.1 nm, respectively. The instrument sampling unit consists of three independent detectors: VNIR (350–1000 nm), SWIR1 (1001–1800 nm), and SWIR2 (1801–2500 nm). In the VNIR band, the spectral resolution (half-maximum width of a single ray) is about 3 nm, while in the SWIR region the spectral resolution is about 6–10 nm. The main performance parameters of the latest generation of FieldSpec® 4 equipment are shown in **Table 1**. When used in the field, this series of equipment can be carried by a single person, using a contact reflection probe to directly collect spectra, free from the influence of environmental weather, light, etc.

Figure 1. The ASD FieldSpec® portable ground hyperspectral instrument (model FR Pro 3).

Table 1. Performance parameters of ASD FieldSpec® 4 portable ground hyperspectral instrument.

	VNIR	SWIR
Spectral range	350–1000 nm	1001–2500 nm
Spectral resolution	3 nm @ 700 nm	6–10 @ 1400/2100 nm*
Spectral sampling (bandwidth)	1.4 nm	1.1 nm
Sampling frequency	10 spectra·s^{-1}	
Wavelength reproducibility	0.1 nm	
Wavelength accuracy	0.5 nm	
Field of view	25°	
Weight	5.44 kg	

Note: * There are 3 types of spectrometers in the ASD Field Spec® 4. The performance difference between them is that the SWIR band resolution is 6, 8, and 10 nm, respectively.

In the field of non-destructive analysis of cultural relics materials, compared with portable ground hyperspectral instruments, the hyperspectral imaging technology introduced by Goetz et al. in the 1980s was used earlier and more widely [11–15].

Hyperspectral imaging technology can capture hundreds of images and their spectral data in a continuous narrow band, but it cannot work when the surface of the cultural relic is small, highly heterogeneous, and located in a closed space [2]. Portable ground hyperspectral instruments have the advantages of high portability, small probe size, and high spectral resolution, and their application range is wider than that of hyperspectral imaging technology.

Compared with other commonly used spectral technologies, such as fiber optic reflectance spectroscopy (FORS), short-wave infrared spectrometer, multispectral imaging technology and infrared spectroscopy technology, portable ground object hyperspectral instrument also shows certain performance advantages or characteristics. FORS technology and ground object hyperspectral instrument belong to the same reflectance spectroscopy technology and have similar working principles. Existing commercial miniature FORS spectrometers can be customized for different application scenarios by adjusting the basic components. The operating software can also be customized. They are comprehensive in functions, small in size (the whole device weighs 3.5 kg), and easy to operate [16]. Compared with portable ground hyperspectral instruments, they are superior in size; however, their wavelength response range usually does not exceed 200 to 1100 nm, and the lack of short-wave infrared bands restricts their application scope. Miniature portable short-wave infrared spectrometers are also used in the analysis of cultural relics materials [17,18]. The spectrometer is smaller in size (60 g) and is highly portable. It can be used directly by connecting to a computer via a USB interface. However, its spectral response range does not include the visible light-near infrared band (only 1200–2200 nm), so it cannot be used for accurate analysis of the color of cultural relics, and its spectral resolution is slightly poor (~10 nm). Compared with multispectral imaging technology, the spectral bandwidth obtained by portable hyperspectral instrument is narrow and continuous [2,19]. Compared with infrared spectroscopy technology, portable hyperspectral instrument does not require sampling and sample preparation, and compared with the application wavelength in the mid-infrared region (2.5–25 μm), its working range in visible light-near infrared-short-wave infrared enables it to directly use natural light as a light source, which is particularly suitable for non-destructive analysis of light- and heat-sensitive cultural relics. In addition, while collecting spectral data, remote transmission and analysis of data can be achieved by using remote sensing technology in the same spectral band (0.38–3.0 μm) [20], which is unmatched by traditional spectral technology. The above performance advantages lay the foundation for the successful application of portable ground hyperspectral instrument in the analysis of cultural relics materials.

3. Application of portable ground hyperspectral instrument in the analysis of cultural relics

3.1. Analysis of cultural relics materials

3.1.1. Analysis of inorganic materials

The application of portable hyperspectral spectrometers in the analysis of inorganic cultural relics can be traced back to 2010, when Camaiti et al. used ASD spectrometers to analyze the stone and degradation products of the main facade of the Basilica di Santa Maria Novella, a landmark building in Florence, Italy [2,6]. Full-band reflectance spectra were collected from different areas on the church surface (**Figure 2a**). The study found that by monitoring the changes in the absorption peak intensities at 1445, 1489, and 1536 nm in the reflectance spectrum, the degree of transformation of natural marble from calcite to gypsum in an open-air environment can be evaluated; the different particle sizes of gypsum crystals have different effects on the intensity of the characteristic absorption peaks of the spectrum; the carbon-based particles in the black crust on the stone surface absorb the incident light, which will reduce the intensity of the characteristic peaks of the spectrum (**Figure 2b**). This study laid the foundation for the qualitative and quantitative study of stone cultural relics using portable hyperspectral instruments. Subsequently, Suzuki et al. simulated the gypsum process of carbonate open-air cultural relics under acid rain erosion and proposed a semi-quantitative model for predicting the degree of gypsum [21]. By collecting full-band reflectance spectra of stones with different degrees of gypsum, according to Gaffiey's Gaussian decomposition method of SWIR spectra [22], the spectrum of the 1630–2500 nm band was fitted by nonlinear least squares method under the Levenberg-Marquardt strategy, and the linear combination coefficient K_G that characterizes the degree of gypsum of the stone was calculated. When K_G is between 0 and 0.25, the degree of gypsum of the stone is low; when K_G is between 0.25 and 0.5, the stone is moderately gypsum, and when $K_G > 0.5$, the stone is highly gypsum. The study also pointed out that when using this model to predict the degree of gypsum of cultural relics, it is necessary to consider the physical and chemical characteristics of the cultural relics, such as the difference between the calcite particle size, surface roughness, porosity, etc. and the standard samples used in the model. The smaller the difference, the more accurate the prediction result. Cimino et al. studied the characterization of common soluble salts in stone cultural relics such as Na_2CO_3, Na_2SO_4, and KNO_3 by this technology, and extended it to the in-situ, non-destructive analysis of soluble salts precipitated on the surface of ancient Venetian buildings [23].

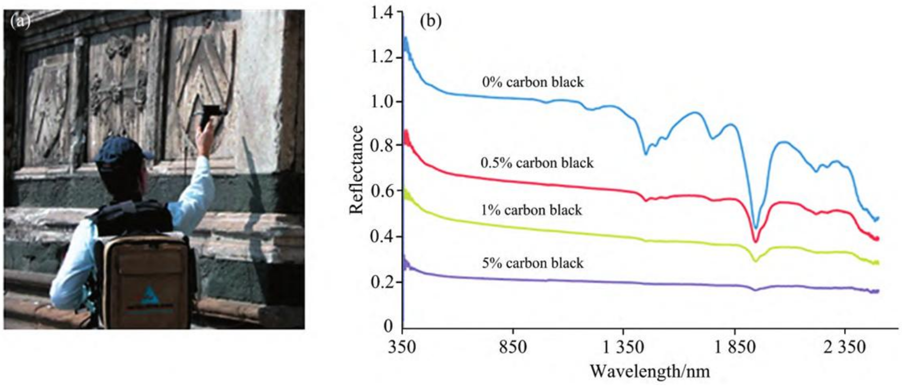

Figure 2. Working photo of the portable ground hyperspectral instrument (**a**) [2]; reflectance spectra of a mixture of gypsum and calcite (1:1) doped with different amounts of carbon black (**b**) [2].

Portable hyperspectral instruments are widely used in the analysis of pigments in painted cultural relics. For the analysis of pigments in precious artworks such as light-and heat-sensitive gold-decorated manuscripts and papyrus paintings, Aceto et al. first made simulated samples on parchment according to the traditional medieval process, then used an ASD spectrometer to collect standard reflectance spectra, and then collected the spectral data of the cultural relics and compared them with the standard spectra [24]. The study established a spectral database based on more than 60 kinds of red, yellow, green, blue, purple, and white pigments/dyes, and achieved non-destructive identification of various pigments in the 15th century gold-decorated manuscripts through the original spectrum and first-order derivative spectrum data of the cultural relics, minimizing the impact of the light source used in the analysis technology on the cultural relics. The study pointed out that compared with the limited spectral range of FORS, the double frequency and combined frequency vibration information of functional groups in the short-wave infrared region (1001–2500 nm) is the fingerprint area for identifying substances containing hydroxyl, sulfate and carbonate. The absorption peaks at 1495, 2285, and 2350 nm can be used to identify pigments containing hydroxyl and carbonate functional groups, such as azurite and malachite (**Figure 3**). At the same time, the distinction of commonly used white pigments can also be quickly achieved: bone white has no absorption peak in the short-wave infrared region; lead white has an absorption peak (1445 nm); gypsum has multiple absorption peaks (characteristic three peaks 1448, 1492, and 1523 nm, and 1942, 2212, and 2268 nm). Aceto et al. [24] also pointed out that the high portability and non-invasive analysis of portable ground feature hyperspectral instruments are particularly suitable for the preliminary analysis of cultural relics with complex components, and can provide a scientific basis for determining the in-depth analysis area or sampling location. Horn et al. used the ASD spectrometer for in-situ analysis of rock painting pigments in the field [25], and used the characteristic peaks at 660, 880 nm and 1410, 2200 nm to respectively identify the main components of red pigment (iron red) and white pigment (kaolinite). Perino et al. used an Avantes spectrometer combined with an X-ray fluorescence spectrometer and a Raman spectrometer to identify blue, green, yellow, and white pigments in late medieval gilded manuscripts [26]. Recently, Radpour et al. also mounted an ASD spectrometer on a scanning platform to study the pigment composition and spatial distribution of tomb murals [27].

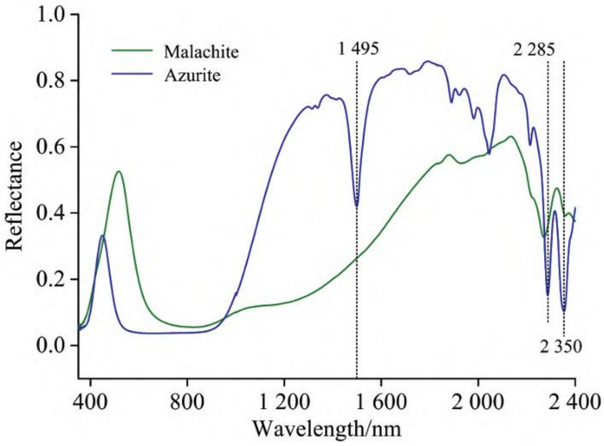

Figure 3. Full-band reflectance spectra of azurite and malachite.

In the analysis of metal artifacts, Liu et al. used an Avantes spectrometer to study the corrosion products of a Ming Dynasty gilt bronze Buddha statue [28]. Based on the positions of the double frequency and combined frequency vibration peaks of hydroxyl and carbonate functional groups in the short-wave infrared region, such as two weak absorption peaks between 1400 and 1600 nm, three strong absorption peaks between 1800 and 2400 nm, two weak absorption peaks at 1422 and 1472 nm, and double peaks at 1918 and 1950 nm, the two main corrosion products of the Buddha statue were identified as chlorantacite/clinoctacrite [$Cu_2(OH)_3Cl$] and azurite [$Na_2Cu(CO_3)_2 \cdot 3(H_2O)$]. Among them, it is the first time that azurite has been identified by a portable ground feature spectrometer. The analysis results have also been verified by X-ray diffraction and Raman spectroscopy. Recently, quantitative research on cultural relics materials has gradually emerged by combining portable ground feature hyperspectral instruments with a variety of advanced data processing methods. For the quantitative analysis of the components of binary mixed pigments, Pallipurath et al. first decomposed the characteristic peaks of the first-order derivative variation spectrum into the sum of multiple Gaussian functions through a fitting program to identify the color transition region of the original spectrum, and then determined the mass fraction of each component in the mixture based on the different contributions of different pigment characteristic peaks to the transition boundary characteristics [29]. This method has been successfully applied to the quantitative analysis of red pigments in medieval illuminated manuscripts in the Fitzwilliam Museum at Cambridge University. In addition, Lyu et al. conducted qualitative and quantitative analysis of mixed pigments used in Chinese paintings during the Qing Dynasty by extracting endmembers from the full-band reflectance spectrum of mixed pigments, comparing the spectra with those of standard substances, and calculating the ratio derivative spectrum [30].

3.1.2 Analysis of organic materials

Usually, accurate identification of organic cultural relics relies on invasive or destructive analytical techniques such as gas chromatography-mass spectrometry, high performance liquid chromatography, and infrared spectroscopy, and non-invasive techniques are often not possible. However, by using short-wave infrared fingerprint area combined with chemometrics and other methods, portable ground feature hyperspectral instruments provide a new way to identify organic materials such as proteins, polysaccharides, and oil cements with similar chemical compositions, as well as textiles.

Ricciardi et al. were the first to combine ASD spectrometer with near-infrared imaging. They not only discovered egg yolk cement on a 15th-century parchment manuscript for the first time, but also determined the distribution range of the cement through imaging [31]. Different from the spectral characteristics of cements such as egg white and gum arabic, egg yolk contains lipids and has two strong absorption peaks at 2306 and 2305 nm (the combined frequency peaks of C-H stretching and bending vibrations), and two weak absorption peaks in the range of 1729 and 1760–1763 nm (the first harmonic frequency peaks of CH_2 stretching vibrations). This study pioneered the use of portable hyperspectral spectrometers to identify organic cultural relics. Subsequently, Dooley et al. [32] and Gabrieli et al. [33] used similar methods to study the cementing materials of medieval woodcuts and illuminated manuscripts, and identified hide glue, egg yolk and gum arabic and their distribution ranges. Pallipurath et al. combined ASD spectrometer with Raman spectrometer to identify protein, polysaccharide and oil cementing materials in the mixture of lead pigment (red lead, white lead and yellow lead) and cementing materials, and sorted out the characteristic peaks of cementing materials in the short-wave infrared fingerprint region (**Table 2**) [34].

Table 2. Characteristic peak positions (nm) of organic cement reflectance spectra and their interpretation [34].

Gum arabic	Egg yolk	Whole egg	Flaxseed oil	Poppy oil	Walnut oil	Peak resolution
	1210					Secondary octave peaks of –CH_3, –CH_2–, and –CH=CH–
1456	1414					First octave peaks of –OH
	1724	1725	1723		1721	First octave peaks of –CH_3, –CH_2–, and –CH=CH–
	1759	1759	1755		1757	
1933	1933	1933	1922		1922	The combined frequency peak of –OH
	2058	2058				The combined frequency peak of –NH
2103			2131			The combined frequency peak of –CH=CH–
2330	2306	2306	2302	2302	2302	The combined frequency peak of –CH_3 and –CH_2–
	2348	2348	2347	2344	2345	

The author's team used an ASD spectrometer to systematically study the spectral characteristics of three commonly used binders in China and the West, namely egg yolk, rabbit skin glue, and linseed oil, mixed with a variety of common pigments such as cinnabar, azurite, lapis lazuli, and iron yellow [19,35]. The study found that although the spectral characteristics of the short-wave infrared fingerprint region will undergo a series of changes when the binder is mixed with different pigments, such as the disappearance of the shoulder peak and the shift of the absorption peak, the position of the C–H combined frequency and harmonic peaks remains unchanged. This spectral change pattern provides a basis for identifying cementing materials in the mixture. At the same time, the first-order derivative spectrum of the mixture spectrum can assist in the accurate characterization of each component through waveform, inflection point position, peak intensity ratio and other characteristics, and reduce the mutual interference between the absorption peaks of pigments and cementing materials. Horn studied the changes in spectral characteristics of iron red mixed with protein and oil cementing materials before and after accelerated ultraviolet aging [36]. The experiment found that after about 100 years of accelerated ultraviolet aging in an aging test chamber [36], the positions of the characteristic peaks of the lipid components of egg yolk (CH_2 stretching and bending vibration) remained basically unchanged, such as the characteristic double peaks at 1725 and 1759 nm, and the characteristic double peaks at 2306 and 2346 nm; the characteristic peak of the lipid components of linseed oil shifted from 2306 nm to 2301 nm; and the lipid characteristic peak of sandalwood oil at 2304 nm disappeared. This study has a good enlightenment effect on the analysis of cementing materials of painted cultural relics that are severely deteriorated, have low cementing material content and contain iron red pigment.

Amato et al. used principal component analysis (PCA) to reduce the dimensionality of the spectral data obtained by the ASD spectrometer and distinguished linseed oil and poppy oil, two oil painting cements with very similar chemical compositions, through non-destructive analysis methods [37]. Although the original spectra and first-order derivative spectra of linseed oil and poppy oil are highly similar, after PCA is used to reduce the dimension of the first-order derivative spectra in the 1650–2500 nm band, the two are clearly distinguished in the score diagram (**Figure 4a**). The study pointed out that the main basis for distinguishing the two quick-drying oils is the different types of unsaturated fatty acids contained in them. In the PCA analysis, the double peaks at 1724 and 1754 nm (the first harmonic peaks of C–H_2 asymmetric and symmetric stretching vibrations) are the main loads affecting the results (**Figure 4b**).

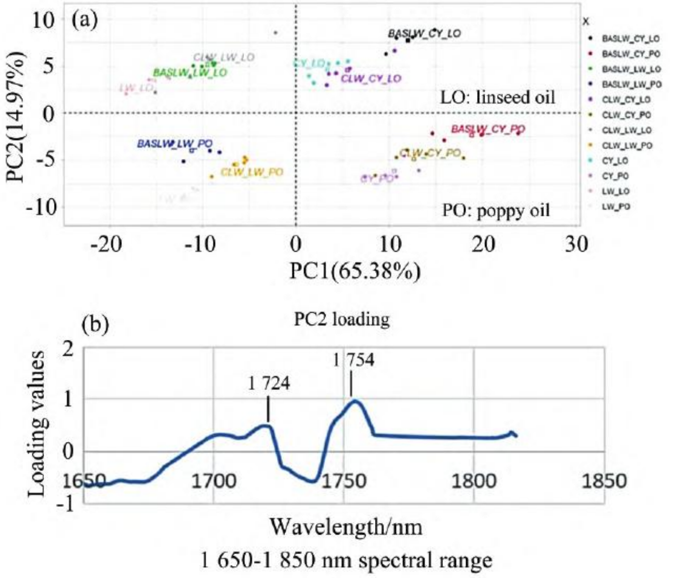

Figure 4. Score diagram (**a**) and loading diagram (**b**) obtained by PCA processing the first-order derivative spectrum of the reflectance spectrum in the 1650–1850 nm band [37].

In the analysis of textile cultural relics, non-destructive identification can also be achieved by using the characteristic peaks of cotton, linen, silk, wool, etc., in the short-wave infrared region and combining them with principal component analysis and other methods. Zhao et al. collected the full-band reflectance spectra of four natural fibers and established a classification model through PCA. The study pointed out that the spectral characteristics of the 1850–2500 nm band are the key to fiber identification [38]. Ding et al. found that the spectra of silk and wool in the shortwave infrared region are significantly different, and their characteristic peaks are located at 2058 (amid A/II combined frequency peak) and 2200 nm (amid B/II combined frequency peak), 2052 (amid A/II combined frequency peak), and 2177 nm (amid B/II combined frequency peak), respectively. Although the full-band spectra of cotton and linen are very similar and cannot be directly identified, an identification model can be established with the help of infrared spectroscopy and its processing software [39]. This method has a good effect in the identification of fibers of ancient or modern textile relics.

3.2. Analysis of cultural relics protection materials

In the field of outdoor immovable cultural relics protection, it is important to monitor the aging and degradation of the protective materials on the cultural relics and their degree of loss, and to perform periodic maintenance in a timely manner. However, how to characterize the protective materials in situ, accurately and non-destructively is a difficult problem. Existing technical means such as portable infrared spectrometers and in-situ hydrophobicity testing methods are applicable to a small spatial range and cannot provide spatial distribution information of protective materials in a larger range.

In order to evaluate the durability of the weathering-resistant material (fluoroelastomer, polyhexafluoropropylene-vinylidene fluoride) on the facade of the 17th-century sandstone Baroque church (Chiesa dei Santini Michele e Gaetano) in Florence, Italy after 20 years of aging in the natural environment, our team developed a material analysis method for cultural relics protection based on a portable ground hyperspectral instrument [2,40]. Firstly, in the laboratory, different amounts of anti-weathering materials were coated on the same stone as the church to make simulated samples. Then, an ASD spectrometer was used to collect spectra to study the corresponding relationship between the characteristic peaks and their intensities and the amount of material used. Afterwards, spectra were collected from different areas of the church surface and compared with the spectral data of the simulated samples. The experimental results show that in the short-wave infrared fingerprint region, the intensity of the absorption peak at 2256 nm (the combined frequency peak of C–H and C=O stretching vibration) is positively correlated with the residual amount of anti-weathering material. This conclusion was verified by the “Pipette” in-situ surface hydrophobicity test, that is, the area with high absorption peak intensity at 2256 nm has high residual amount of anti-weathering material, which shows strong hydrophobicity. Using this method to investigate the entire area of the church’s facade, the spatial distribution of the residual amount of protective materials can be obtained, which provides an important basis for the church's routine maintenance. This study has opened up a new way for in-situ, non-destructive analysis of protective materials on cultural relics.

3.3. On-site restoration of cultural relics and real-time monitoring

During the restoration process of cultural relics, in order to timely evaluate the real-time effects of mechanical, physical or chemical restoration methods and their impact on the cultural relics themselves and avoid “protective damage”, it is very necessary to develop an analytical technology that can monitor the changes in the structure and composition of the material of the cultural relics in real time on site. Due to the characteristics of portable ground hyperspectral instrument such as high portability, in-situ, non-destructive and rapid analysis, it shows strong application potential in real-time monitoring of cultural relics restoration.

Cleaning the aged and yellowed varnish layer on the surface of oil paintings is a destructive and irreversible restoration operation. If it is not done properly, it will cause serious damage to the painting layer and its value. When using Er:YAG laser to clean the varnish layer on the surface of the laser-sensitive pigment layer (containing –OH and –NH functional groups), our team innovatively used an ASD spectrometer to monitor the shape and characteristic peak intensity of the reflectance spectrum of the varnish layer and the painting layer, avoiding excessive cleaning and determining the optimal cleaning conditions [41]. In this study, two of the most photosensitive pigments, cinnabar and lead white, and frankincense/PB67 resin were used to make simulated tempera samples. Under isopropyl alcohol wetting, the effect of cleaning frankincense resin with Er:YAG laser at a power of 0.7 W (100 mJ, 7 Hz) was obvious. The characteristic peaks of the resin at 1703, 1745 nm (first harmonic peak of C–H stretching vibration) and 1923 nm (combined frequency peak of O–H asymmetric stretching and bending vibration) were broadened and the peak intensity was significantly reduced (**Figure 5c, f**). However, under this cleaning condition, the surface layer was damaged and turned dark and black (**Figure 5b, e**). When the laser energy dropped to 50 mJ (10 Hz), the intensity of the characteristic peak of mastic resin decreased, but it was stronger than the peak intensity after high-energy laser cleaning. Under this condition, after repeated operations, the cleaning effect of high-energy laser can be achieved, while ensuring that the picture layer is free from laser ablation. Compared with natural resin, the synthetic resin PB67 varnish layer can withstand higher laser energy. When the laser energy is 100 mJ (10 Hz), the cleaning effect is good and the picture layer is intact.

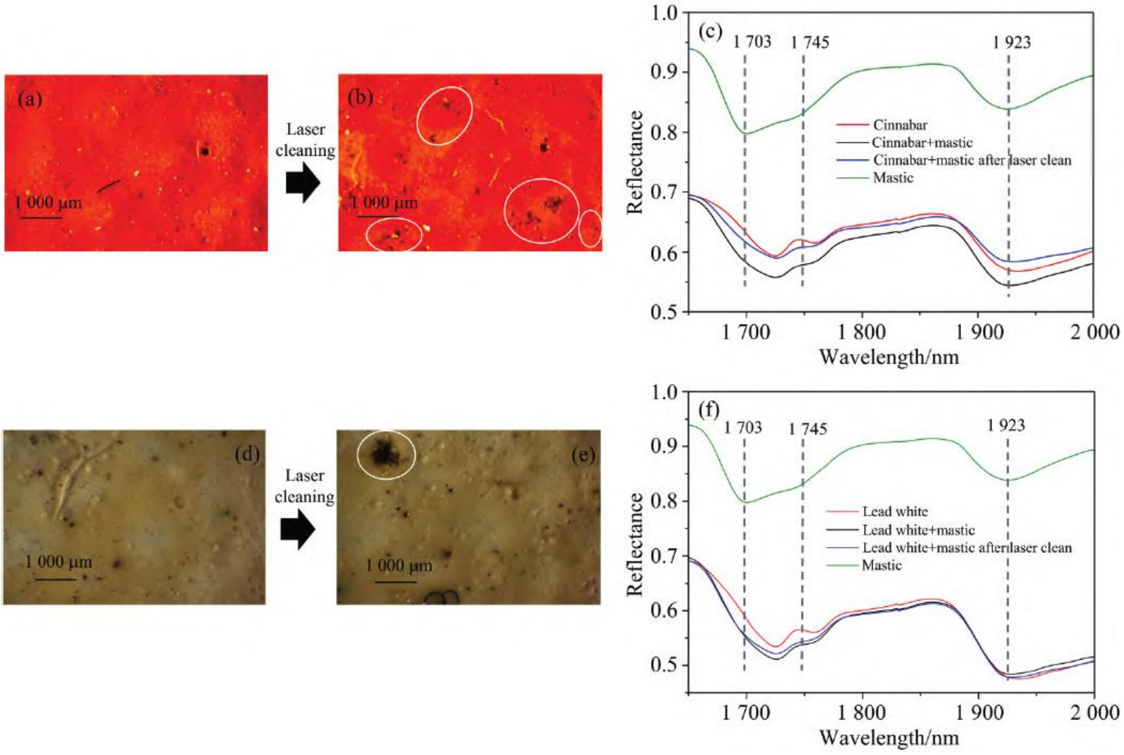

Figure 5. Microscopic photographs of the surface of red lead and white lead tempera before (**a**, **d**) and after (**b**, **e**) laser cleaning, and the changes in the surface reflectivity spectrum before and after cleaning (**c**, **f**).

Taking advantage of the fact that a portable ground-based spectrometer can simultaneously obtain spectral information in the visible light and short-wave infrared regions, Vettori et al. monitored the effects of three (laser, chemical, and microbial) surface cleaning methods on stone artifacts in situ and non-destructively, and semi-quantitatively analyzed the amount of black crust removed/residue on the surface [42].

First, the spectral information in the visible light region (390–780 nm) was converted into the standard three-dimensional color space CILL*a*b*, and the cleaning effect was evaluated by calculating the color change (ΔE) on the surface of the cultural relics before and after cleaning. Then, according to the previous study of Suzuki et al. [21], the short-wave infrared region was used for semi-quantitative analysis of the calcite and gypsum content after cleaning. The specific method was as follows: a standard model for evaluating the relative content of gypsum and calcite was established through gypsum and calcite benchmark compounds [21]; the spectrum in the 1630–2500 nm region was fitted with the gypsum and calcite spectral components with linear combination coefficients k_g and k_c, respectively; the k_g/k_c value was calculated to determine the residual amount of black crust and verify the cleaning effect. The study found that after surface cleaning, k_g/k_c changed from >1 to <1; the smaller the k_g/k_c value, the better the cleaning effect and the lower the residual amount of black crust. The research and technical results have been put into practice in the stone component repair project of the Cathedral of Santa Maria del Fiore in Florence, Italy.

4. Discussion

4.1. Establishment of standard spectrum library

Matching the acquired spectral data of cultural relics with the spectral features of the standard spectral library is an effective means to improve the efficiency of identifying cultural relics materials. In the field of cultural relics material analysis, the standard spectral libraries commonly used by European and American cultural relics protection scholars are the “Spectral Library” compiled by the United States Geological Survey (USGS) and the “SpectralDB” compiled by the Institute of Applied Physics of the Italian National Research Council (CNR-IFAC). However, the above two spectral libraries still have their limitations. For example, the limited standard materials (“Spectral Library” only contains inorganic minerals, “SpectralDB” only contains commonly used pigments), the narrow spectral range (“SpectralDB” has a wavelength range of 270 to 1700 nm), the low spectral resolution, and only the original reflectance spectra, which restrict their large-scale application and promotion in the analysis of cultural relics. Although some materials have been supplemented in recent studies [43], there is no report on the full-band reflectance spectral database of organic cultural relics materials and commonly used cultural relics protection materials, which should attract the attention of scholars at home and abroad. In addition, since the derivative transformation spectrum can effectively assist in the characterization of substances by amplifying the characteristic signals of the original spectrum, the establishment of a corresponding spectral library also has high application value.

4.2. Unification and standardization of spectral preprocessing

Similar to the analytical process of other more mature spectral technologies, preprocessing of the acquired full-band reflectance spectrum is also very necessary. On the one hand, for qualitative analysis, proper preprocessing can reduce and eliminate the influence of various non-target factors on the spectrum, highlighting the characteristic spectrum information of the target analyte; on the other hand, for quantitative analysis, spectrum preprocessing helps to establish a stable and reliable quantitative analysis model.

In the analysis of cultural relics, curve smoothing, baseline correction, Kramers-Kronig correction, envelope removal, data derivation, etc., are commonly used. However, different scholars apply preprocessing methods differently. Some scholars do not use preprocessing methods, and directly perform qualitative analysis such as waveform, absorption peak position and intensity on the average spectrum obtained after multiple measurements [24]; some scholars first use 1–2 preprocessing methods [26,44], and then perform qualitative/quantitative analysis. The pigment spectral library established by Aceto et al. all used raw spectra without preprocessing [24], while Pottier et al. used two preprocessing methods, namely curve smoothing and baseline correction, for a certain band in order to improve the signal-to-noise ratio of the spectrum and enhance the intensity of specific absorption peaks (**Figure 6**) [44]. In fact, whether or not to use a spectrum preprocessing method or which method to use will affect the accuracy of the analysis results to varying degrees. Zhang et al. found in their study on the identification of mural pigments [45] that the reflectivity, absorption peak intensity and width of the spectrum curve changed after the envelope was removed. In addition, the standardization of spectral preprocessing also directly affects the application value of the standard spectral library. Therefore, the preprocessing methods of the included spectra should be clarified and unified for users' reference.

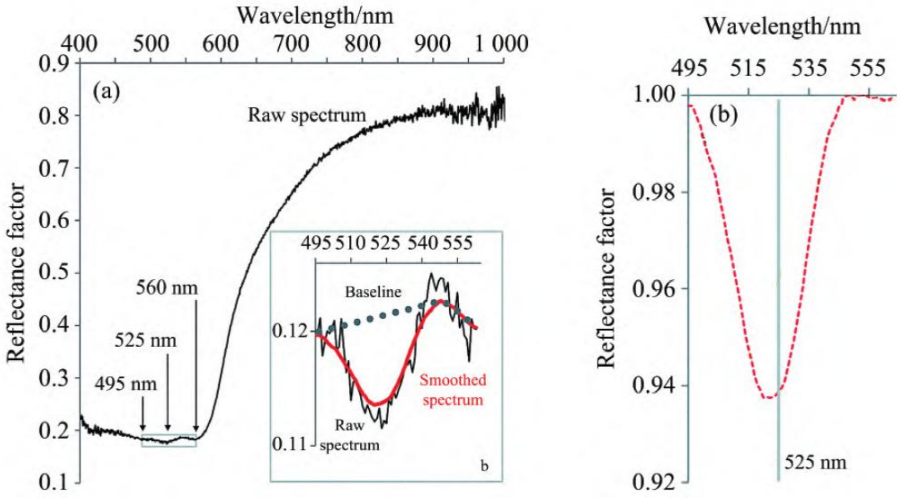

Figure 6. Curve smoothing (**a**) and baseline correction (**b**) of the original reflectivity spectrum [44].

5. Conclusion and outlook

Portable hyperspectral instrument is a non-invasive and non-destructive analysis technology that can be used in situ on cultural relics or field sites. It has the characteristics of wide spectral band range and high portability. It has high feasibility and unique advantages in the study of cultural relics materials. This paper reviews the research progress of cultural relics material analysis based on portable hyperspectral instrument in the past decade, including the application status in the analysis of cultural relics materials, analysis of cultural relics protection materials and in-situ monitoring of cultural relics restoration. However, as a developing analytical technology, the use of portable hyperspectral instruments to accurately characterize cultural relics still faces some challenges. First, the materials that make up cultural relics are complex and diverse, and the content of various materials varies greatly. At present, further research is needed on the detection limits and influencing factors of different brands of instruments and different cultural relics materials (organic materials, inorganic materials, and composite materials) to improve the accuracy of analysis and clarify its scope of application. Secondly, in terms of spectrum processing, there are many methods for preprocessing spectra, but as mentioned above, there is a lack of corresponding standards for spectrum processing, which affects the accuracy of qualitative and quantitative analysis, as well as the repeatability of research results. Finally, the establishment of a spectral library of commonly used cultural relic materials with unified standards still needs to be further improved to meet the actual needs of research on various types of cultural relic materials.

With the continuous deepening of research and application of portable ground hyperspectral instruments, as well as the cross-application of multidisciplinary theories and methods in cultural relics and archaeological research, the following development trends are foreseeable:

(1) Expand its application in the analysis of fragile, light- and heat-sensitive organic cultural relics. The current research objects are mainly stone cultural relics, oil paintings, and other common western cultural relics. By taking advantage of its performance, its application in the analysis of organic cultural relics such as paper archives, bamboo slips, and films will be further expanded.

(2) Combined application with other analytical techniques. The portable ground feature hyperspectral instrument is highly portable and does not require sampling. It can be combined with other non-destructive/mini-destructive techniques for detailed analysis after preliminary overall analysis, which can not only support each other but also enhance the depth of research.

(3) In-depth research on quantitative analysis. With the development of advanced data processing methods, there is a broad prospect for quantitative research on the composition and content of each component in mixed cultural relic materials by using neural networks, deep learning, and mixed pixel decomposition to analyze spectral data.

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References

1. Tejedor B, Lucchi E, Bienvenido-Huertas D, et al. Non-destructive techniques (NDT) for the diagnosis of heritage buildings: Traditional procedures and futures perspectives. Energy and Buildings. 2022; 263: 112029. doi: 10.1016/j.enbuild.2022.112029
2. Camaiti M, Benvenuti M, Costagliola P, et al. Hyperspectral sensors for the characterization of cultural heritage surfaces. In: Masini N, Soldovieri F (editors). Sensing the Past: From Artifact to Historical Site. Springer, Cham; 2017. pp. 289–311. doi: 10.1007/978-3-319-50518-3_13
3. Ricciardi P. UV-visible-near IR reflectance spectrophotometry in a museum environment. In: Adriaens M, Dowsett M (editors). Spectroscopy, Diffraction and Tomography in Art and Heritage Science. Elsevier; 2021. pp. 103–131. doi: 10.1016/B978-0-12-818860-6.00003-9
4. Liang H. Advances in multispectral and hyperspectral imaging for archaeology and art conservation. Applied Physics A. 2012; 106: 309–323. doi: 10.1007/s00339-011-6689-1
5. Deng B, Guo H, Wang C, et al. Applications of remote sensing technique in archaeology: A review (Chinese). National Remote Sensing Bulletin. 2010; 14(1): 187–206. doi: 10.11834/jrs.20100115
6. Camaiti M, Vettori S, Benvenuti M, et al. Hyperspectral sensor for gypsum detection on monumental buildings. Journal of Geophysics and Engineering. 2011; 8(3): S126–S131. doi: 10.1088/1742-2132/8/3/S12
7. Clark R. Spectroscopy of rocks and minerals and principles of spectroscopy. In: Rencz AN, Ryerson RA (editors). Remote Sensing for the Earth Sciences, 3rd Edition. John Wiley & Sons, Inc.; 1999.
8. Ramakrishnan D, Bharti R. Hyperspectral remote sensing and geological applications. Current Science. 2015; 108(5): 879–891.
9. Workman J Jr., Weyer L. Practical Guide to Interpretive Near-Infrared Spectroscopy, 1st Edition. CRC Press; 2007. doi: 10.1201/9781420018318
10. Beć KB. A simple guide to complex world of overtone and combination bands: Theoretical simulation and interpretation of NIR spectra–summary of the workshop at NIR-2021 Beijing Conference. NIR News. 2021; 32(7–8): 15–18. doi: 10.1177/09603360211060966
11. Goetz AF, Vane G, Solomon JE, et al. Imaging spectrometry for Earth remote sensing. Science. 1985; 228(4704): 1147–1153. doi: 10.1126/science.228.4704.1147
12. Cucci C, Delaney JK, Picollo M. Reflectance hyperspectral imaging for investigation of works of art: Old master paintings and illuminated manuscripts. Accounts of Chemical Research. 2016; 49(10): 2070–2079. doi: 10.1021/acs.accounts.6b00048
13. Picollo M, Cucci C, Casini A, et al. Hyper-spectral imaging technique in the cultural heritage field: New possible scenarios. Sensors. 2020; 20(10): 2843. doi: 10.3390/s20102843
14. Cucci C, Casini A. Hyperspectral imaging for artworks investigation. In: Data Handling in Science and Technology: Hyperspectral Imaging. Elsevier; 2019. pp. 583–604. doi: 10.1016/B978-0-444-63977-6.00023-7
15. Gao Z, Du M, Cao N, et al. Application of hyperspectral imaging technology to digitally protect murals in the Qutan temple. npj Heritage Science. 2023; 11: 8. doi: 10.1186/s40494-022-00847-7
16. Lin W, Peng Y, Wang C. Design of portable device for rapid nondestructive detection of fresh meat quality (Chinese). Transactions of the Chinese Society of Agricultural Engineering. 2014; 30(7): 243–249. doi: 10.3969/j.issn.1002-6819.2014.07.029
17. O'Brien NA, Hulse CA, Friedrich DM, et al. Miniature near-infrared (NIR) spectrometer engine for handheld applications. Proceedings of SPIE. 2012; 8374: 837404. doi: 10.1117/12.917983
18. Catelli E, Sciutto G, Prati S, et al. A new miniaturised short-wave infrared (SWIR) spectrometer for on-site cultural heritage investigations. TALANTA. 2020; 218: 121112–121121. doi: 10.1016/j.talanta.2020.121112
19. Wang C, Tie F, Zhao X, et al. Preliminary study on the non-invasive characterization of organic binding media employing a portable hyperspectral sensor (Chinese). Spectroscopy and Spectral Analysis. 2021; 41(9): 2886. doi: 10.3964/j.issn.1000-0593(2021)09-2886-06

20. Campbell JB, Wynne RH. Introduction to Remote Sensing, 5th Edition. The Guilford Press; 2011.
21. Suzuki A, Vettori S, Giorgi S, et al. Laboratory study of the sulfation of carbonate stones through SWIR hyperspectral investigation. Journal of Cultural Heritage. 2018; 32: 30–37. doi: 10.1016/j.culher.2018.01.006
22. Gaffey SJ. Spectral reflectance of carbonate minerals in the visible and near infrared (0.35-2.55 microns); calcite, aragonite, and dolomite. American Mineralogist. 1986; 71(1-2): 151–162.
23. Cimino D, Falchi L, Corradini M, et al. Reflectance spectroscopy as a non-invasive technique for preliminary characterization of soluble salts on historical masonries. In: Osman A, Moropoulou A (editors). Advanced Nondestructive and Structural Techniques for Diagnosis, Redesign and Health Monitoring for the Preservation of Cultural Heritage. Springer, Cham; 2022. pp. 28–34. doi: 10.1007/978-3-031-03795-5_4
24. Aceto M, Agostino A, Fenoglio G, et al. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. Analytical Methods. 2014; 6: 1488–1500. doi: 10.1039/C3AY41904E
25. Horn KR, Walker G, Winton V, et al. Field characterisation of rock art paintings using non-invasive reflectance spectroscopy in the search for organic paint binders at Genealogy and Stickman Rockshelters in the Weld Range (Western Australia). Journal of Archaeological Science: Reports. 2020; 34: 102617. doi: 10.1016/j.jasrep.2020.102617
26. Perino M, Pronti L, Di Forti LG, et al. Revealing artists' collaboration in a 14th century manuscript by non-invasive analyses. Minerals. 2021; 11(7): 771. doi: 10.3390/min11070771
27. Radpour R, Delaney JK, Kakoulli I. Acquisition of high spectral resolution diffuse reflectance image cubes (350–2500 nm) from archaeological wall paintings and other immovable heritage using a field-deployable spatial scanning reflectance spectrometry hyperspectral system. Sensors. 2022; 22(5): 1915. doi: 10.3390/s22051915
28. Liu W, Li M. Wu N, et al. A new application of Fiber optics reflection spectroscopy (FORS): Identification of "bronze disease" induced corrosion products on ancient bronzes. Journal of Cultural Heritage. 2021. 49: 19–27. doi: 10.1016/j.culher.2021.03.007
29. Pallipurath AR, Skelton JM, Ricciardi P, et al. Estimation of semiconductor-like pigment concentrations in paint mixtures and their differentiation from paint layers using first-derivative reflectance spectra. Talanta. 2016; 154: 63–72. doi: 10.1016/j.talanta.2016.03.052
30. Lyu S, Liu Y, Hou M, et al. Quantitative analysis of mixed pigments for Chinese paintings using the improved method of ratio spectra derivative spectrophotometry based on mode. Heritage Science. 2020; 8: 31. doi: 10.1186/s40494-020-00372-5
31. Ricciardi P, Delaney JK, Facini M, et al. Near infrared reflectance imaging spectroscopy to map paint binders in situ on illuminated manuscripts. Angewandte Chemie (International Edition) 2012; 51(23): 5607–5610. doi: 10.1002/anie.201200840
32. Dooley KA, Lomax S, Zeibel JG, et al. Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy. Analyst. 2013; 138: 4838–4848. doi: 10.1039/C3AN00926B
33. Gabrieli F, Dooley KA, Facini M, et al. Near-UV to mid-IR reflectance imaging spectroscopy of paintings on the macroscale. Science Advances. 2019; 5(8): eaaw7794. doi: 10.1126/sciadv.aaw7794
34. Pallipurath A, Skelton J, Ricciardi P, et al. Multivariate analysis of combined Raman and fibre-optic reflectance spectra for the identification of binder materials in simulated medieval paints. Journal of Raman Spectroscopy. 2013; 44(6): 866–874. doi: 10.1002/jrs.4291
35. Wang C, Salvatici T, Camaiti M, et al. A new application of hyperspectral radiometry: the characterization of painted surfaces. EGU General Assembly. 2016; 18: 18255.
36. Horn KR. Time takes its toll: Detection of organic binder media in ochre paints with visible near-infrared and short-wave infrared reflectance spectroscopy. Journal of Archaeological Science: Reports. 2018; 21: 10–20. doi: 10.1016/j.jasrep.2018.06.033
37. Amato SR, Burnstock A, Michelin A. A preliminary study on the differentiation of linseed and poppy oil using principal component analysis methods applied to fiber optics reflectance spectroscopy and diffuse reflectance imaging spectroscopy. Sensors. 2020; 20(24): 7125. doi: 10.3390/s20247125
38. Zhao H, Wang Y, Liu S, et al. Spectral reflectance characterization and fiber type discrimination for common natural textile materials using a portable spectroradiometer. Journal of Archaeological Science. 2018; 111: 105026. doi: 10.1016/j.jas.2019.105026
39. Ding L, Gong T, Yang Q, et al. Non-destructive fiber type identification in ancient textiles using portable near- infrared fiber optic reflectance spectroscopy (Chinese). Science of Conservation and Archaeology. 2021; 33(4): 128–136.

40. Vettori S, Pecchioni E, Camaiti M, et al. Portable hyperspectral device as a valuable tool for the detection of protective agents applied on hystorical buildings. EGU General Assembly. 2012; 14: 9459.
41. Wang C, Cao Y, Tie F, et al. Er:YAG laser cleaning of painted surfaces: Functional considerations to improve efficacy and reduce side effects. Coatings. 2021; 11(11): 1315. doi: 10.3390/coatings11111315
42. Vettori S, Verrucchi M, Di Benedetto F, et al. Hyperspectral sensor: A handy tool to evaluate the efficacy of cleaning procedures. Journal of Cultural Heritage. 2021; 49: 79–84. doi: 10.1016/j.culher.2021.02.012
43. Maynez-Rojas MA, Casanova-González E, Ruvalcaba-Sil JL. Identification of natural red and purple dyes on textiles by Fiber-optics Reflectance Spectroscopy. Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy. 2017; 178: 239–250. doi: 10.1016/j.saa.2017.02.019
44. Pottier F, Kwimang S, Michelin A, et al. Independent macroscopic chemical mappings of cultural heritage materials with reflectance imaging spectroscopy: case study of a 16th century Aztec manuscript. Analytical Methods. 2017; 9(42): 5997–6008. doi: 10.1039/C7AY00749C
45. Zhang C, Hu Y, Hou M, et al. Pigment identification of colored relics based on improved spectral absorption feature fitting algorithm (Chinese). Journal of Spatio-Temporal Information. 2017; 24(3): 119–123. doi: 10.3969/j.issn.1672-1586.2017.03.023