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Diagnosis of Pigment Materials Affected by Air Pollution and Clay Minerals in Sabil Alkazlar.

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## Diagnosis of Pigment Materials

### Affected by Air Pollution and Clay Minerals in Sabil Alkazlar

THE Arabic word Sabil stands for public drinking fountain. Sabil Alkazlar (fig. 1) is one of the Ottoman historical buildings that have survived in historic Cairo. It is located at 30° 01' 59.42" N and 31° 15' 13.29" E; in Alsoyofeyya Street behind Alsultan Hassan mosque. It was established in 1617 AD by Mustafa Agha Pasha Alkazlar. The façade, internal units and the ceiling of the building are exposed to different weathering agents.

Research is lacking concerning the techniques and painting materials used in wall paintings dated to the Ottoman period in Egypt. Therefore this study was carried out to verify the effect of air pollution and clay minerals on the deterioration of the wall paintings in Sabil Alkazlar.

### Sampling and Methodology

The plasters and pigment materials used in Sabil Alkazlar were sampled for laboratory analyses to determine their chemical composition. X-ray diffraction (XRD) analysis was performed using powdered samples of the pigment materials and plasters using a Philips (PW1840) diffractometer with Ni-filtered Cu-K $\alpha$  radiation. The samples were scanned over the 5-70° 2 $\theta$  intervals at a scanning speed of 1.2° min<sup>-1</sup>. A quantitative estimate of the abundance of

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the mineral phases was derived from the XRD data using the intensity of certain reflections and external standard mixtures of minerals compared to the JCPDS standards of 1967. The detection limits of the method were  $\pm 1$  w/w %.

Samples of plaster and pigments were examined by SEM-EDAX using a Fei company SEM (version quanta 200), with specifications of: KeV 24.98; tilt (0.00); take-off: (36.47); ampt (35.0); detector type (SUTW-sapphire); resolution (129.87). Cross sections were carried out using a stereo microscope type Stemi dr 1663 Zeiss. Moreover FTIR and UV analyses were carried out to identify the binder used in both plaster and pigment materials.

Concerning clay mineralogy, the grain size determination of the plaster sample was performed according to the classification of Folk.<sup>1</sup> A 20g split of the sample was subjected to the chemical treatment described by Jackson.<sup>2</sup> The  $< 2 \mu\text{m}$  fraction of the sample was separated into three fractions. Untreated mounts of clay fractions were prepared for XRD analysis. The untreated mounts were examined after treatment with ethylene-glycol solution to distinguish the expandable mineral phases, and heated for two hours at  $550^\circ\text{C}$  to differentiate between kaolinite and chlorite.<sup>3</sup> Semi-quantitative estimates of the mineral abundance based on the peak area of the untreated mounts were made from the XRD data using the method described in Biscaye.<sup>4</sup>

## Results

### *Plaster Sample*

The XRD analysis of the rendering layer applied to the wooden ceiling of Sabil Alkazlar; revealed the presence of gypsum, anhydrite, dolomite, quartz, aluminum oxide, microcline, halite, bone black, yellow ochre and hematite (fig. 2). SEM-EDAX of the same sample showed the presence of: 43% oxygen, 18% calcium, 13% silicon, 11% carbon, 3% iron, 5% aluminum, 2% sulfur, 2% magnesium, 1% chlorine, 1% potassium and 1% sodium (fig. 3).

### *Pigment Samples*

#### *Black Pigment Sample*

XRD analysis of a black pigmented plaster sample from the ceiling proved that the used pigment material is bone black  $[\text{C}.\text{Ca}_3(\text{PO}_4)_2]$ . The sample contains also gypsum, dolomite, quartz, halite, orpiment, cinnabar and aluminum oxide (fig. 4). The SEM-EDAX of the sample revealed the presence of about 65% carbon, 28% oxygen, 1% chlorine, 1% sodium, 1% calcium, 1% phosphate, 1% sulfur and traces of aluminum, silicon and magnesium (fig. 5).

1. Folk, *Petrology of Sedimentary Rocks*.

2. Jackson, "Soil Chemicals Analysis", p. 690.

3. Pehlivanoglou, Tsirambides, Trontsios, "Origin and Distribution of Clay Minerals", p. 61-73.

4. Biscaye, "Mineralogy and Sedimentation", p. 803-831.

### *Golden Pigment Sample*

Based on the XRD analysis, the golden pigment material used in Sabil Alkazlar's ceiling is gold (Au) mixed with traces of copper. The analyzed sample contains gypsum as a major constituent, in addition to anhydrite, dolomite, quartz, aluminum oxide, microcline, halite, yellow ochre and hematite (fig. 6). The SEM-EDAX of the same sample detected the presence of about 47% gold, 23% carbon, 18% oxygen, 7% calcium, 1% potassium, 1% quartz, 1% sodium, 1% iron and traces of copper, aluminum and magnesium (fig. 7).

### *Red Pigment Sample*

XRD analysis of the red pigment material in Sabil Alkazlar's ceiling revealed the presence of natural cinnabar (HgS). The sample also contains gypsum, anhydrite, dolomite, quartz, aluminum oxide, microcline, halite, lead sulfide, yellow ochre and hematite (fig. 8). The SEM-EDAX for the same sample detected the presence of about 30% carbon, 19% mercury, 17% oxygen, 15% lead, 6% sulfur, 3% calcium, 3% chlorine, 2% potassium, 1% sodium, 1% iron, 1% silicon, 1% magnesium and 1% aluminum (fig. 9).

### *Clay Mineralogy*

A plaster sample taken from the eastern corner of the Sabil's ceiling was separated for the identification of its clay mineral content. The untreated phase of the sample showed the presence of an unidentified clay layer at 7.26 Å and a layer of kaolinite at 12.28 Å. In the glycolated phase, the sample showed the presence of a smectite–illite mixed layer at 5.35 Å and a layer of kaolinite at 12.28 Å. In the heated phase kaolinite disappeared and a smectite–illite mixed layer was detected at 8.76 Å.

### *Binder Samples*

Four samples were analyzed using FTIR in order to identify the medium used in both the rendering layer and pigments in Sabil Alkazlar. Functional groups and wave numbers were measured. Animal glue binding was found on the FTIR charts. Based upon the results, it has been proved that rabbit skin glue was the paint medium used to mix and fix the pigments to the plaster, and it was also used to mix the components of the plaster layer together and fix them to the wooden ceiling (fig. 10). A standard sample of rabbit skin glue was prepared for comparison (fig. 11). The result was also emphasized by the UV analysis (fig. 12) which proved that the used medium was rabbit skin glue.

### *Cross Section*

The benefit of studying the cross-sections of the ground and paint layers reveals the painter's technique, the structure of the paint layers, the mixture of the pigment grains, the density of the colors and the construction of the layers which in turn helps to determine the artistic school to



which the monument belongs.<sup>5</sup> It is well-known that the decoration of ceilings is done through one of two techniques. The first and most common technique is the outlining of the design and the shape of ornamentation followed directly by the application of the pigments on the paint ground. The second technique which is rarely used involves applying different color grades and several pigments followed by coloring the upper layer with the desirable color grade. The latter technique is more advanced since it shows the experience and skill of the artist. In order to determine if the first or second technique was used, a bulk sample was taken from the ceiling's golden pigment (fig. 13a). The cross section of the golden sample (fig. 13b) revealed that the artist applied a thin sheet of gold over a thick layer of a red pigment which is composed of hematite and silica grains.

A bulk sample of the ceiling's black and red pigments was tested (fig. 14a). The black pigment was examined under a light microscope (fig. 14b). The results showed that the layered structure consists of 5 layers: the upper layer is black; the fourth and third layers are gray; the second is creamy and the lowest layer is red. XRD analysis revealed that the black pigment is bone black and the red pigment is natural cinnabar. Both pigments appeared in all layers with variable ratios. This sample confirmed that the artist used the multi-layer technique. The sample from the red pigment (fig. 14c) revealed the presence of a thin red upper layer followed by a thicker layer; the third layer is creamy in color and is thicker than the previous two layers. The final lowest layer is the thickest layer and it is the plaster layer which precedes the paint ground. It can be concluded that the painting layers of the Sabil Alkazlar's ceiling was composed of a wooden support upon which the plaster layer was composed of two layers (*gesso grosso* and *gesso sotile*), and a pigment layer carried out using the tempera technique.

## Discussion

### *Plaster and Soluble Salts*

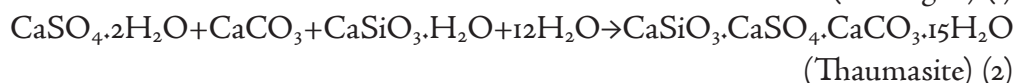
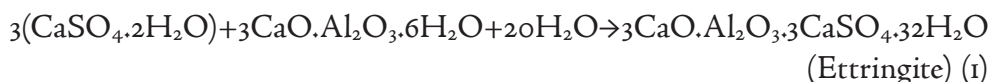
1. The XRD and SEM-EDAX analyses indicate that gypsum and anhydrite are the dominant compounds in the plaster layer. Two destructive expansive reactions are usually taking place in the presence of gypsum leading to the formation of ettringite and thaumasite. The latter forms in historic mortars and plasters by the reaction of gypsum and calcium aluminum hydrates in a moist condition.<sup>6</sup> Sabil Alkazlar is not immune of that effect because of its location in historical Cairo which suffers from the continuous increase of water table. The formation of ettringite or thaumasite leads to the complete destruction of the material.<sup>7</sup> Fissuring and cracking phenomena are widely observed in the plastered ceiling and walls of Sabil Alkazlar (fig. 9). The possibility of ettringite formation in historic mortars or plasters due to air pollution effect was previously discussed by Sabbioni<sup>8</sup> as showed in reaction (1) & (2).

5. Vasilescu, "Examples of Application of Some Modern Techniques", p. 39-48.

6. Böke, Akkurt, "Ettringite Formation", p. 1457-1464.

7. Van Balen *et al.*, "Environmental Deterioration".

8. Sabbioni *et al.*, "Atmospheric Deterioration", p. 539-548.



2. Charola and Centeno state that the dehydration of gypsum to hemihydrate does not occur on monuments.<sup>9</sup> This does not preclude that gypsum, particularly in cryptocrystalline forms, may partially dehydrate and eventually rehydrate giving rise to further contraction–expansion cycles.<sup>10</sup> This hypothesis is supported by the detection of both anhydrite and gypsum in the plaster layer of the Sabil Alkazlar, which may refer to a phase metamorphosis of the calcium sulphate compounds in that layer.

3. Anhydrite was detected abreast with gypsum in the rendering layer of the Sabil Alkazlar's ceiling. It is our position that the material used was anhydrite and the effect of the slight humidity started the anhydrite to absorb water molecules and return partly to gypsum in an uncompleted hydration process. This change is usually followed by an increase in the volume of anhydrite. During the transformation of anhydrite to gypsum, a volume expansion of up to 61% is possible. This develops hydration pressure which depends on the temperature and humidity of the air.

4. The presence of hematite and goethite (yellow ochre) in the plaster is due to one or more of the following:

a. The presence of crushed pottery which was added to the plaster to improve its thermal properties. The amount of iron present in Nile clays used in pottery making contains about 2.5% iron oxides.<sup>11</sup> Hematite as a natural component of the Egyptian red clay together with other iron oxides or oxy-hydroxides such as goethite [ $\text{FeO}(\text{OH})$ ] are responsible for the color of many soils.<sup>12</sup>

b. The crushed brick which is known as Horasan in Turkey and Homra in Arab countries was added to mortars and plaster prior to the advent of Portland cement to give them the desired characteristics of good cohesion, low porosity and high mechanical properties.<sup>13</sup>

c. Hematite and goethite pigments were added to the plaster layer to give the reddish color which provided a high covering power to the pigments used in the paint layer. It was also used to reduce the amounts of pigments used (cinnabar, bone black, gold) which have a higher economic value. This may also explain why the amount of phosphate and sulfur are low in the analyzed samples, as the analyzed samples are used in its bulk form (a plaster covered with the pigment material) in which the pigments are greatly diluted. On the other hand the amount of carbon is high because it is due to the presence of many sources of carbon such as pigment material and soot.

9. Charola, Centeno, "Analysis of Gypsum-Containing Lime Mortars", p. 269-278.

10. Charola, "Salt Deterioration", p. 10-24.

11. Eissa *et al.*, "X-ray and Derivatographic Studies", p. 775-778.

12. Smitt, Cox, Davies, "Salt Transport".

13. Böke, Akkurt, *Cement and Concrete Research*, 33, p. 1457-1464.

5. Orpiment was mixed with goethite and hematite which was added to the plaster layer for the aforementioned reasons listed above in point 4.

6. Crushed dolomitic limestone and sand were added to the plaster as filling materials.

7. The presence of aluminum oxide and microcline in the plaster indicates the presence of clay minerals.

8. Halite was detected in all examined samples. Growth of halite crystals appears also in most SEM micrographs. The water table in Cairo has risen significantly over the last decades and in a growing number of cases the water table has reached the ground floor of the monuments. An insufficient sewage system and the leaking of sewage have increased the ground water level. Salt solutions from the subsurface intrude by capillary rise in the walls of the monuments where salts, especially halite, precipitate on the plaster surface or in the pore spaces of the plaster close to the surface.<sup>14</sup> A number of factors influence salt crystallization damage in porous materials including: (1) pore size and porosity, (2) the nature of the salt including the ease with which it achieves high saturations by evaporation, variations in environmental temperature and the energy difference between the crystal and the pore wall, (3) the transport of the solution in terms of the supply rate of the solution and the evaporation of water and (4) strength, which is the material's resistance to crystallization pressure.<sup>15</sup> There is high possibility for plaster detachment due to the chemical and climatic effect, especially if the salts crystallize between the plaster layers or between the support and the plaster. Mortar and plaster falling and friability are visible phenomena in the Sabil Alkazlar. In addition, salt crystals are precipitated at the surface where they retain moisture on the wall and reduce the moisture gradient further.

### *Pigments and Medium*

9. The presence of bone black in the plaster is due to the penetration of the pigments into the plaster layer as the pigment was used in a diluted state.

10. Lead sulfide was detected in the cinnabar red sample as a consequence of the effect of air pollution, which will be discussed below.

11. Pure gold was used as gilding material in the Sabil Alkazlar wall paintings. Traces of copper were mixed with gold for solidification purposes.

12. Ottoman gilding of artifacts (tiling technique) included adding colors to the tiles, painting in red and black terracotta, and then coating the tiles with gold leaves.<sup>16</sup> The same layer structure was used in the gilding technique in the Sabil Alkazlar.

13. Rabbit skin glue was the medium used with pigments and plaster in the studied monument.

14. Fitzner, Heinrichs, La Bouchardiere, "Limestone Weathering of Historical Monuments in Cairo", p. 217-239; *Geological Society, Special Publication*, p. 205.

15. Benavente *et al.*, "The Influence of Petrophysical Properties", *Environmental Geology* 52, p. 215-224.

16. Gündes, Oktuğ, Özden, "Tales of Tiles in Ottoman Empire", p. 1-7.

## Clay Minerals

14. Because of the strong bonding between  $O^{2-}$  and  $OH^-$  of silica tetrahedral and alumina octahedral respectively, kaolinite does not exhibit swelling in water.<sup>17</sup> But with acid rain which is assumed in the polluted air of Cairo, kaolinite can form aluminum sulfate which provides the necessary nutrient for the sulfur oxidizing bacteria. This is particularly dangerous especially for the cinnabar in the Sabil Alkazlar. The decay effect in this instant depends on the presence of sulfur in this pigment.

15. Kaolinite can also form X-ray amorphous hydrated silicon dioxide which leads to plaster cracking as the silica crystals are harder than those of plaster. This process may also be followed by crystal deformation.

16. Smectite-illite mixed layers are able to swell more than kaolinite according to the 2:1 composition. When water is absorbed, swelling starts to appear on the wall paintings surfaces in microscopic cracks and fractures. This is shown in the SEM micrographs of the red pigment (fig. 9).

17. The presence of Na, Ca and Mg minerals in smectite encourage the formation of trona ( $Na_3HCO_3CO_3 \cdot 2H_2O$ ), thenardite ( $Na_2SO_4$ ), Mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ) and halite (NaCl) salts in connection with air pollution and microorganisms. These salts are very hygroscopic. They keep the walls and plasters of the Sabil Alkazlar wet for long periods. Macro scale experiments confirmed that mirabilite (crystallizing at  $RH > 50$  per cent) and thenardite (crystallizing at  $RH < 50$  per cent) tend to form subflorescence in highly localized areas under conditions of constant RH and temperature. This crystallization pattern is more damaging than that of halite, since halite tends to grow as efflorescence or by filling the smallest pores of the stones and plasters.<sup>18</sup>

18. When the clay minerals are impacted by the relative humidity, they dissolve or wash up leaving voids. Those voids are then filled with crystallized salts if they are internal or with dust and fine sand if they are external creating a deformation of wall paintings surface. This phenomenon can be seen all over the façade of the Sabil.

## Air Pollution Effect

Air pollution was first recognized in the 16th century by Leonardo da Vinci. Air pollution resulting from anthropogenic sources such as electric utilities, domestic heating, car and airplane transportation have increased the atmospheric concentration of inorganic and organic compounds in the form of gases, aerosols or particulate matter and their deposition on stone and wall paintings surfaces. The Sabil Alkazlar is surrounded with all these sources as it is located in the center of historic Cairo. In addition there is a neighboring bakery, whose impact is seen in the high ratio of carbon which was detected in all of the examined samples, even

17. Turer, "Effect of Heavy Metal", p. 421-425.

18. Rodriguez-Navarro, Doehne, "Salt Weathering", p. 191-209.

in those samples that have no black pigment material. The complex physical and chemical interactions of these agents with the mineral material have dramatically accelerated the decay of the building materials.<sup>19</sup> Particulate pollutants vary enormously in size and are especially dangerous to objects because they attract moisture and gaseous pollutants. Dust can be an abrasive agent. Removing dust involves washing, wiping, or shaking, all of which accelerates deterioration and increases the risk of physical damage to wall paintings.<sup>20</sup> Dust precipitated on the wall paintings of the Sabil (fig. 1) and in the micro cracks (fig. 9).

Sulfides in the air reacted with pigments such as lead white to form lead sulfide. This black pigment caused the graying of white areas according to the following reaction:  $Pb_2 + S_2 \rightarrow PbS$  (black). Other pigments may react with sulfides in a similar manner. For example, azurite blue ( $2CuCO_3 \cdot Cu(OH)_2$ ) turns brown or dark green due to the formation of black copper sulfide. Little is known about the effects of air pollution on hydraulic mortars and almost no quantitative data are available. In fact, only ground and sea water are considered as the possible sources of atmospheric sulfate, while the effects of sulfur (wet and dry deposition) on such materials are neglected.<sup>21</sup> The presence of ammonia in the atmosphere increases significantly the oxidation efficiency of  $SO_2$  due to increased solubility of this gas. With regards to the sulfur dioxide influxes on buildings and structures, the presence of edges and corners increases turbulence and exposure to pollutants. Stalactites and high relief decorations as basic elements in Ottoman architecture help air pollutants to precipitate upon the walls and facades in the Sabil Alkazlar. Thus the air pollutants start to act as a decay factor in reaction with moisture.

Cairo is a megacity with high air pollution which can vary greatly from one day to another. Across the seasons, there are different sources of pollutants as well as natural factors that determine their impact on the urban areas. Each of these factors needs to be considered for an integrated approach to the problem.<sup>22</sup> Air pollution is also a basic source of salts impacting the historic buildings in Cairo.<sup>23</sup> Halite that was detected in the ceiling plaster of the Sabil Alkazlar is a result of these sources. The effect of the soluble salts depends on:

- a. The solubility factor of the salt and its ability to transfer from the groundwater into the building materials.
- b. The porosity of the building materials.<sup>24</sup> Chemically, salts in reaction with the pigment components play a role as a catalyst in the discoloring phenomenon (fig. 1).

The outdoor air pollutants, such as sulfur dioxide and ozone, have been recognized as threats to cultural property for a long time. Surveys of air pollutant levels inside buildings and

19. Warscheid, Braams, "Biodeterioration of Stone", p. 343-368.

20. Boston Museum of Fine Arts, Department of the Interior, Departmental Manual, Museum Property Handbook, (411 DM, Vol. I), Chapter 5 Environmental Agents of Deterioration, 1993, USA.

21. Van Balen *et al.*, *European Commission*.

22. Nakashima *et al.*, "Making Cities Work".

23. Fitzner, Heinrichs, La Bouchardiere, *Limestone Weathering*, p. 217-239.

24. Moussa *et al.*, "Impact of Soluble", p. 292-308.



of the corresponding indoor/outdoor concentration ratios have been carried out.<sup>25</sup> Among air pollutants likely to be found in Cairo, lead undoubtedly deserves attention. Lead is ubiquitous in indoor air in Cairo and historic buildings are no exception including the Sabil.<sup>26</sup>

The values of atmospheric lead in four different areas—residential, traffic, industrial and mixer—in Cairo from 1999 to 2002 were measured and the results varied from 1.08 µg/m<sup>3</sup> in residential areas to 14.05 µg/m<sup>3</sup> in industrial areas. It was 1.80 µg/m<sup>3</sup> and 1.26 µg/m<sup>3</sup> in traffic and mixed areas respectively.<sup>27</sup>

Lead originates outdoors and has also been detected in the present study in the Sabil Alkazlar on its wall paintings. The effect of atmospheric lead on cinnabar has been detected for the first time. In the red sample, lead was detected by SEM-EDAX. In addition lead sulfide was detected by the XRD analysis of the same sample. Cinnabar, in this case, is darkened by contact with lead in the air due to the formation of black lead sulfide. In the case of impure cinnabar that contains free sulfur, the darkening phenomenon can be quickly noticed. In water color paint films, vermilion is often seriously blackened.

## Conclusions

Based on the results of the aforementioned analyses, the plaster in the Sabil Alkazlar is anhydrite plaster mixed with sand and dolomite and the anhydrite has been partially hydrated into gypsum. Aluminum oxide and microcline were also detected in the plaster to indicate the presence of clay minerals. Black pigment in the Sabil is bone black. Red pigment in the Sabil Alkazlar is natural cinnabar, while the golden pigment is pure gold with traces of copper for solidification purposes of the gilding material. Wall paintings in the Sabil Alkazlar were applied using the multi-layer technique which is one of the techniques used in Ottoman paintings. *Gesso grosso* and *gesso sotile* style were used and the tempera technique was applied used rabbit skin glue medium.

Pigment materials in the Sabil Alkazlar are highly affected by soluble salts, air pollution and clay minerals present in building materials. Sodium chloride (halite) was detected in the analyzed samples as a consequence of the effect of the continuously rising water table in Cairo. Atmospheric lead was found to react with the free sulfur in the cinnabar to form lead sulfide which is responsible for the darkening of these pigments. Clay mineral separation of the plaster layer showed that the plaster contained kaolinite in addition to a smectite-illite mixed layer. The wall paintings in the Sabil Alkazlar are deteriorating due to the action of these compounds especially in the saturation and desiccation cycles. Swelling of clay minerals results in a net of micro cracks on the painting surface in the Sabil Alkazlar.

25. Charola, "Review of the Literature".

26. Moussa, "Assessing the Decay Agents".

27. Sharaf *et al.*, "Evaluation of Children's Blood", p. 414-419.

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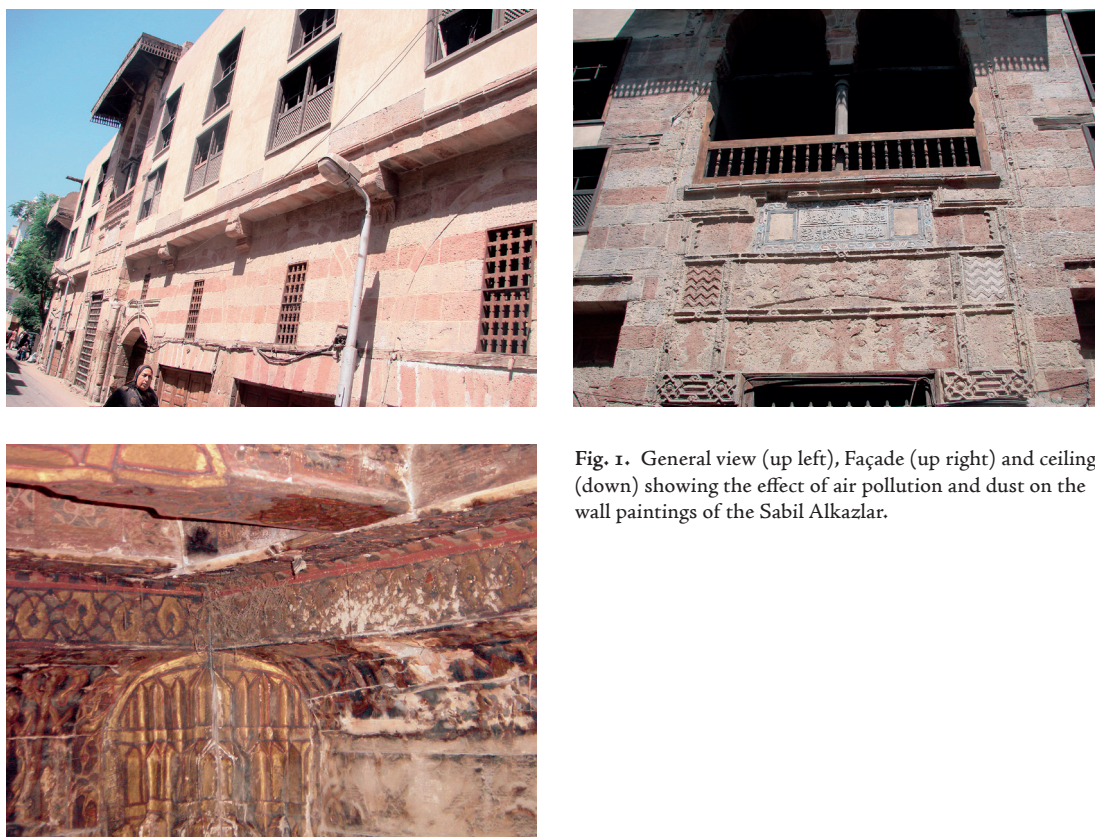


Fig. 1. General view (up left), Façade (up right) and ceiling (down) showing the effect of air pollution and dust on the wall paintings of the Sabil Alkazlar.

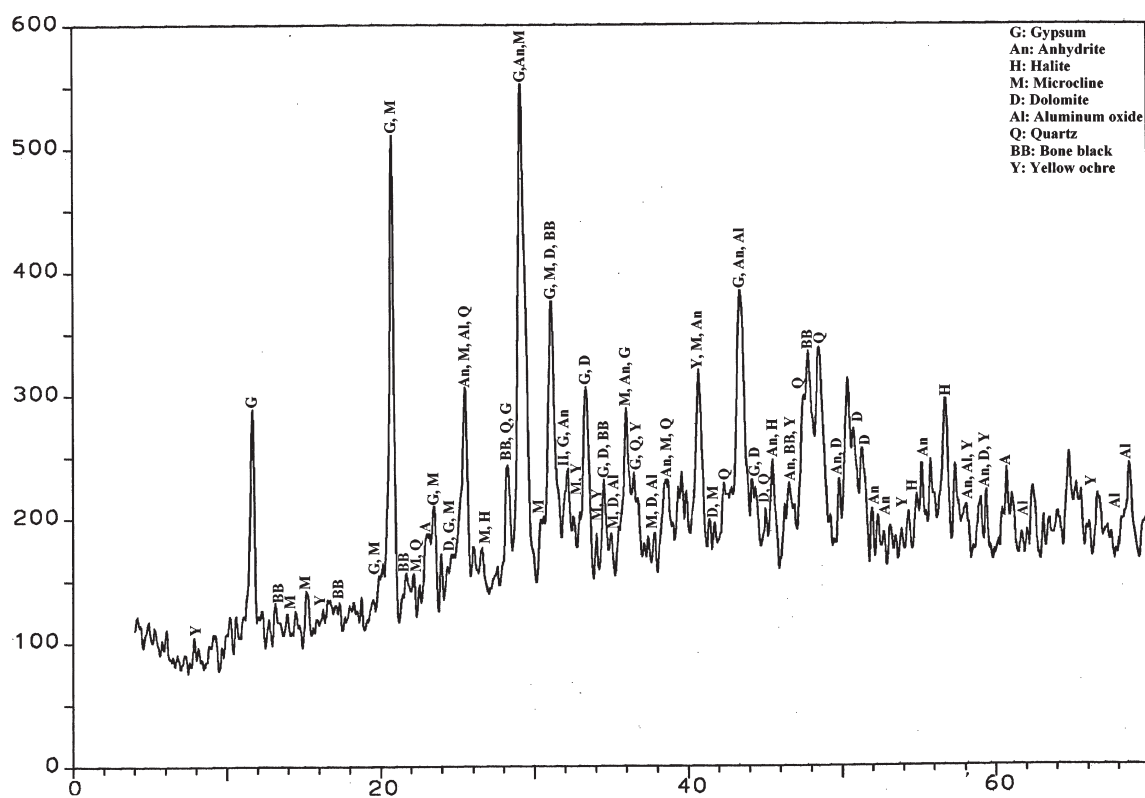


Fig. 2. XRD pattern of the studied plaster sample from the Sabil Alkazlar.

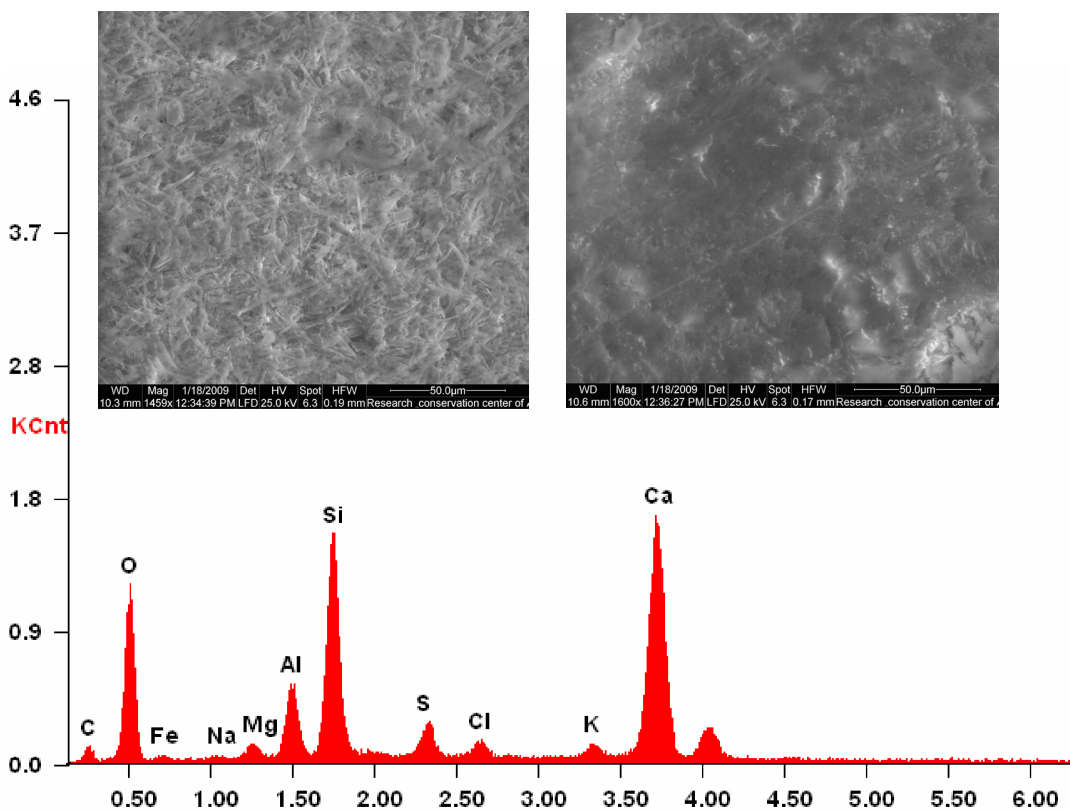


Fig. 3. SEM-EDAX spectra and micrographs of the studied plaster sample from the Sabil Alkazlar.

The micrograph (left) shows the gypsum crystals which are the main components of the plaster, while the micrograph (right) shows the growth of anhydrite and halite crystals inside gypsum.

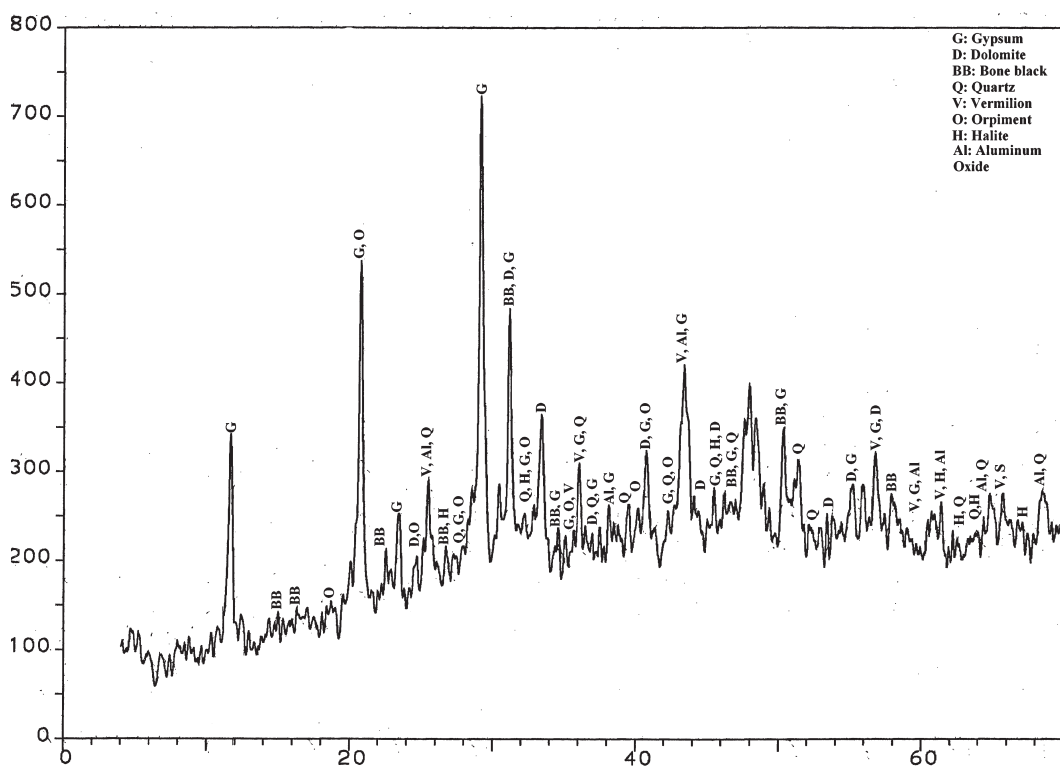


Fig. 4. XRD pattern of the studied black pigment sample from the Sabil Alkazlar.

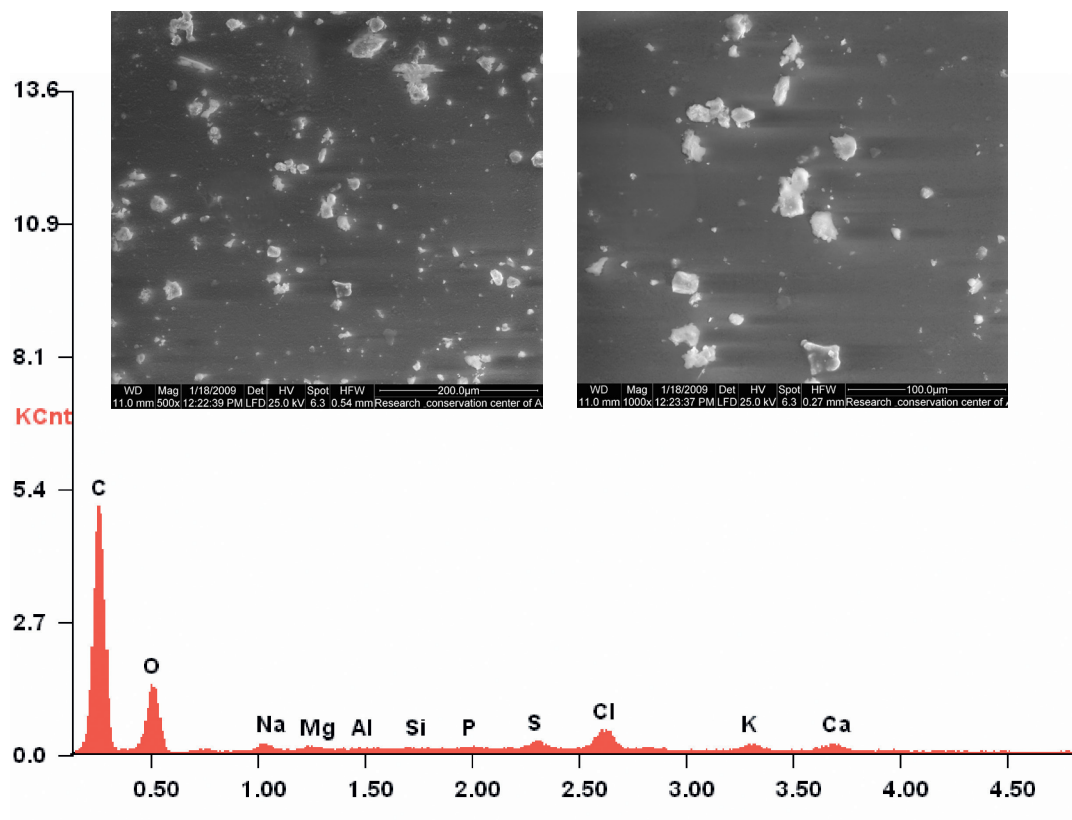


Fig. 5. SEM-EDAX spectra and micrographs of the studied black pigment from the Sabil Alkazlar. The micrographs show the growth of halite crystals upon pigment surface (efflorescence).

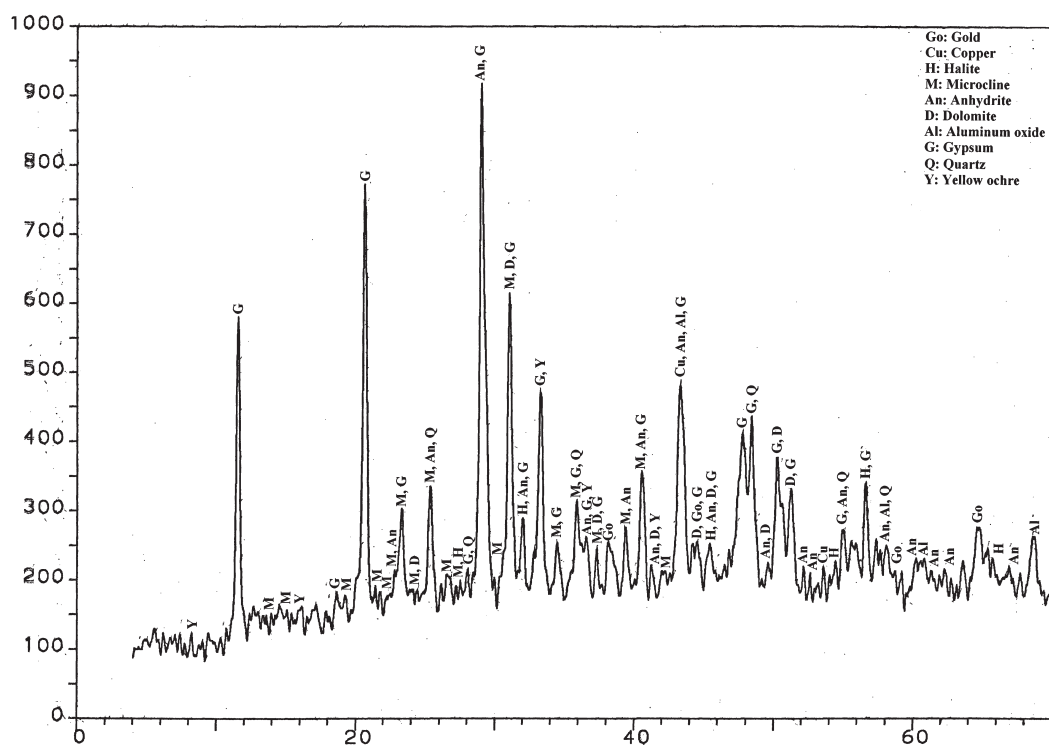


Fig. 6. XRD pattern of the studied golden pigment sample from the Sabil Alkazlar.

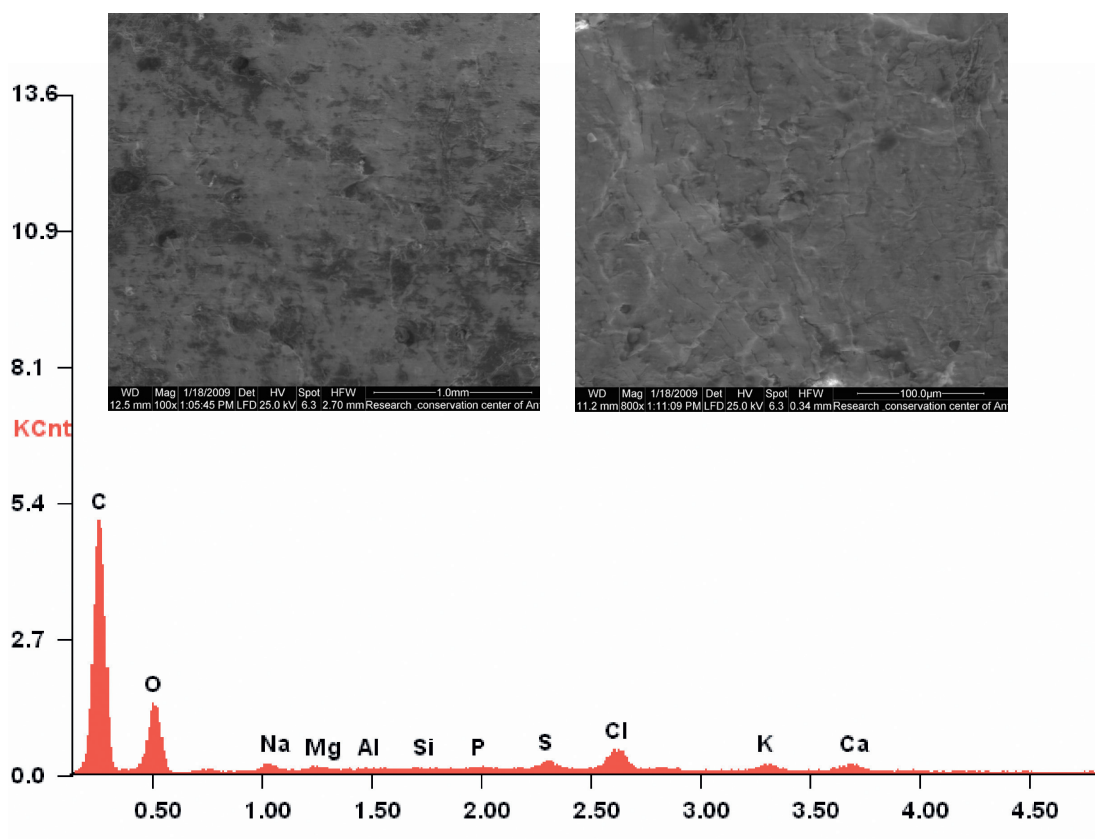


Fig. 7. SEM-EDAX spectra and micrographs of the studied golden pigment from the Sabil Alkazlar. The micrographs show the presence of blisters which can be explained due to hammering of gold leaves.

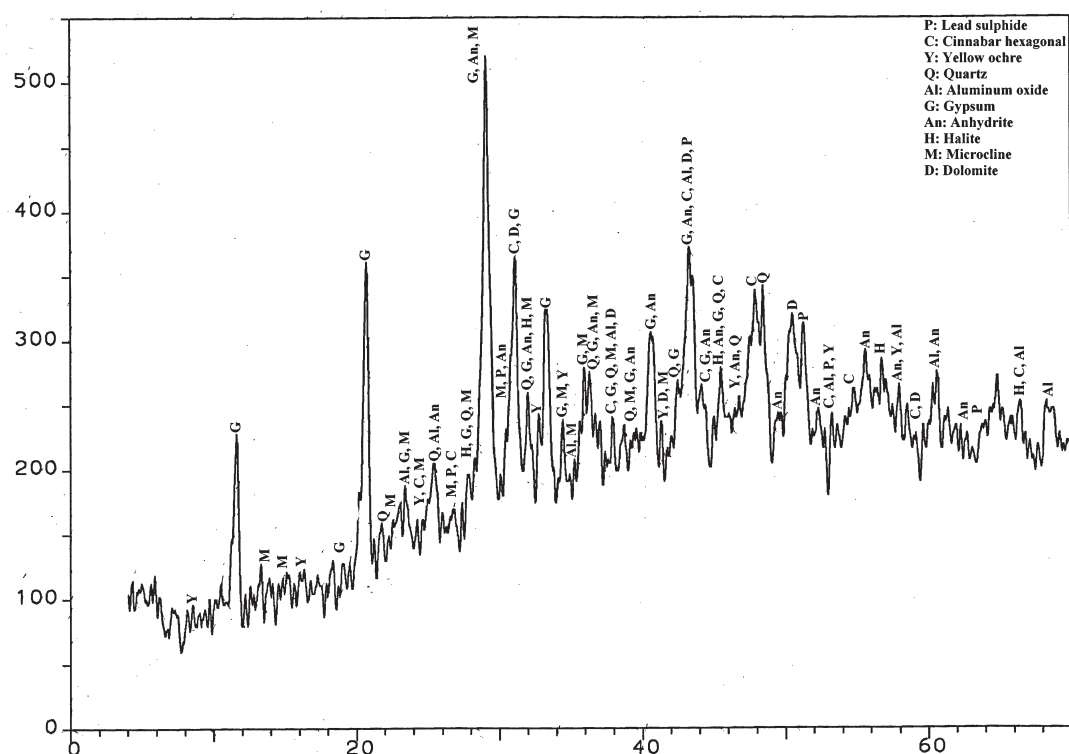


Fig. 8. XRD pattern of the studied red pigment sample from the Sabil Alkazlar.



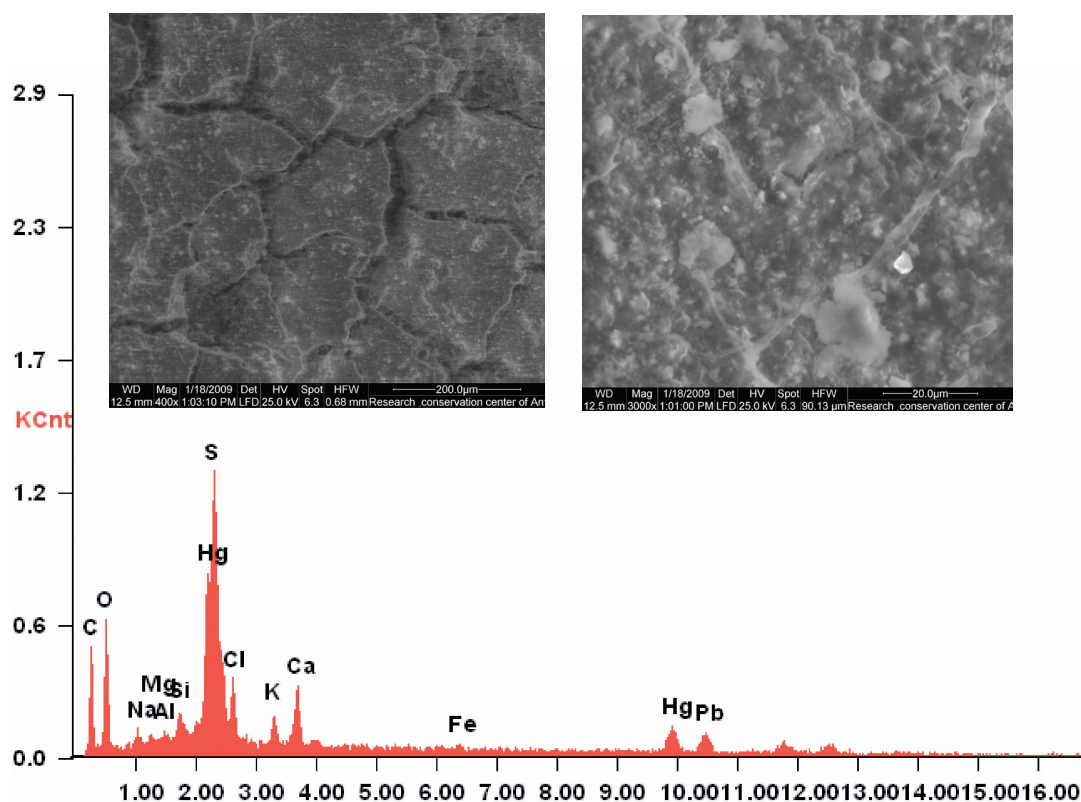


Fig. 9. SEM-EDAX spectra and micrographs of the studied red pigment from the Sabil Alkazlar. The micrographs show a net of micro cracks in the pigment surface due to clay minerals effect; these cracks are filled with salt crystals and dust.

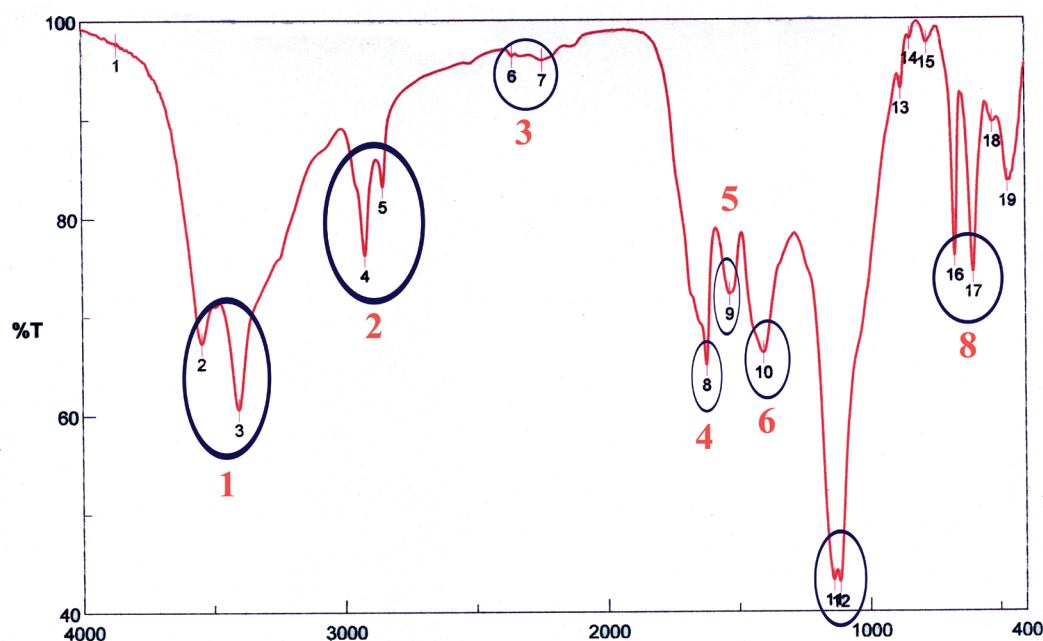


Fig. 10. FTIR spectrum of the binding medium used with the red pigment in the Sabil Alkazlar.

[1] Asymmetric and symmetric OH stretching bands of both animal glue and gypsum (splitting of the band is due to presence of gypsum). N-H stretching band of animal glue is over lapped by OH bands.

[2] Asymmetric and symmetric CH stretching bands of aliphatic groups of animal glue.

[3] Combination or overtones bands.

[4] Carbonyl stretching band of animal glue (amide I) + S=O stretching of  $\text{SO}_4^{2-}$  of gypsum.

[5] Combination of C-N stretching band and N-H bending band (amide II) of animal glue.

[6] C-H bending + OH bending band.

[7] Asymmetric  $\text{SO}_4^{2-}$  stretching band of gypsum.

[8]  $\text{SO}_4^{2-}$  bending band of gypsum.

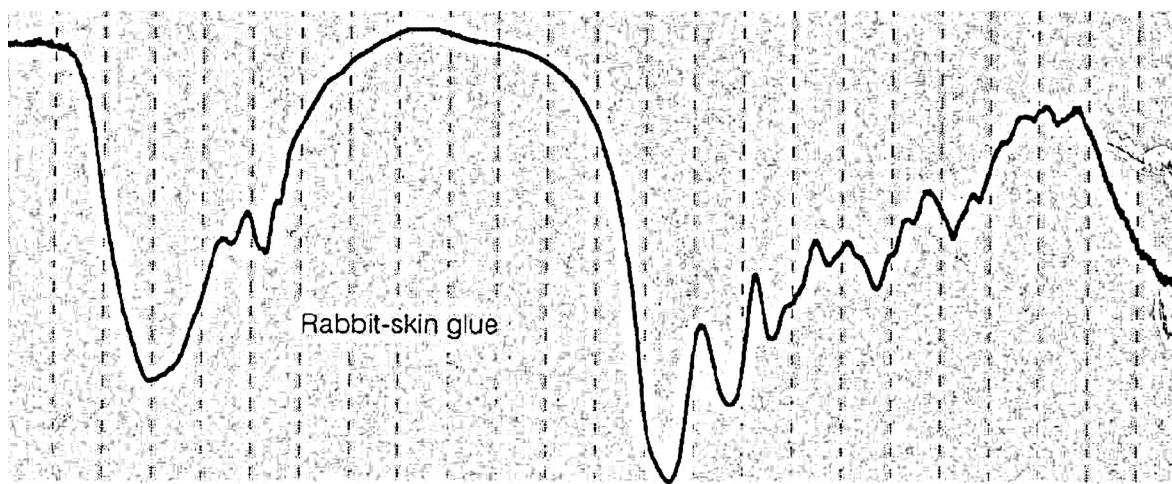


Fig. 11. FTIR standard of rabbit skin glue.

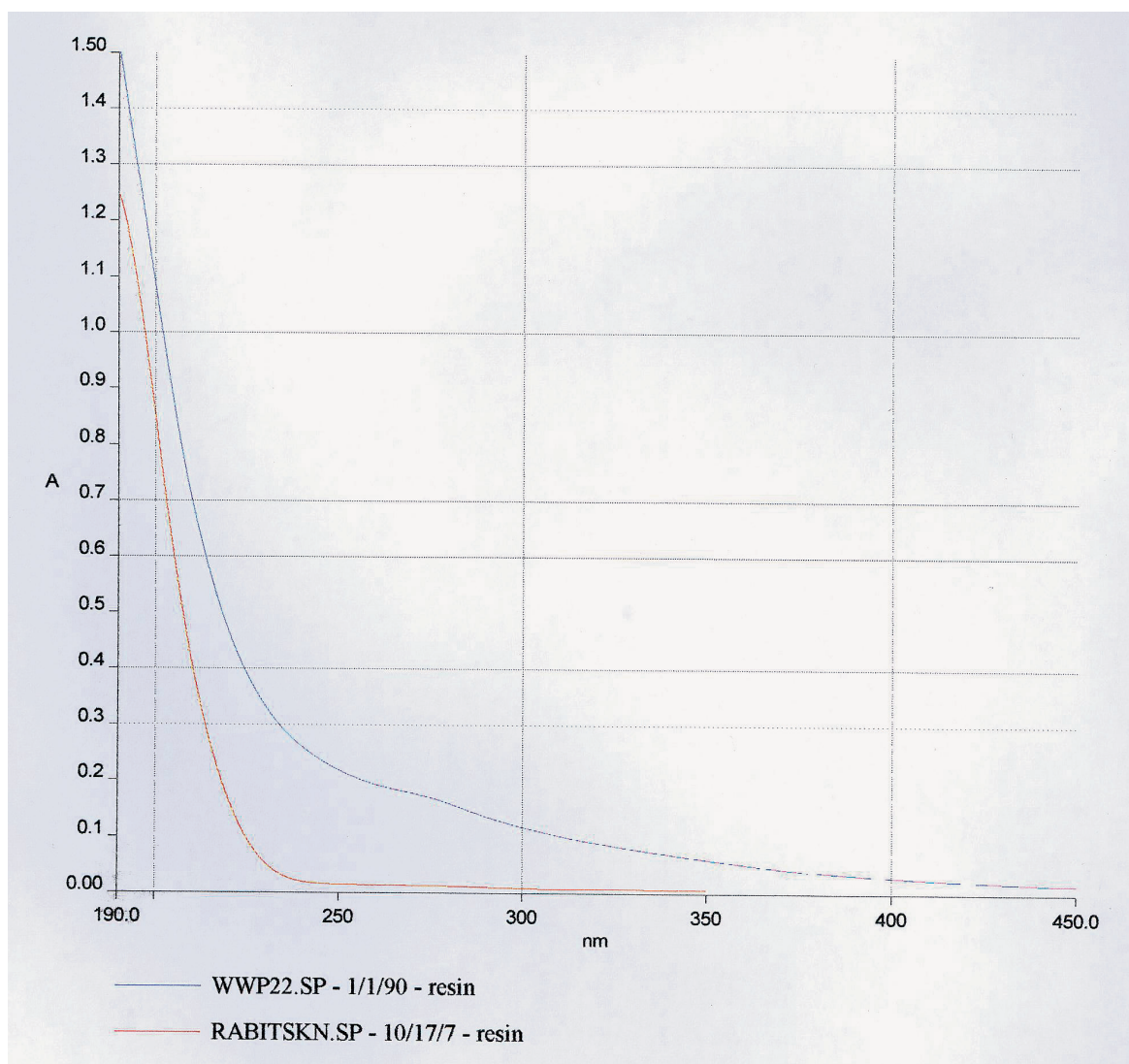


Fig. 12. UV spectrum of the binding medium used with the red pigment in the Sabil Alkazlar, proves that it is rabbit skin glue.

[1] Analyzed sample.

[2] Standard of rabbit skin glue.



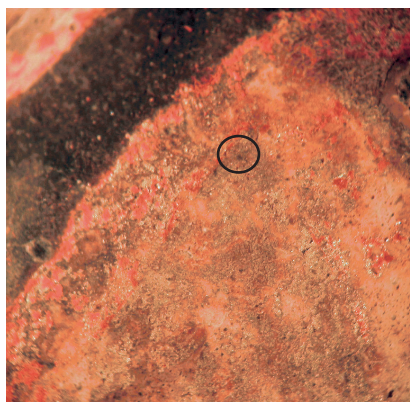


Fig. 13a. Shows the bulk sample of the ceiling's golden pigment from which the cross section was prepared (the cycles shows the exact place).

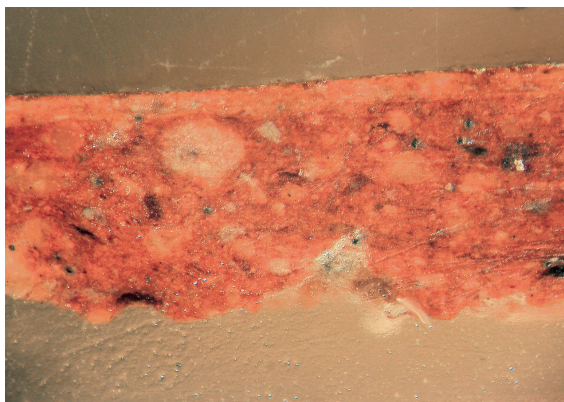


Fig. 13b. Cross section of the golden pigment in the Sabil Alkazlar (125X).



Fig. 14a. Shows the bulk sample of the ceiling's black and red pigments from which the cross section was prepared (the cycles shows the exact place).

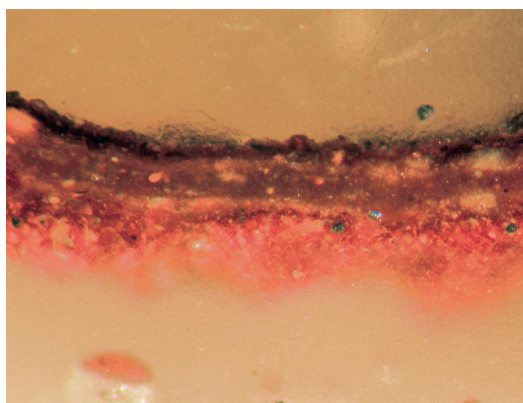


Fig. 14b. Cross section of the black pigment in the Sabil Alkazlar (125X).

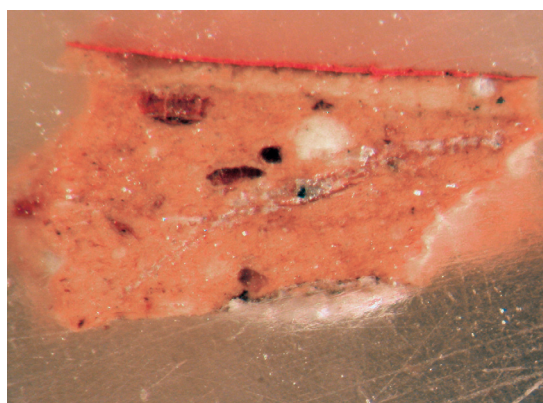


Fig. 14c. Cross section of the red pigment in the Sabil Alkazlar (125X).