

# Comparative study of pigments used in 16th–17th century CE tempera mural art from Malayadipatti and Adiyamankottai temple, Tamil Nadu, India

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**Eight micro-samples from mural paintings of Malayadipatti and Adiyamankottai temples in Tamil Nadu, India were studied using binocular microscopy, thin film crystal X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, micro-Raman spectroscopy and field emission scanning electron microscopy to understand the original constituent materials of the pigments, binders and the methods of painting. Red paint had a mixture of cinnabar and hematite. The yellow colour resulted from orpiment. Orange hues were produced a mixture of orpiment and hematite. Grey colour was produced by a mixture of calcium carbonate and manganese dioxide. Black tones were prepared primarily using lamp black. The minerals used in both the temples were nearly identical. The appearance of proteinaceous materials/oils as a binding medium in all samples indicated the use of a tempera wall painting technique. These findings help improve our understanding of the methods and materials used in mural arts and serve as a guide for their future restoration.**

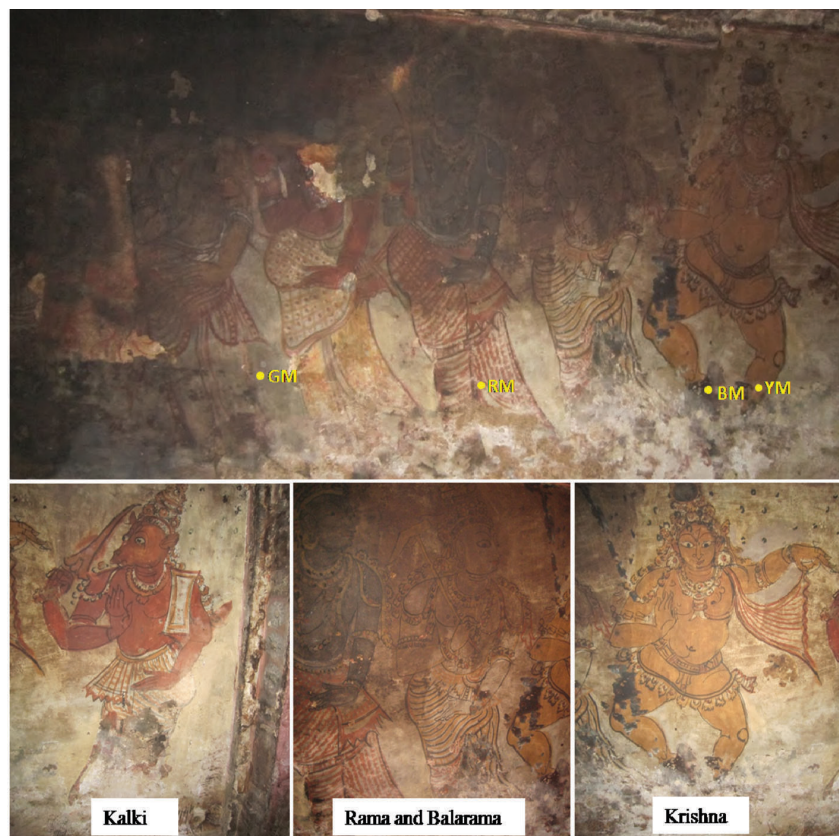
**Keywords:** Art restoration, binders, mural paintings, pigments.

THE Malayadipatti rock-cut temples are situated in the granite hillocks, south of the Malayadipatti village (10.2781°N; 78.6156°E) Tiruchirappalli district, Tamil Nadu, India. There are two temples at Malayadipatti, one for Lord Shiva and the other for Lord Vishnu. These two temples are on the same hillock. According to epigraphic notes<sup>1</sup>, the Shiva temple was built by Kuvavan Sattan and the deity is known as Vakeeswarar. The Vishnu temple is generally known as Olipathi Vishnu Gruham, located near the western end of the hillock. Painted stucco, numerous sculptures, and paintings on the walls and ceiling adorn the rock-cut Vishnu temple. Lord Vishnu in a reclining pose, moolavar,

the presiding deity is beautifully carved into the 4.572 m. The sanctum, mukha-mandapa; and ardha-mandapa are all part of the rock-cut temple. Paintings, sculptures and stucco work cover almost the entire interior surface of the temple. Lord Vishnu and Goddess Lakshmi are depicted in the sculptures. Lord Shiva, Lord Narasimha, Lord Brahma, and other Gods can also be found. These sculptures are completely covered with stucco which is painted. These works of art seem to date from the 16th to 17th century CE<sup>1</sup>. However, the drawings in the temple are not in good condition. Smoke, soot and oil vapours have caused much of the destruction. Lord Vishnu in Matsya avatar (fish incarnation) is painted on the far left, while Lord Narasimha (man-lion incarnation) is painted on its right. The representation of Lord Narasimha here is unusual; he is depicted with a lion's body and a human head, which is not common elsewhere. Figure 1 represents paintings of Lord Rama with a bow, Lord Balarama holding a plough, a dancing Lord Krishna and Lord Kalki avatar<sup>2</sup>.

The Chenraya Perumal Temple is situated in Tamil Nadu's Dharmapuri district, in the town of Adhiyamankottai (12.395067°N; 78.110786°E). Murals of the temple depicting episodes from the *Mahabharata*, Viswaroopa darshan of Lord Krishna and *Ramayana* adorn its interiors from the 17th century CE (Vijayanagara Empire)<sup>3,4</sup>. The ardha mandapam of this temple is about 3.048 m long. A massive portrait of Lord Vishnu (Viswaroopa), spans the entire 3.048 m ceiling. The body of Lord Vishnu is covered with figures of several animals, humans, plants, birds and various other living beings. This is to indicate that Lord Vishnu is the creator and protector of all lives and the encompasses everything around him. Scenes from the *Mahabharata* and *Ramayana* are depicted in other paintings. The murals on the walls and those near the window have faded. Only the fast red colour remains in the paintings near the window. Many other colours have faded (Figure 2)<sup>4</sup>. The Vijayanagara Empire was one of India's last great periods

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**Figure 1.** Paintings show the dancing Krishna and Kalki, Rama with bow, and Balarama holding plough, Malayadipatti temple, Tamil Nadu. Location of analysed points marked with sample code.

of history and culture. Painting, like all other art forms, was encouraged during this period. Paintings from this period can be found in numerous temples throughout South India<sup>5</sup>.

The rapid deterioration and decay of the murals is due to adverse environmental conditions such as temperature, precipitation, humidity, moisture and condensation, which are influenced by factors such as altitude, land and water, ocean currents, latitude, prevailing winds, mountains as barriers, and for land areas, surface cover and local topography (presence or absence of vegetation and its nature, wetness or dryness), as well as air pollution. Another factor contributing to degradation is the chemical action of light, which is known to cause dramatic changes in pigments and binding media<sup>6-8</sup>. The climate of Tamil Nadu varies from dry sub-humid to semi-arid<sup>9</sup>. The average temperature and relative humidity in the state are 22.6°C and 69.8% respectively<sup>10</sup>, which promote both biological attack and chemical disintegration. Most of the chemical disintegration reactions are dependent on the presence of moisture, which is intensified by biological attack and increase in temperature. Tropical temperature is ideal for cryptogamic growth (algae, fungi, lichens, and mosses). These conditions also favour the growth of insects such as white ants (termites) and bacteria, which are feared not only in the tropics but also elsewhere<sup>8</sup>. The underlying essence of the materials, as well as the materials surrounding the pigments also cause degradation and alteration in the hues of

these murals. The painted surface layer as the outermost layer of mural paintings is subjected to deterioration, which induces several types of structural damage such as flaking of paint, cracking, exfoliation and discoloration of paints, staining, formation of blisters on the paint layer, and detachment of paint layer from the support<sup>11</sup>.

Identification of pigments is one of the most significant analytical tasks in the characterization of ancient paintings, since it offers a wealth of knowledge about its provenance, date of manufacture, painting traditions and trade. Paint pigments and other materials are also important in terms of art history and conservation. They are particularly important while selecting the best materials and methods for art restoration<sup>12-14</sup>. The present study aims to compare pigment samples from Malayadipatti and Adhiyamankottai, to learn more about the artists' ability, material composition of paints, preparation techniques and painting. The samples were analysed using binocular microscopy (BM), thin-film X-ray diffraction (TF-XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy, and field emission scanning electron microscopy (FESEM). This combination of techniques allows us to characterize the organic and inorganic components of various pigments, as well as learn more about their association. The findings of this study shed light on the differences in artistic style and colour palette in these two localities.



**Figure 2.** Image shows the beautiful mural paintings from Adhiyamankottai, Tamil Nadu. Location of analysed points marked with sample code.

**Table 1.** List of pigment samples, their sample code and identified pigments

Observed colour	Sample code	Location	Identified pigments
Red	RM	Malayadipatti	Cinnabar + hematite
Red	RA	Adhiyamankottai	Hematite
Yellow	YM	Malayadipatti	Orpiment
Orange	OA	Adhiyamankottai	Orpiment + hematite
Grey	GM	Malayadipatti	Calcium carbonate + manganese dioxide
Grey	GA	Adhiyamankottai	Calcium carbonate + unidentified pigment
Black	BM	Malayadipatti	Lamp black
Black	BA	Adhiyamankottai	Lamp black

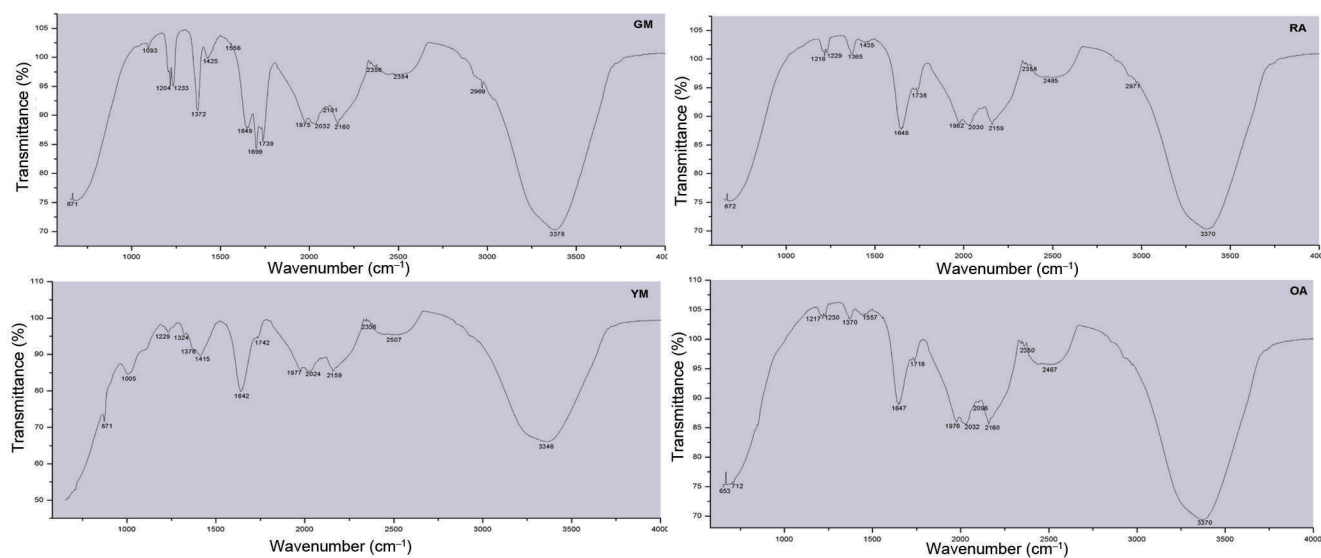
## Materials and methods

Eight pigment – four from each location, viz. Malayadipatti and Adhiyamankottai – were extracted from the temple walls (Figures 1 and 2). Sample selection was made to represent different colours (red, orange, yellow, black and grey), learn about painting techniques, and the composition of materials used in the temple wall paintings which are particularly crucial for a comparative study. Table 1 gives the sample codes for all the samples. Small amounts of sample were directly used in analytical studies.

Small samples were extracted from the both temples as it is necessary to study about the pigments and paintings

and further to preserve the murals. Since the demand for use of the samples in other instruments is high, we have chosen a few tests that yield good results and help characterize the pigments. As a result, we have extracted a micro-samples to determine the exact pigment composition used in two temples.

The samples were imaged under transmitted light for high-quality resolution with stereo-binocular microscope (Leica Z6APO) connected to a digital camera. The Leica Application Suite was used to obtain 3D high-resolution digital imagery from the Leica DFC camera. PANalytical X'Pert Pro X-ray diffractometer (Bragg–Brentano geometry) working at 45 kV and 40 mA using  $\text{CuK}\alpha$  (1.54) radiation



**Figure 3.** Fourier transform infrared spectroscopy of studied pigment sample GM, YM, RA and OA.

was used for XRD analysis of thin films of the pigment samples. High Score (PANalytical) PDF-2 database of 2005 was used to identify the mineral phases. The Artax 200 XRF spectrometer (Bruker, Germany) was used, which was equipped with an SDD detector system, and a Molybdenum X-ray tube was used for analysing the samples. The source was run at 50 kV voltage, 700 mA current, 100 sec acquisition time, 4519–7105 cps pulse density and 1.9% dead time. The instrumental configuration allowed identification of elements with atomic number ( $Z$ ) greater than 13. The spectra were directly obtained from the micro-samples. A PerkinElmer Frontier FTIR spectrometer was used to perform FTIR analysis. The spectra were obtained using 32 scans with a spectral resolution of  $4\text{ cm}^{-1}$  over a range  $600\text{--}4000\text{ cm}^{-1}$ . The pigments were examined with a Renishaw Raman inVia Reflex microscope. The power was set between 10 and 100 mW to avoid degradation of the samples. The resolution was  $4\text{ cm}^{-1}$  for each wavelength; 1–5 scans of 10–60 sec each were averaged. FE-SEM analysis was performed to determine surface morphology using a JEOL JSM-7610F scanning electron microscope in high vacuum mode, Peltier-cooled, octane plus model ( $30\text{ mm}^2$  and 127 eV resolution) at 100 V to 3.9 kV. The electron acceleration voltage was set at 15 kV to ensure generation of X-rays with a beam current of 1 nA (electrostatic unit) and a short dead time.

## Results

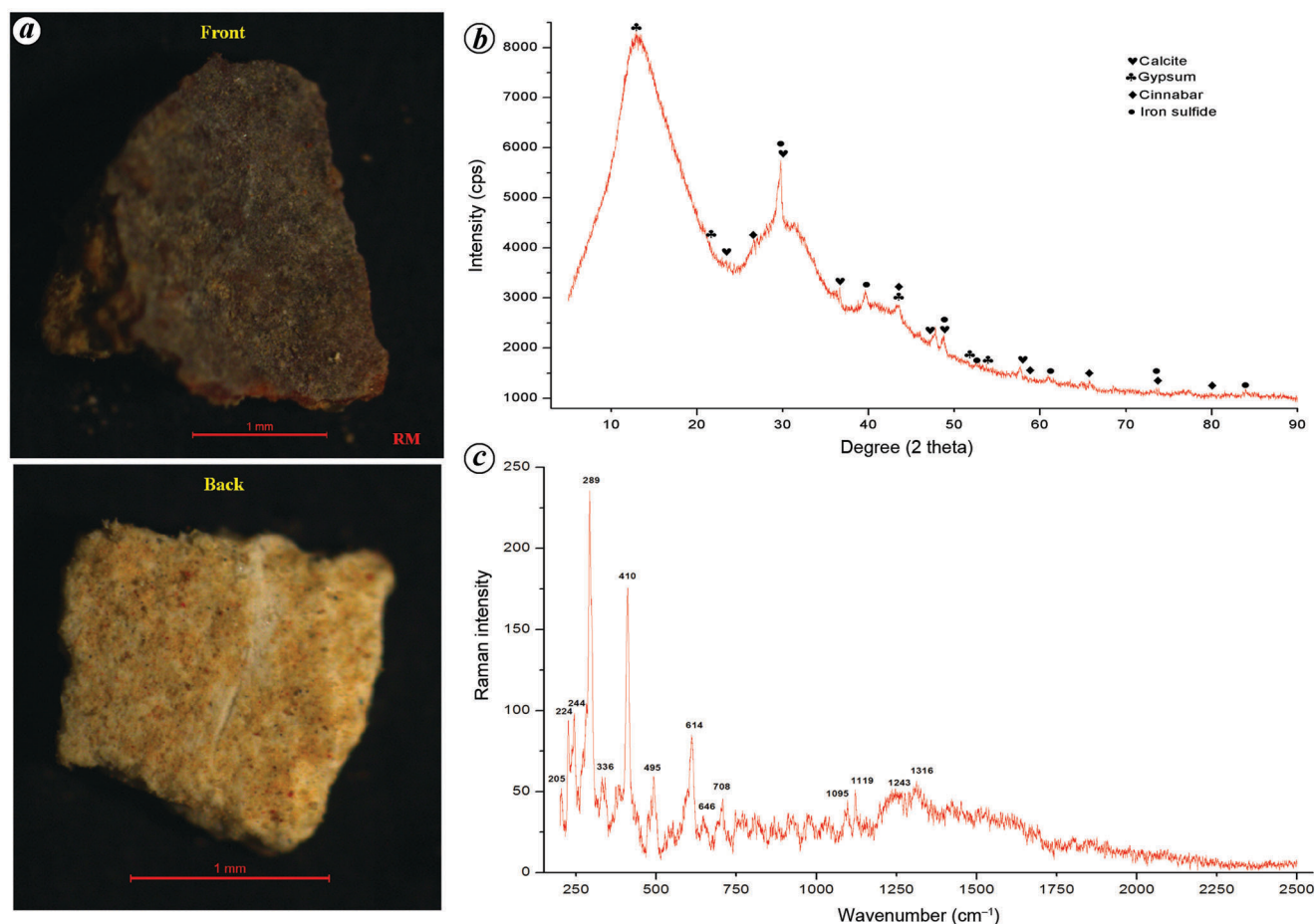
### Painting technique

Binocular images of the pigment samples from Malaya-dipatti and Adhiyamankottai revealed that the paintings were made with a thin paint layer on the top of a sheet of

fine plaster. The boundaries between the fine plaster and paint layers were examined to determine the painting techniques. Borderlines differentiated the plaster and paint layers in both the temples. Borderlines may indicate that the pigments were mixed with binders (organic materials) and then applied on dry plaster surfaces, a technique known as *Tempera*. FTIR spectroscopic study (Figure 3) was used to analyse the organic materials in the paintings. Protein and oil were present in the FTIR spectra of all the paint layers. Indian murals are usually *tempera* paintings, in which the pigments are fixed to the base of the dry plaster with gum, glue or other water-soluble adhesives<sup>15</sup>.

### Pigment layers

**Red pigment layer:** Figure 4a shows binocular images of sample RM. A dark brown to black crust can be seen on the front surface of the red pigment layer of the Malaya-dipatti Vishnu temple. This is considered to be black soot accumulated on the paint layer as a result of oil-lamp burning in the temple. It is worth noting that pilgrims in India often light ghee, oil lamps inside the temples; indeed, the remains of some oily accretions, grime and soot that had accumulated on the temple walls can still be seen. Carbon, hydrogen, nitrogen and sulphur (CHNS) analysis confirmed the presence of 3.18 wt% of carbon on the surface of the RM sample, indicating the deposition of black soot (Figure 5a). The results obtained from CHNS analysis were confirmed by SEM analysis, which showed pits, thus confirming the deposition of soot (Figure 5b). XRF analysis, indicated that mercury in conjunction with iron ochre played a key role in producing the red colour. Ca was utilized as a ground (base), while Cl and S were involved in atmospheric processes (Table 2). Additionally, the pigment contained Si, Mn and



**Figure 4.** (a) Binocular image; (b) X-ray diffraction spectra; and (c) Raman spectra of sample RM.

K in the form of clay. The XRD analysis showed the presence of cinnabar, calcite, gypsum and iron sulphide (Figure 4b). Raman spectrum clearly showed peaks for hematite at 224, 244, 289, 495, 646 and 1316  $\text{cm}^{-1}$  (Figure 4c)<sup>16</sup>. Thus it can be concluded that hematite with cinnabar was present in the sample for producing red colour to enhance the specific tone and hue of the paintings. Presence of gypsum was confirmed by peaks at 410 and 495  $\text{cm}^{-1}$  (ref. 17). Peaks for cinnabar were seen at 336  $\text{cm}^{-1}$  (ref. 18).

Binocular images of the RA sample showed no deposition/accretion on the pigment layer (Figure 6a). Although the RA micro-sample was taken from one location for testing, it was observed that there was no soot deposition in the temple. The presence of Ca, Fe, and Sr in XRF elemental analysis of the red layer of RA suggested that hematite is the main component for producing the red colour (Table 2). Ca and Sr were part of the base of the pigment layer. The significant percentage of Sr (7.72 wt%) suggested that seashells or strontium compounds were used in the mortar preparation of the Chenraya Perumal Temple. XRD spectra showed the presence of hematite, aragonite, and strontium iron oxide (Figure 6b). The presence of aragonite rather than other calcium carbonate polymorphs supports

that calcium was the organic precipitate<sup>19</sup>. Aragonite and strontium may be organic. Although strontium is commonly found in shells consisting of aragonite, it is not always present, and though it may be one of the factors leading to aragonite formation, others must also exist<sup>20</sup>. The Raman spectrum of the RA sample surface revealed bands characteristic of hematite. Hematite has  $D^{63d}$  crystal space group. Seven phonon lines are expected in the Raman spectrum – two  $A_{1g}$  modes (225 and 498  $\text{cm}^{-1}$  respectively) and five  $E_g$  modes (247, 293, 299, 412, 613  $\text{cm}^{-1}$  respectively). All the seven peaks are seen in the spectrum (Figure 6c), with slight changes in wavenumber ( $\text{cm}^{-1}$ )<sup>16</sup>. The peak at 1313  $\text{cm}^{-1}$  indicates the presence of gypsum. Results of the FTIR spectroscopic study indicate that the normal mode of hematite shows six infrared active vibrations – two  $A_{2u}$  and four  $E_u$  at 672  $\text{cm}^{-1}$  ( $A_{2u}$ ), while calcium carbonate shows vibrations at 1365 and 1435  $\text{cm}^{-1}$  (Figure 3)<sup>21</sup>.

*Yellow pigment layer:* XRF analysis indicates that the pigment contains high amounts of As, Fe and Ca, and a low amounts of S, Mn, K, Cl and Ti (Table 2). The presence of orpiment is indicated by the chemical composition and yellow hue of the sample. Peaks at 871  $\text{cm}^{-1}$  for calcium

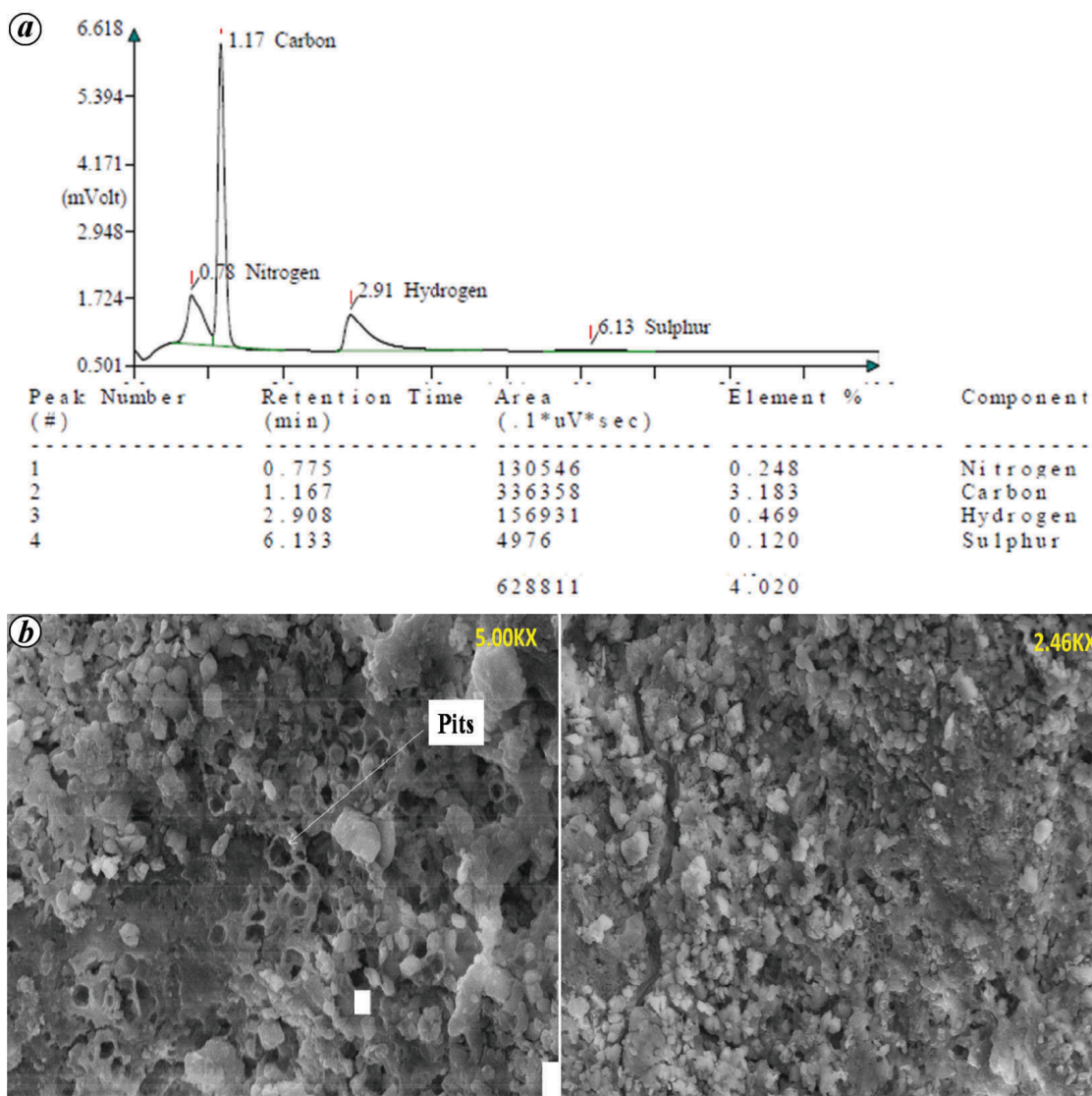
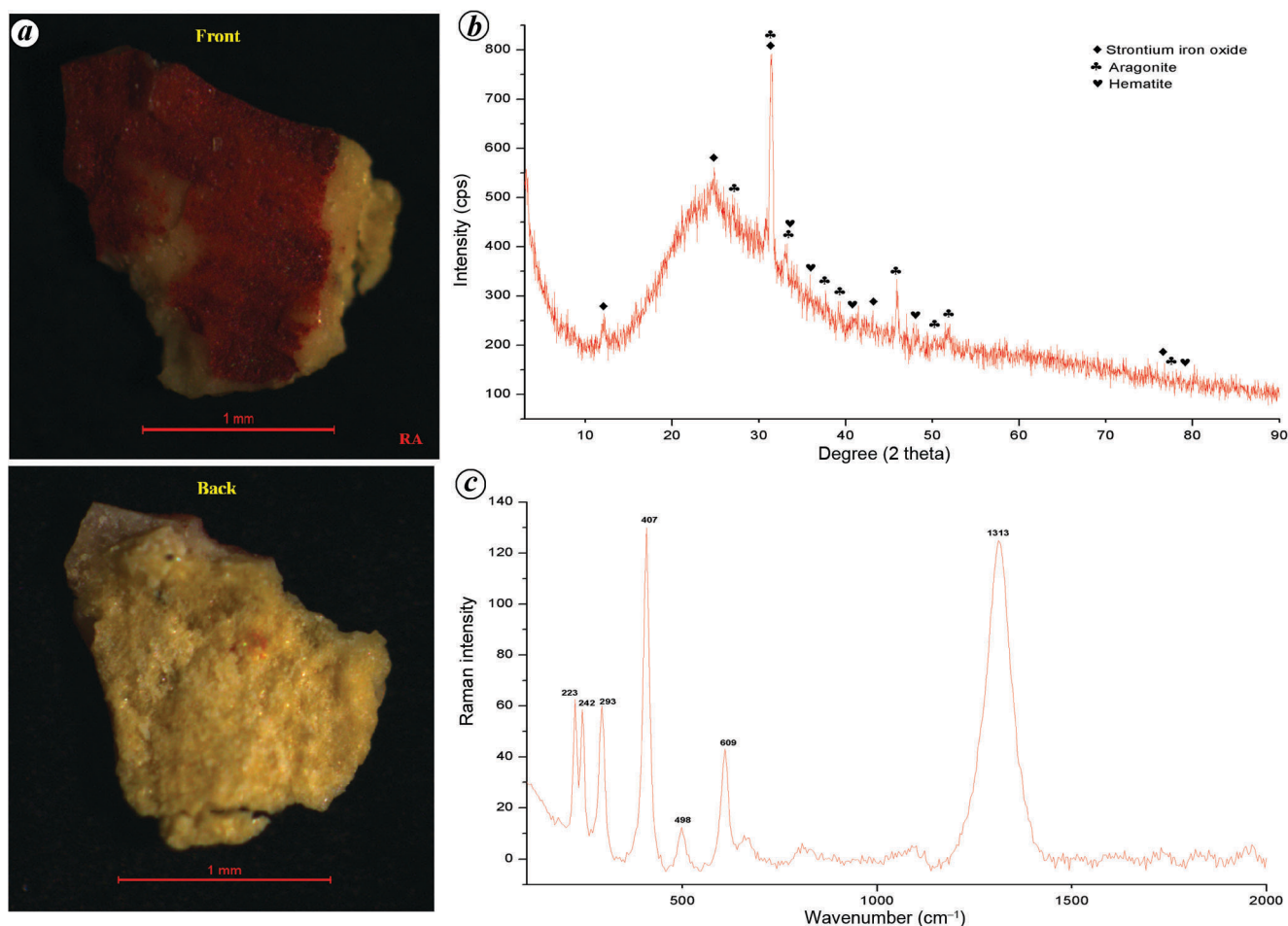


Figure 5. a, CHNS graph with results; b, scanning electron microscopy (SEM) images at different magnification of sample RM.

Table 2. Chemical composition (wt%) of the analysed pigments using X-ray fluorescence from two locations, viz. Madadipatti and Adhiyankottai, Tamil Nadu, India

Elements	Maladipatti				Adhiyankottai			
	RM (wt%)	GM (wt%)	YM (wt%)	BM (wt%)	RA (wt%)	GA (wt%)	OA (wt%)	BA (wt%)
Ca	64.13	64.46	51.99	56.23	57.89	78.70	50.05	76.52
Fe	12.28	28.07	9.83	26.13	36.12	10.64	21.75	8.72
Hg	15.72	—	—	2.34	—	—	—	—
Mn	1.74	1.14	1.34	—	—	—	—	—
Si	1.53	0.99	—	—	—	—	—	—
S	1.95	1.78	2.57	—	1.27	1.10	1.23	0.86
Cl	0.89	1.14	1.00	—	—	—	—	—
K	1.76	2.42	1.13	4.70	—	1.81	1.96	2.09
Pb	—	—	—	5.80	—	—	—	—
Zn	—	—	—	1.91	—	—	—	—
Cu	—	—	—	1.62	—	—	—	—
Ti	—	—	0.77	1.27	—	0.97	0.69	—
As	—	—	31.37	—	—	—	17.89	3.27
Sr	—	—	—	—	7.72	6.78	6.43	8.54



**Figure 6.** (a) Binocular image; (b) X-ray diffraction (XRD) spectra; and (c) Raman spectra of sample RA.

carbonate and  $980\text{ cm}^{-1}$  for gypsum were observed in the FTIR analysis (Figure 3). However, there was a noisy peak and no phases were observed in the Raman and XRD analysis respectively. The reasons behind these findings remain ambiguous and lack a clear explanation.

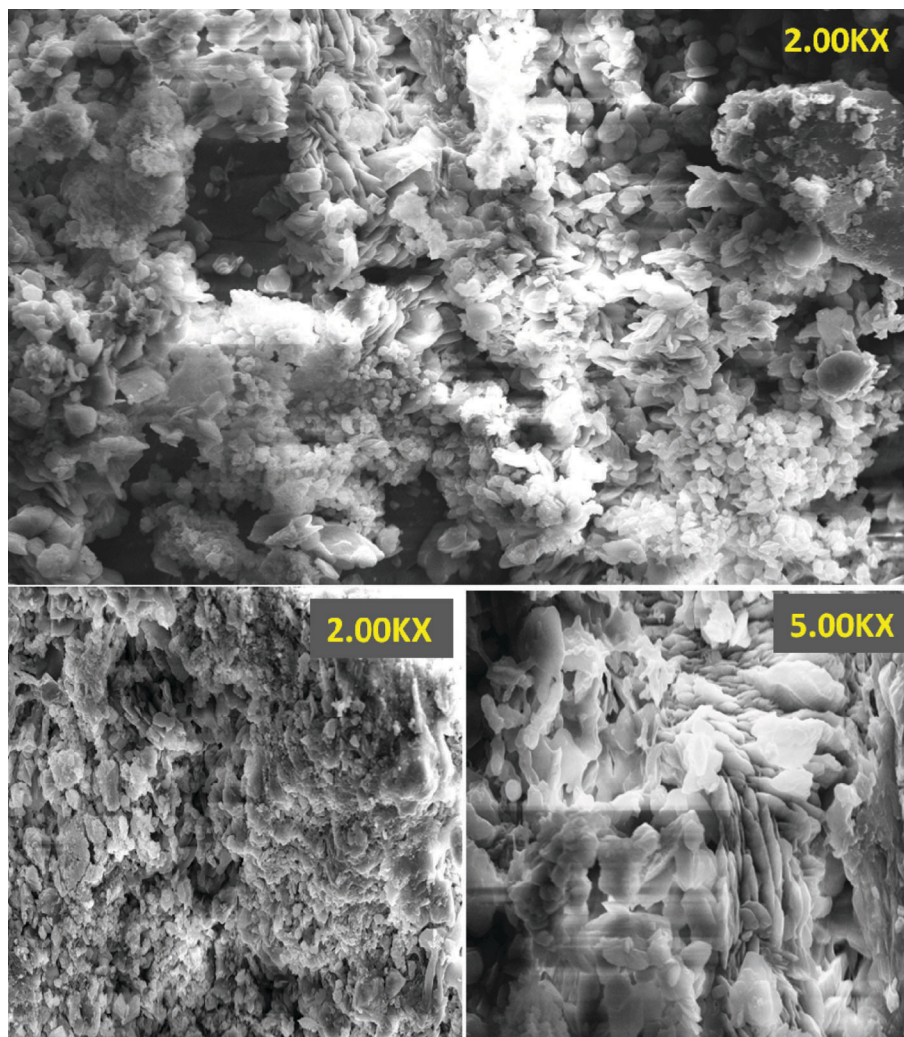
**Orange pigment layer:** The elemental composition of the orange pigment layer revealed that it is mainly composed of Ca, As and Fe and moderate amounts of Sr, K, Pb and Ti. According to XRF analysis results, orange paint in OA sample is composed of a mixture of hematite and orpiment. Results of the analysis revealed the presence of aragonite, calcium – strontium sulphate, claudetite, hematite and ferrobustamite. Claudetitean arsenic oxide, is associated with orpiment, an arsenic sulphide<sup>22</sup>. The Raman spectrum of the orange layer reveals typical hematite bands at 224, 294, 406 and  $611\text{ cm}^{-1}$ , as well as a band at  $345\text{ cm}^{-1}$  attributed to orpiment<sup>23</sup>. According to these findings, the orange hue is achieved using a combination of hematite and orpiment. Gypsum shows bands at 492 and  $1084\text{ cm}^{-1}$  (ref. 24).

**Grey pigment layer:** Results of XRF analysis for GM showed the major elements Ca, Fe and K along with minor

elements S, Mn, Cl and Si (Table 2). The high percentage of Ca and Fe confirms the presence of calcium carbonate and iron-containing compounds. Peaks corresponding to ferrobustamite, quartz, magnetite, calcium carbonate and gypsum are seen in the XRD images. Manganese is present in pyrolusite and magnetite, both of which are black<sup>25</sup>. Peaks for gypsum at 414, 1009 and  $1134\text{ cm}^{-1}$ , and calcium carbonate at  $710\text{ cm}^{-1}$  were identified in the Raman spectra. However, there was no band in the spectra that could be assigned to any gray pigment. SEM images of GM showed a well crystallized and more compact structure of calcium carbonate particles (Figure 7). The grey pigment is due to a mixture of calcium carbonate and manganese minerals.

Results of XRF analysis indicate the presence of Ca, Sr and Fe as major components along with minor components of K, S and Ti (Table 2). No XRD, FTIR and Raman analyses data were obtained.

**Black pigment layer:** Minute deposition of soot, dust and dirt particles can be seen in some areas on the its surfaces. XRF data showed the presence of major elements Fe, Ca, Pb, K, Mn and Hg with traces of Zn, Cu and Ti (Table 2),

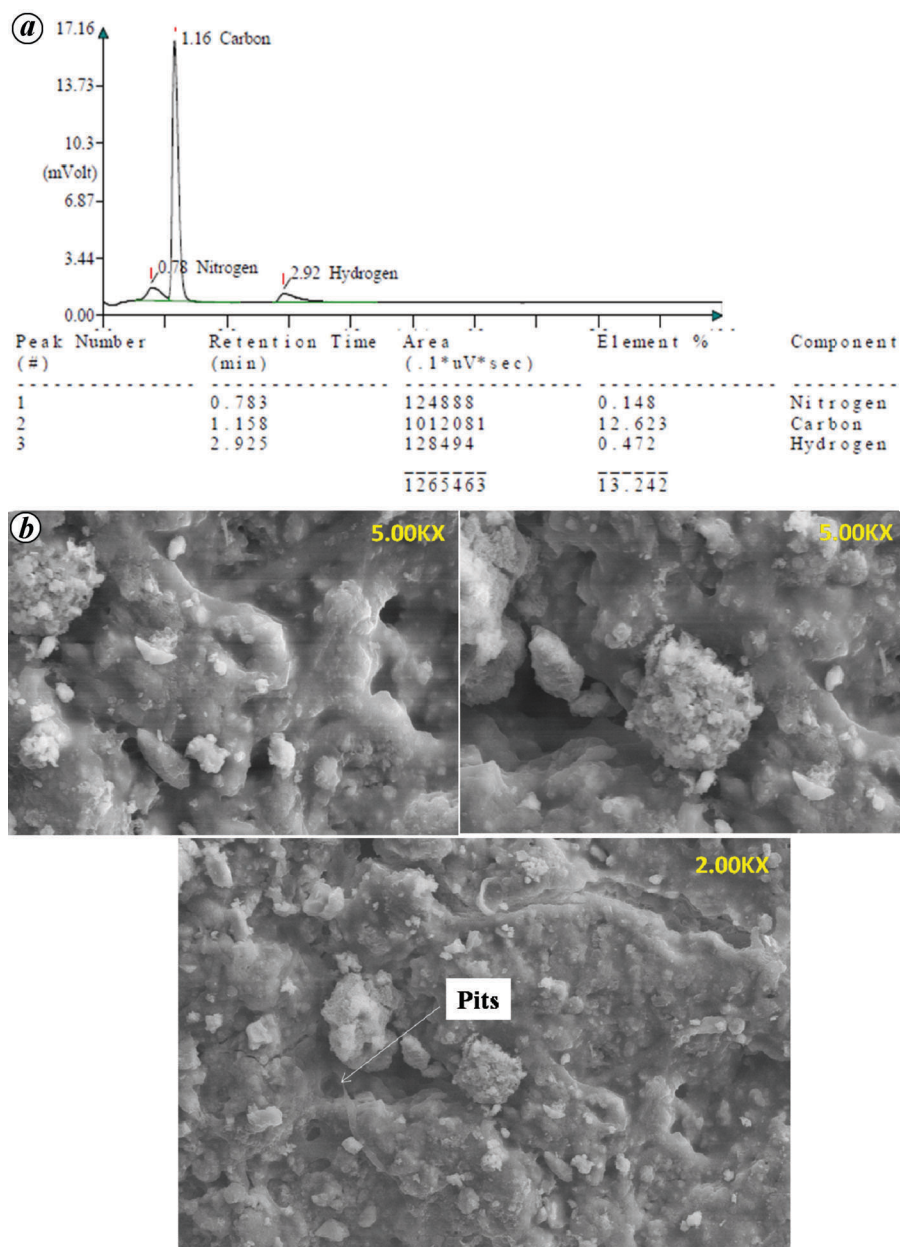


**Figure 7.** SEM images show the compact calcium carbonate formation in the GA sample at different magnifications.

which indicate that the black colour is due to the mixing of all elements containing pigments. However, the XRD pattern and infrared spectra of the BM sample did not show any crystalline phases, suggesting that this pigment is mostly made up of amorphous carbon compounds. Other black pigments that could impart black hue include carbon black or soot, bone black, manganese oxide and ivory black. Phosphorus and manganese were not found in the present study, ruling out the use of bone and ivory black<sup>26</sup>. The high iron content indicates the presence of ferrous oxide. Due to the geochemical affinity of copper for lead, the minor component of Cu with Pb in the black pigment sample may be linked to lead-rich minerals<sup>27</sup>. CHNS analysis indicated a high concentration of carbon (12.62 wt%), confirming that the pigment is carbon black (Figure 8 a). Carbon-based black pigments from combustion of vegetable oils have been used since antiquity. The application of black pigment was preferred for outlining the panels in ancient Indian decorative art<sup>11</sup>. The Raman spectra showed characteristic peaks for lamp black at 1141, 1390, 1509

and 1535  $\text{cm}^{-1}$ . The peak at around 1535  $\text{cm}^{-1}$  was due to the occurrence of carbon in hexagonal graphite sheet mode. In single perfect crystal graphite, this band is the only signal, corresponding to an ideal graphitic lattice vibration mode with  $E_{2g}$  symmetry. The peak at 1390  $\text{cm}^{-1}$  is due to disorder, which corresponds to a graphitic lattice vibration mode with  $A_{1g}$  symmetry. It is known as the ‘disorder-induced’ or D (disorder) mode. At 1509 and 1141  $\text{cm}^{-1}$ , weaker disorder bands D3 and D4 are present respectively, but D2 (shoulder of G mode) is absent in the spectra<sup>28,29</sup>. The spectra also show additional bands at 284 and 390  $\text{cm}^{-1}$  due to iron oxide present in the sample. Therefore, carbon black is the primary component for producing black colour. The structure of lamp black can be observed under SEM (Figure 8 b). The particles are highly irregular and formless, and at higher magnification pits are seen. Under a binocular microscope, the smooth application of black pigment is evident on the front surface of sample BA, while quartz grains (ranging in colour from brown to cream brown) are visible on the back surface. Results of





**Figure 8.** (a) CHNS graph with results and (b) SEM images at different magnification of sample BM.

XRF analysis reveal the presence of Ca, Sr, As, Fe, K and S (Table 2). This indicates that the black pigment comprises calcium carbonate, iron oxide, arsenic oxide, and potassium, with minimal traces of sulphur. Interestingly, no signals were detected in the XRD and FTIR analyses, but the Raman spectra displayed multiple peaks.

The Raman spectrum shows two broad and overlapping bands at around  $1569\text{ cm}^{-1}$  (G band) and  $1360\text{ cm}^{-1}$  (D band) depicting the lamp black. It is worth noting that when a sample contains additional compounds, the parameter values of Raman bands within the  $1000\text{--}1900\text{ cm}^{-1}$  range can be influenced. Peaks at  $600$  and  $872\text{ cm}^{-1}$  affirm the presence of iron oxide and calcium carbonate respectively.

*FTIR spectroscopic study of the binders:* The binders in samples GM, YM, RA and OA were studied using FTIR spectroscopy. The data in Table 3 and Figure 3 present the results. Medium intensity wave bands at  $600\text{--}700\text{ cm}^{-1}$ , indicate the presence of calcium oxalate polymorphs in most the samples except YM. Calcium oxalate formation may be due to the addition of organic matter. The band at  $669\text{ cm}^{-1}$  indicates the presence of iron oxide in sample OA. Calcite bands at  $712$ ,  $871$ ,  $1093$ ,  $1365\text{--}1372$  and  $1425\text{--}1435\text{ cm}^{-1}$  and a weak silica band at  $1005\text{ cm}^{-1}$  were also observed. The amide-I band at  $1642\text{--}1660\text{ cm}^{-1}$  correlated with C=O stretching was seen in all the samples, while the amide-II band at  $1556\text{--}1557\text{ cm}^{-1}$  from N-H bending

**Table 3.** Assignment of bands and organic groups on micro-samples of the pigment samples analysed using FTIR spectroscopy

Malayadipatti		Adhiyankottai		
GM Wavenumber (cm <sup>-1</sup> )	YM Wavenumber (cm <sup>-1</sup> )	Binders	RA Wavenumber (cm <sup>-1</sup> )	OA Wavenumber (cm <sup>-1</sup> )
671	—	← Calcium oxalate polymorphs	→ 672	653/663/673
—	—	Iron oxide	→ —	669
—	—	Calcite	→ —	712
—	871 ←	Calcite	→ —	—
—	1005 ←	Silica	→ —	—
1093	—	Calcite	→ —	—
1204	—	—	→ —	—
1217	1217	—	→ 1216	1217
1233	1229	—	→ 1229	1230
—	1324	—	→ —	—
1372	1376 ←	Calcite	→ 1365	1370
—	1415	—	→ —	—
1425	—	← Calcite	→ 1435	—
—	—	Amide-III	→ 1455	—
—	—	—	→ 1463	—
1556	—	← Amide-II	→ —	1557
1649	1642 ←	Amide-I	→ 1648	1647
1699	—	—	→ 1655	1654
—	—	—	→ 1719	1718
1739	1742 ←	Ester	→ 1737	1736
1975	1977	—	→ 1977	1976
2032	2024	—	→ 2030	2032
—	—	—	→ 2097	2096
2101	—	—	→ —	—
2160	2159	—	→ 2159	2160
2342	2342	—	→ 2341	2341
—	—	—	→ 2349	2350
2358	2356	—	→ 2358	2359
2370	2371	—	→ 2369	—
2384	—	—	→ —	—
—	—	—	→ 2485	2467
—	2507	—	→ —	—
2969	—	—	→ —	—
3378	3346 ←	N-H stretching	→ 3370	3370

(with a contribution from C–N stretching) was observed in samples GM and OA. The amide-III band at 1455 cm<sup>-1</sup> was present only in sample RA. Additionally, the N–H stretching band near 3346–3370 cm<sup>-1</sup> ( $\nu_{\text{O-H}}$ ) confirmed the presence of an amide. FT–IR peaks, confirmed the presence of proteins (amides) and clay minerals (silica and ferrous oxide). However, no peaks in the range 2711–2788 cm<sup>-1</sup> were observed, indicating that carbohydrates/polysaccharides were absent in the pigment samples<sup>30</sup>. The samples also exhibited notable absence of key characteristic signals. These include the primary hydroxyl band (OH) at 3410 cm<sup>-1</sup>, fatty acid (CH<sub>2</sub>) signals at 2924 and 2854 cm<sup>-1</sup>, as well as the sulphate (SO<sub>4</sub><sup>2-</sup>) signal at 1118 cm<sup>-1</sup>. Notably, across all samples, ester (C=O) signals were consistently observed within the range 1739–1743 cm<sup>-1</sup>, indicating an oil-like component. This may be attributed to the presence of triglycerides found in the egg. Significantly, the shape and wavenumber of these ester signals closely resemble those of the reference binder. The absence of aliphatic CH stretching signals (at 2924 and 2853 cm<sup>-1</sup>) effectively

rules out the possibility of drying vegetable oil<sup>31</sup>. Consequently, FTIR spectra of the four samples consistently exhibit bands linked to amides and esters, implying that the binders likely utilized proteinaceous material or oils.

Studies have highlighted the utilization of regionally accessible herbal extracts in artistic and structural contexts<sup>32,33</sup>. These extracts include a diverse range plant molasses, aloe vera, cacti juice, leaf extracts and boiled banana solution, as well as oils derived from sources like tung trees, fish and animal fat. Moreover, unconventional materials such as blood from various animals have also been documented. These unconventional materials were used due to their remarkable water-repellent and wetness-resistant characteristics. Especially, lime mortar fortified with organic components gained prominence in ancient construction practices due to its augmented performance in challenging environmental conditions. The synergistic blend of lime and organic matter enhanced both the longevity and robustness of structures from the bygone era<sup>34</sup>.

## Discussion

The painting technique and pigment palette were almost similar in both Maliyadipatti and Adhiyamankottai temples, but there are dissimilarities in the plaster. Mud plaster layer as arriccio and lime wash layer as intonaco were used in the Malayadipatti temple, whereas rough lime plaster layer as arriccio and fine lime plaster layer as intonaco were used in the Adhiyamankottai temple. In arriccio painting, a layer of relatively coarse plaster is applied to the wall before a smooth top layer (the intonaco) that forms the painting surface is provided. In intonaco the finish coat of plaster upon which painting is done is made of roughly one part lime putty and one part aggregate (usually salt-free river sand, but also pozzolana (volcanic ash, marble powder etc.). Furthermore, gypsum and calcium carbonate have been used as the base for the pigments. It is known that gypsum is produced by sulphating of lime either by environmental contamination or water penetration through the painted plaster surface. This phenomenon is extremely dangerous for artworks, because it can cause the paint film to detach. If the painter had used gypsum during the execution of murals, it is very difficult to distinguish the same with the gypsum produced by sulphating of lime in analysis. As a result, one of the most difficult diagnostic challenges is determining whether the gypsum in wall paintings is due to modification processes or not<sup>35</sup>. Strontium in the Adhiyamankottai temple samples in addition to calcium carbonate and gypsum, as revealed by XRF analysis, suggests that the plastering material may have been produced from seashells. No separate analysis for of ground (base) and plaster was done in the present study. The pigment colours in the Malayadipatti temple samples were deep and dull, a rough surface, while in the Adhiyamankottai temple samples, the colours were intense and bright on a smooth surface.

## Conclusion

Study of mural paintings in the Malayadipatti and Adhiyamankottai temples shows that different pigment constituents were used. The colour palette comprised predominantly mineral pigments, hematite, cinnabar, orpiment, manganese oxide, calcium carbonate and lamp black. Calcium carbonate and gypsum were used as a ground (base) for the pigments. The tempera technique was executed in both the temples with the use of protein and oil as binders. Some pigments such as red and yellow showed slight masking by dust and dirt. The multidisciplinary approach adopted in this study highlights the importance of such studies in the context of conservation of wall paintings.

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