

**Examination of Pigments and
Organic Binding Media Applied On
Ancient Egyptian Wall Paintings
Dating from The New Kingdom
(1348 – 1320 B.C.)**

by

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Abstract

It is fact that little analytical work has been carried out on the identification of organic binding media used on ancient Egyptian wall paintings.⁽¹⁾ This paper contains results of tests of organic binding media and pigment samples taken from the wall paintings of Horemheb tomb from the eighteenth-dynasty, New Kingdom (1348-1320 B.C.).

Analysis was carried out using IR spectrophotometry, X-Ray diffraction, thin layer and paper chromatography, microchemical and microscopic analysis.

Introduction

The tomb of Horemheb (No. 57, valley of the kings, Luxor 1348-1320 B.C.) has been recognised as one of the Egypt's most valued artistic treasures. It was discovered by the American archaeologist Theodor Davis and his assistant Edward Ayrton on 25th Feb. 1908.⁽²⁾ The tomb contains some of the best scenes of the eighteenth dynasty wall paintings (Fig. 1-2). The wall paintings in the tomb are carved in relief and skilfully painted in colours which retain their remarkable brightness. The tomb is constructed on two parallel axes, the first containing corridors, chambers and stairways, and the second containing a set of chambers, corridors, and a burial chamber (Fig. 3).

Characteristic pigment samples were taken from different locations on the wall painting of the tomb, then subjected to analysis using the following methods.

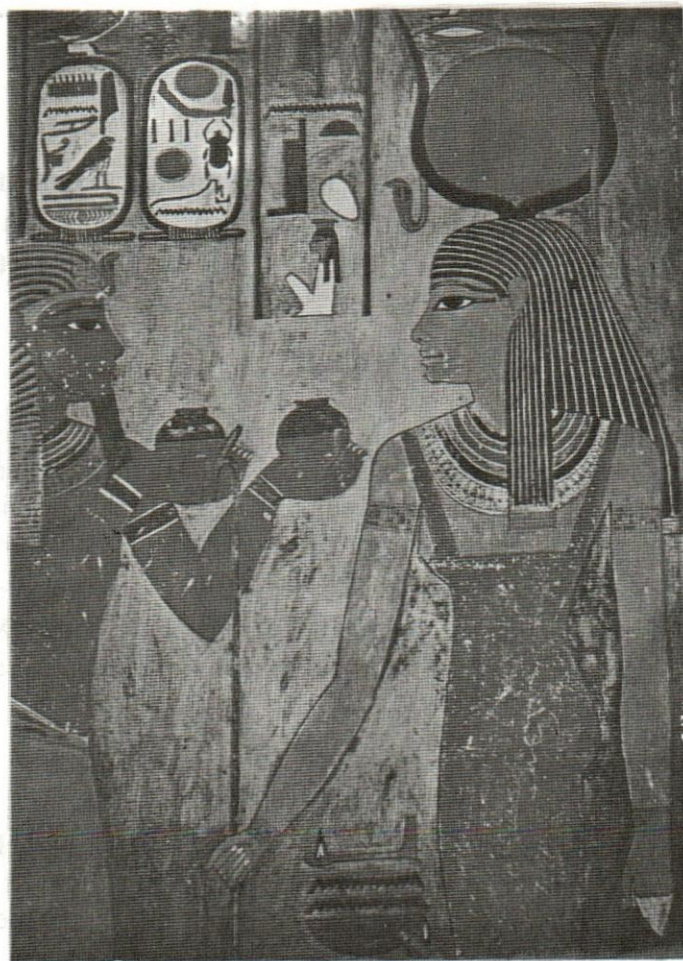


Fig. (1) : Painting fragment from the Tomb of Horemheb.

Pigments	IR spectrophotometry, X-Ray diffraction, microchemical and microscopic analysis.
Binding media	IR spectrophotometry, thin layer and paper chromatography.

The aim of the present work is to identify pigments and organic binding-media used in the Horemheb tomb.

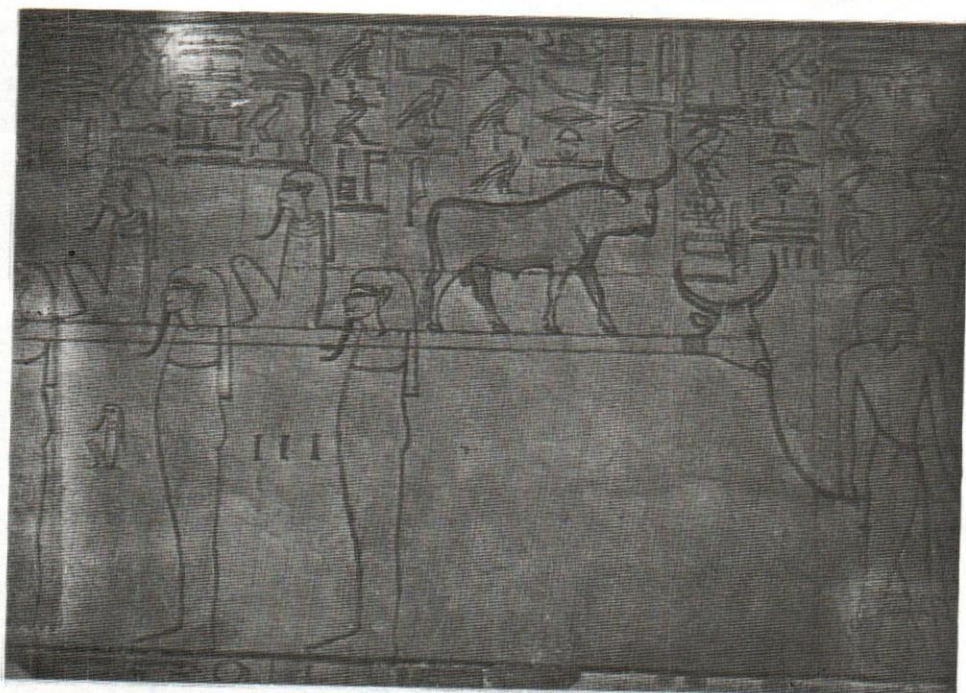


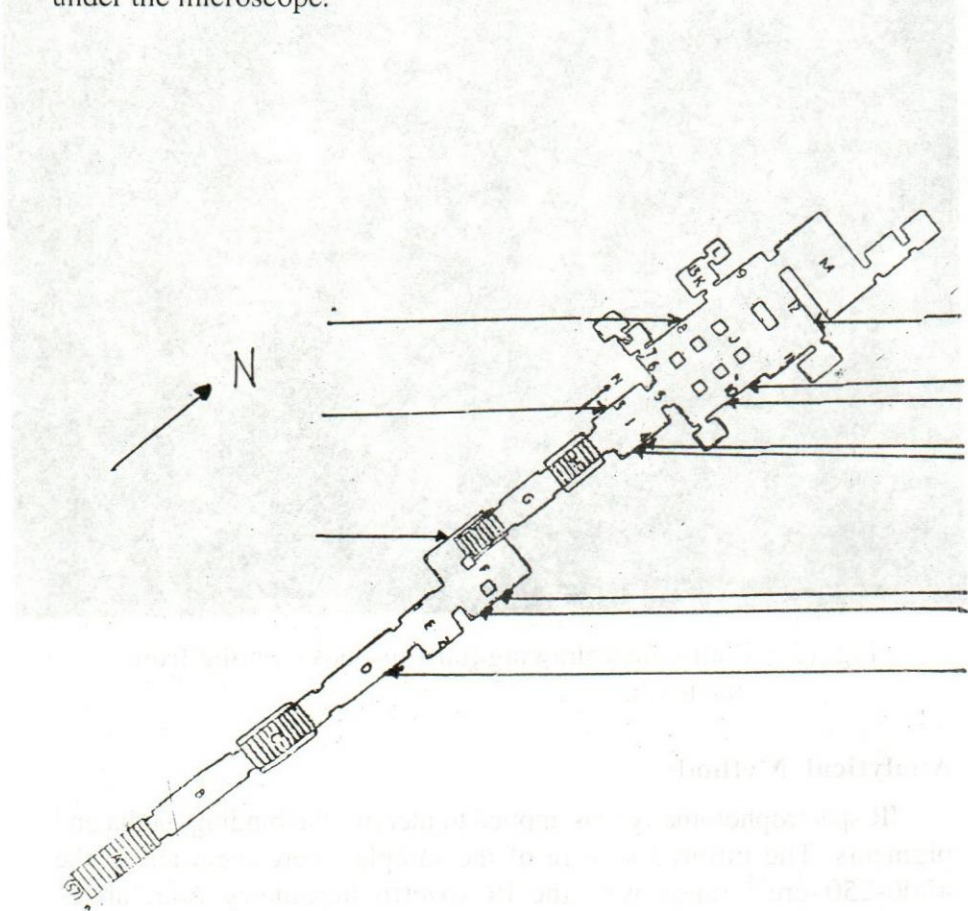
Fig. (2) : Preliminary drawing (un-finished) painting from the tomb.

Analytical Methods

IR spectrophotometry was applied to identify the binding media and pigments. The infrared spectra of the samples were recorded in the $4000-250\text{ cm}^{-1}$ range with the IR spectrophotometry Acculab G, Beckman Inc. USA. The identification of the constituents of samples was based on the occurrence of specific absorption bands related to the composition of samples. This method allows the analysis of very small samples (3-5 mg) which can be mixed with potassium bromide and pressed into a disc. The spectra obtained were characterised by comparison with literature data.

The microscopical examination was applied to identify pigments. The samples were mounted on glass slides embedded in Canada balsam (refracture index $n_p = 1.545$) and were observed by the Polarising microscope (Laboval, C, zeiss, Germany) with magnification up to 600x. The typical microchemical reaction and spot tests were employed.

The reaction of the pigment samples with acids were also observed under the microscope.



(Fig. 3) : Plan of the Tomb of Horemheb, the positions from where the pigment samples were taken are remarked, with arrows.

In order to identify the organic binding media, a set of analytical methods were applied. The presence of carbohydrates and proteins was verified by progressive paper chromatography, while esters and fatty acids were examined by thin layer chromatography.⁽³⁾

Microchemical tests were also carried out for all samples on cross sections immersed in epoxy resin.

X-Ray diffraction was carried out by analysing the curves registered on an X-Ray diffractometer HZG4/A-2 by continuous registration and by the following condition : radiation $\text{Cu K}\alpha$ - parameter of the lamp : 10, 20, 30 mA° 20, 40 Kv - proportional counter; rate of counter shift $1^\circ/\text{min}$ -rate of paper 12 mm/min.

Experiment and Results :

PIGMENT :

The pigments reported in Horemheb tomb are red, yellow, white, blue and black. More than five characteristic pigment samples were examined by IR spectrophotometry. The IR spectra of the pigments are shown in (Table 1). The analysis showed the red pigment to be ochre with the highest percentage of kaolinite and iron oxide. The yellow pigment was revealed to be ochre consisting mostly of kaolinite and traces of quartz and calcite. The IR spectra of the white pigment shows the absorption bands at 2520 cm^{-1} , 1795 cm^{-1} and 1430 cm^{-1} characteristic for the CaCO_3 type of calcite which proves the presence of cal. carbonate as a white pigment. The spectra of the blue pigment shows the presence of silicate and quartz. The method of FIR (Fourier IR) (being of higher precision than the standard IR technique) was used to examine the composition of the blue pigment. However the blue pigment was revealed to be Egyptian blue (Fig. 4, 5, 6).

Microscopic and microchemical analysis :

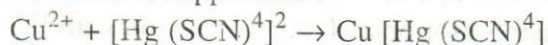
Microscopically, natural forms of red pigment are heterogeneous in composition and particle size. Elongated, red and dark brown, lustrous particles of hematite Fe_2O_3 can be seen. The yellow pigment is heterogeneous in particle size and in composition, pale yellow and dull yellow particles are sensibly isotropic. Tests for Fe^{-3} on with $\text{Fe}(\text{Cn})_6$ shows the yellow pigment to be ochre Fe OOH , while the white pigment particles are quite homogeneous, and are highly birefracting. The chemical test for the white pigment was shown by dissolution in HCl. With effervescence of CO_2 and by treating the pigment with dilute H_2SO_4 it gives characteristic - "wheatsheaf" - formation of needless

“gypsum”. The black pigment consists of very small opaque particles. These particles were found to be carbon black C. The results of chemical reactions are given below :

Colour of pigment	Peak Intensity cm^{-1}	Mineral	Pigment
Yellow	3695 - 3625 - 1040 - 1010 - 910 1430 - 875 - 712 800 - 780 540 - 460	Kaolinite Calcite Quartz Iron Oxide	Yellow Ochre Fe OOH
Blue	1470 - 1380 - 1320 - 1180 - 1165 - 1150 - 1100 - 1005 - 960 - 850 - 775 - 750 - 670 - 625 - 600 - 575 - 525 - 475. 1430 - 875 - 712.	Silicate Calcite	Egyptian Blue $\text{CaCuSi}_4\text{O}_{10}$
Red	1795 - 1430 - 875 - 712. 3695 - 3625 - 1040 - 1010 - 910. 3550 - 3400 - 1150 - 1120. 1100 - 800 - 780. 540 - 460.	Calcite Kaolinite Gypsum Quartz Iron Oxide	Red Ochre Fe_2O_3
White	2520 - 1795 - 1430 - 875 - 712.	Calcite	Calcium Carbonate “chalk” CaCO_3

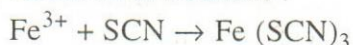
Tab. (1) : IR Spectrum results of pigment samples.

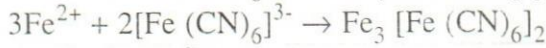
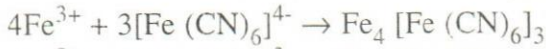
– Reaction of copper ions :



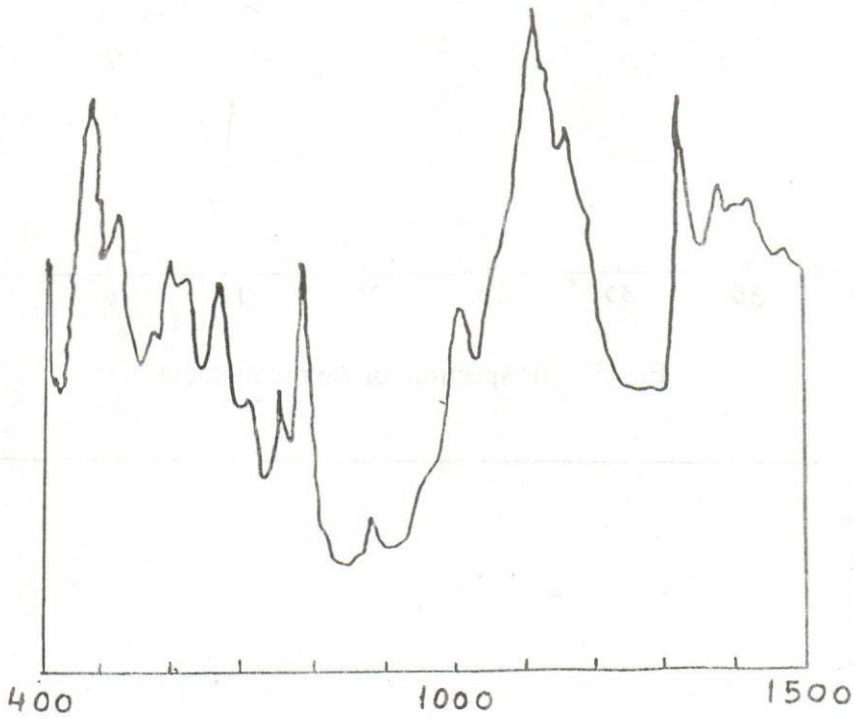
With borax it gives blue colour when heated and green colour when cool.

– Reaction of iron ions :



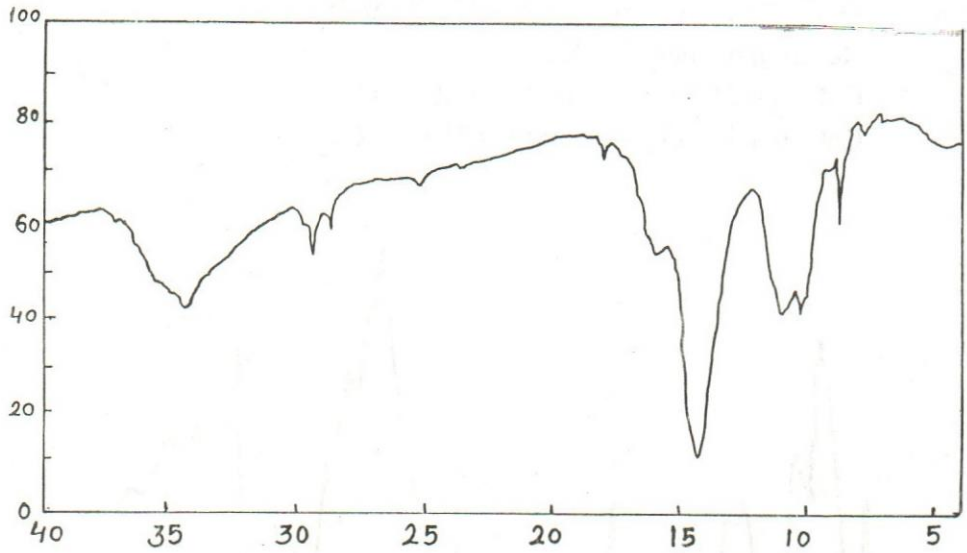


- Reaction of chalk CaCO_3 :

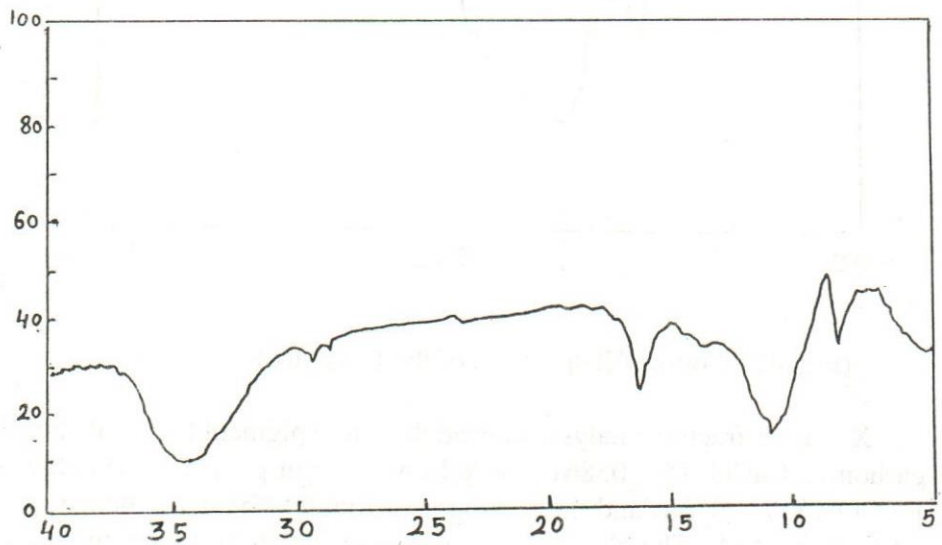


(Fig. 4) : Fourier IR spectrum of the Egyptian blue pigment.

X-Ray diffraction analysis showed the white pigment to be calcium carbonate CaCO_3 (5 - 0586). The yellow pigment proved to be ochre $\text{Fe}(\text{OOH})$ (17 - 0536) and the red pigment found to be ochre hematite Fe_2O_3 (13 - 534). The blue material was identified as an Egyptian blue $\text{CaCuSi}_4\text{O}_{10}$ (12 - 512). Egyptian blue was the first artificial pigment manufactured in Egypt as early as the fourth dynasty. It has been studied by many investigators since last century.⁽⁴⁾



(Fig. 5) : IR spectrum of the red pigment.



(Fig. 6) : IR spectrum of the white chalk.

ORGANIC BINDING MEDIA :

Before the paint media can be examined, it is necessary to determine whether micro-organisms are present and if so, to give their characteristics and to evaluate the influence of their content on the results of chromatography tests.⁽⁵⁾ However, direct analysis using a biological microscope and the growing of special culture media for bacteria and fungi showed the absence of micro-organisms.

The IR spectrum presents the following absorption frequency bands : 1070 cm^{-1} , 1220 cm^{-1} , 1385 cm^{-1} , 1440 cm^{-1} , 1620 cm^{-1} and 2930 cm^{-1} characteristic for carbohydrate and vegetable tannin (plant gums).

Chromatography tests were applied to determine simple sugars extracted with ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$ for 4 hours. The extracts were developed twice after 24 hours in ethyl acetate, pyridine and water ($3*6 : 1 : 1*15$ respectively).

After simple sugars had been extracted (except pentose and ketohexose), the samples were hydrolysed in H_2SO_4 for 6 hours at 105°C to test for compound sugars Hydrolyzates were neutralized with solid barium carbonate BaCO_3 and the precipitated barium sulphate BaSO_4 was isolated by filtration. Then the simple sugars glycuronic acid, arabinose, galactose and a small amount of ramnose were identified after the solution had been concentrated. The absence of simple sugars before and their presence after hydrolysis indicates the presence of polysaccharides e.g. plant gums.⁽⁶⁾

Chromatographic analysis chromatograms of amino acids and microchemical reactions allowed the elimination of casein, glutine or egg as paint media.

Discussion and Conclusions

The tomb of Horemheb was cut limestone landslide deposits, while the wall paintings are a relief carved and painted either directly onto the support or on a very thin white priming ground.

According to analysis, the pigments used in the tomb are traditional, red ochre – hematite Fe_2O_3 – yellow ochre – goethite Fe OOH - white chalk CaCO_3 , black carbon C and Egyptian blue pigment $\text{CaCuSi}_4\text{O}_{10}$.

Analysis of paint media from the polychromies in the tomb shows an important quantity of carbohydrates (polysaccharides). The absence of simple sugars excludes honey and plant glue such as linen and corn grain glue. Resin gums can also be eliminated, as they contain a low amount of simple sugars such as fructose. After hydrolysis, galactose and arabinose were identified in important quantities, which implies the use of plant gums.

The results of chromatographic tests are close to those of arabic gum where four simple sugars are present i.g. glycuronic acid, galactose, arabinose and ramnose.⁽⁷⁾ The last sugar – ramnose – was found only in small quantities. In the examined samples, the ratio between galactose and arabinose is about 1 : 1, which corresponds to the proportion of these sugars in arabic gum⁽⁸⁾ (Table 2). Mannose, was found only in very small quantities, which is another proof for arabic gum as an organic binding medium used as a pigment binder in the wall paintings of Horemheb tomb (valley of the kings western bank of the Nile in Luxor).

Table (2)

Type of gum	$\frac{\text{GAL}}{\text{M}}$	$\frac{\text{GAL}}{\text{A}}$	$\frac{\text{GAL}}{\text{K}}$	$\frac{\text{GAL}}{\text{RYB}}$	$\frac{\text{GAL}}{\text{R}}$	$\frac{\text{A}}{\text{M}}$	$\frac{\text{A}}{\text{K}}$	$\frac{\text{A}}{\text{RYB}}$	$\frac{\text{A}}{\text{R}}$
arabic / accacia	—	0.75:1	—	—	5.3:1	—	—	—	7.3 : 1
tragacanth	3.9:1	8.2:1	—	—	1.9 : 1	0.44:1	—	—	0.20:1
sour cherry	4.8:1	0.4 : 1	4.8:1	—	14.5:1	11.7:1	11.7:1	—	35 : 1
plum	2.5:1	0.55:1	5 : 1	—	16 : 1	4.5 : 1	8.8 : 1	—	29 : 1
sweet cherry	2.7:1	0.41:1	2.7:1	—	12.5:1	5.6 : 1	6.6 : 1	—	30 : 1
peach	7.7:1	0.52:1	1.2:1	—	28 : 1	15.3:1	2.4 : 1	—	56 : 1
apricot	4 : 1	0.78:1	3.75:1	12 : 1	10 : 1	5 : 1	4.1 : 1	15.4:1	12.8:1

Where : GAL-a-gelactose, M-d-mannose, A-L-arabinose, K-d-xylose,
RYB-d-ribose, R-L-ramnose.

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1. The first part of the year was spent in the field...

2. The second part of the year was spent in the laboratory...

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