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DECAY OF EMERALD GREEN PIGMENTS ON EASEL PAINTINGS

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Abstract:

Emerald green is one of the pigment of its composition arsenic, copper It is usually used in coloring the areas of trees and clothing, the color by ageing and exposure to inappropriate environmental conditions (temperature, humidity, and ultraviolet) turn Dark brown color caused of changing chemical and structural composition of the paint layer, The changing in colored is not only from medium damage, but there are factors that play an auxiliary role with medium damage, The medium is decomposed and free fatty acids interact with metal ions in emerald green, which leads to the formation of mineral soap that leads to the instability of color particles , the loss of contact between of them it, decompose it and forms a decomposition product of arsenic trioxide(As_2O_3), Which migrates on the surface and interacts with pollutants and discolored green. This article aims to study of the phenomenon of emerald green color change on an oil painting from the 19th century in Al Jazeera museum by the French artist Ad.Monticelli (1824-1886), using an examination by Micro scope Om , PLM ,analysis FTIR , XRD ,and SEM-EDX,. The Analytical XRD analysis showed that the archaeological color sample from emerald green, which has different mineral forms of arsenic damage, such as Copper hydrogen $AsCuHO_3$, lead Arsenite [$Pb_2As_2O_5$], and Clinoclase [$Cu_3AsO_4(OH)_3$] is a mineral water arsenic copper and Arsenicsulfide As_2S_3, FTIR study showed the decomposition products of emerald green, as monocarboxylate, calcium oxalate salts, and arsenic trioxide [As_2O_3].

1. Introduction:

Emerald Green chemical composition is (Copper Trihydrate , $Cu_3(AsO_4)_2.4H_2O$), a common green dye first production by Willem Sattler in 1814, is pigments containing arsenic [1] . It was commonly used in oil painting in the coloring of trees and rocks in the nineteenth century and was favored by artists such as Monet, Cézanne and Van Gogh and Monticelli, [2], who used a mixture colors such as Emerald green mixed

with goethite, azurite, lead white by technique's impasto using a wet technique in wet mixed paint of several different colors [3].

The analyzes performed on his paintings, indicated that the artist has many of his works carry out by impasto technique suffer with fragility and drought and [4] Green is unstable in oil painting, turn to browns, and sometimes is accompanied by other signs of deterioration, such as bleaching and fading.

The color deterioration due to the presence of some elements in its chemical composition, such as copper and arsenic, as they play an important role in the decomposition of organic ingredients and may stimulate the formation of mineral soap [5] Copper ions reduce the bonding of colors with the medium, [6]and copper ions interact with fatty acid groups which is resulting from break down the medium and forming metal soap. [7] These types of copper are chemically unstable and also active, pushing the copper cations moving towards the surface layers where they are exposed to the atmosphere gases, may be interact with hydrogen sulfide to form black copper sulfide [8] which lead to turn green to a dark color and gives a brown color [9]. Darkening also occurs when the painting is exposed to a source that contains light in the visible light area (530-560 nm),[10] because it leads to break down the bonding of the glycerides and are released metal ions result from light oxidation [11]. Darkness sometimes occurs as a result of an increase in the refractive index of the oil medium during the aging [12].

2. Case Study:

2.1. Description of oil Painting of Ad.Monticelli- (1824-1886), in Al Jazeera museum :

The case study used a oil painting applied on wooden, Size (72 cm x 51 cm), Stored in the Al Jazeera museum No. 881 record a museum, The Panel is belonging to the late nineteenth century is called "Lesson Gram", which is a landscape as fig. (1) of painter Adolf Joseph Thomas Monticelli (October 14, 1824 - June 29, 1886) is a French painter for the generation that preceded the Impressionists and Monticelli adopted the practice of introducing elegant fashion characters into his landscape [13].The artist is distinguished in a technical style that uses a greater percentage of pigment., And also a mixture of different colors in the tone of the unit, as a different tone by building thicker and more prominent paint. [14].

Figure 1: shown the panel Measured (72 cm x 51 cm) with detail from the higher left illustrating the darkened and cracked surface of in green area

3. Materials and methods: -

3.1. Materials:

An analytical study was conducted for a sample falling from the edges of the green in the trees area from the upper left side, the visual examination was done using some lenses and photography in natural light and diagonal light using a Sony camera with 100x magnification, The Examination was done using optical microscopy (OM) with a Nikon digital 56 camera DMX 1200F, a mercury lamp, and a halogen lamp, as well as Polarized optical microscopy (PLM) using Axioscope 5 (Zeiss, Oberkuschen, Germany) which is used as a stereo microscope and also for multispectral imaging (, in UV light and in visible light), [15].The sample was prepared as a cross section where a slice of glass was cut on a scale 4 mm x 26 mm x 1 mm then the sample was immersed in an epoxy (No. 27-751) and the mixing ratio (100 ml epoxy: 2 ml hardened) and after hardening and drying the epoxy, the samples are polished with sandpaper (2400, 4000 sizes) moistened with water to obtain a smooth and good surface[16] , The analysis and the examination was carried out using Scanning Electron Microscope (SEM(JEOL 5410 (Japan) magnification up200k with (EDX) Analysis (England) and the creation of a map of the elements on the surface , and The analysis (FTIR) model Cary 630 FTIR spectrometer in the spectral range from 4000 cm $^{-1}$ to 400 cm $^{-1}$[17]

3. Results :-

3.1. Visual examination and Photography:

The examination showed the accumulation of dust on the surface and a change in the color of green to the brown color, especially in the trees area, fig. (2 a) and examination by the oblique light clarified the irregularity of the surface and Opacity was observed, bleaching spots on the surface in parts of the trees in the panel on the left side at the top as fig. (2b).

Figure 2 (a,b) : (a) : shown change in the color with detail from the higher left illustrating the darkened , (b): **shown bleaching spots on the surface and cracked**

3.2. Examination by stereomicroscope:

Green layer appears weaken and cracked and loosed parts of color and it was changed to dark browns and black. Distortion of painting, some areas have white spots and some green areas have different stages of color change as fig. 3 (a-b).

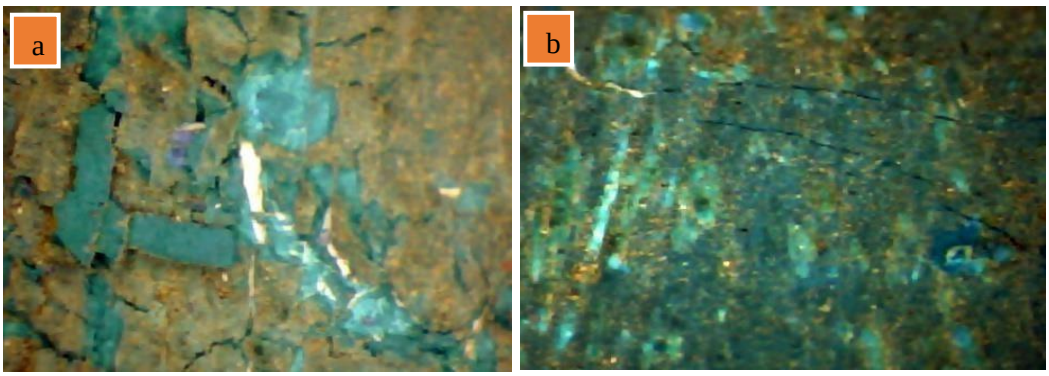


Figure 3 (a,b):(a): shown bleaching spots on the surface and cracked weak and has cracks and loss of color,(b):shown different stages of color change

3.3. Examination by PLM (plane polarized light)-:

The examination showed that the panel layers are four containing a thick first layer of calcite ($CaCO_3$), mixed with coarse particles of lead oxide covered with a thicker less second preparation layer containing calcium carbonate and a little lead and iron and a third layer of colors and a layer Fourth of the varnish and the layer of colors appeared deteriorating , irregular , changed to black , brown and white spot of different sizes and observed in the ground layer large spot and circular transparent resembling bubbles and some particles of blue azurite appear and some round particles of lead , the green pigments are used in admixture with azurite for the deepest greenish blues of the tree , Wherever the copper pigment occurs, the paint appears dark as Fig.4 (a, b)

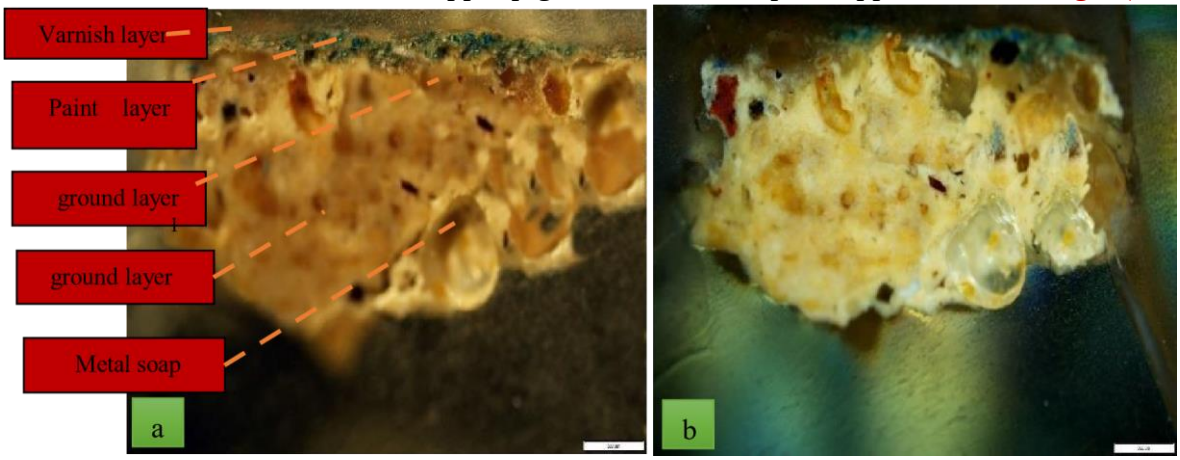


Figure 4 (a, b) Photomicrograph of Cross-section image showing the green paint structures of four layers from the bottom to top coarse ground, fine ground, paint layer and varnish layer (a) under light under PLM (BMM, (b) under UV light

3.4. SEM attached to EDX :-

The results of SEM and EDX are recorded in the table. (1), in addition, fig. (5), and fig. (6- a, b, c, d), and fig.7 showing the chart, photo microphotograph that illustrating the elements of the paint sample.

samples

Table (1) results of EDX analysis of the sample

C	O	Na	Al	Ca	Fe	Cu	As	Au	Pb	Mn	s	Au
45.32	25.34	.56	1.4	5.47	2. 24	9.22	5.32	0.61	2.12	.02	2.4	0. 7

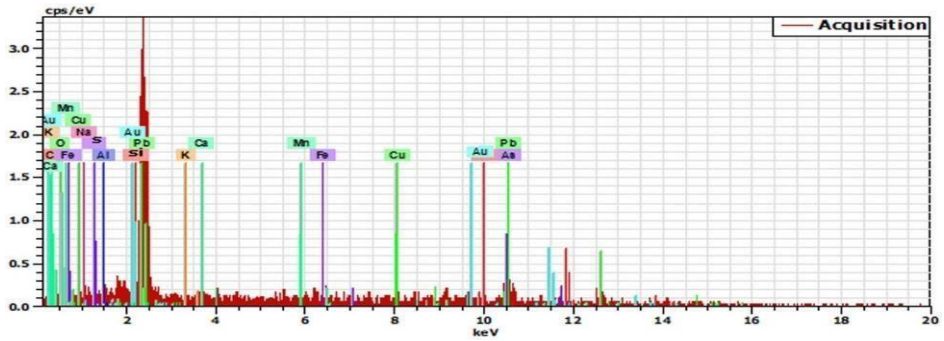


Fig. (5) EDX spectrum of spot analysis from a green sample including copper oxide and arsenite oxide indicating Emerald green pigment

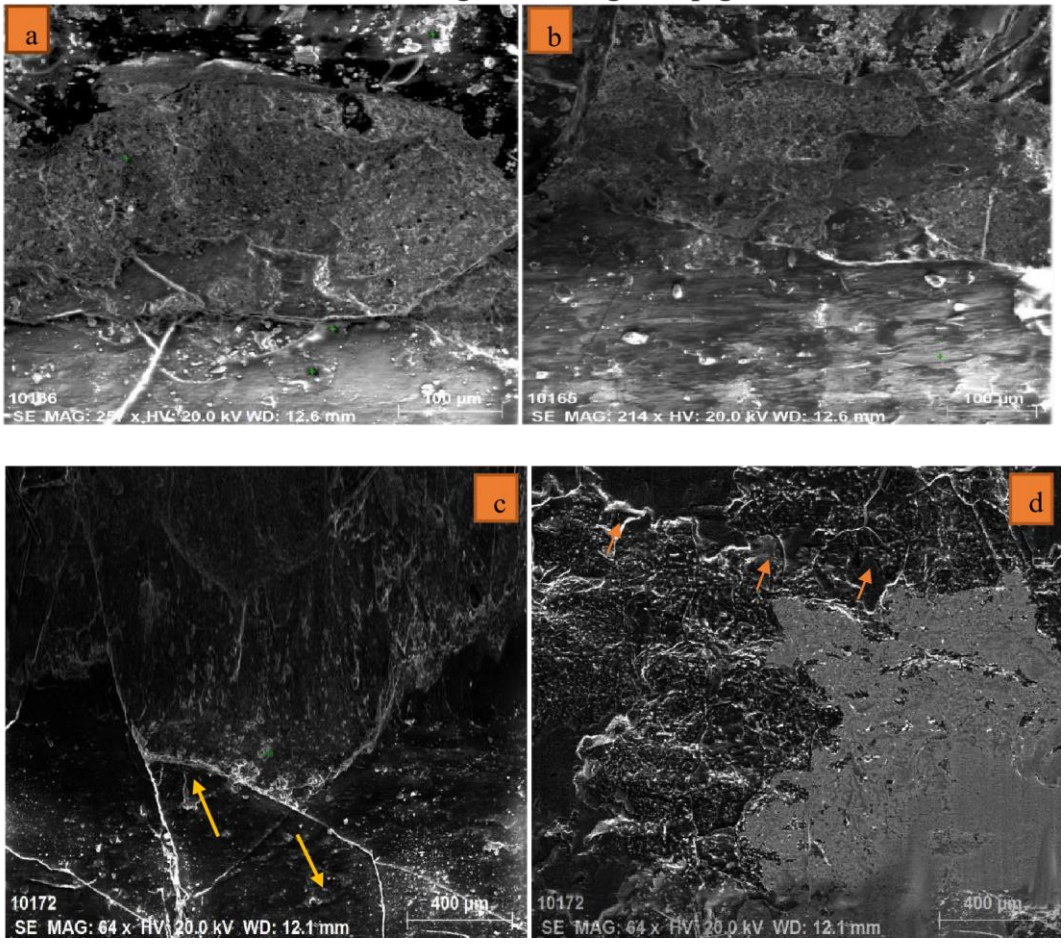


Fig. (6- a, b ,c, d)SEM image1000X (a) showing decomposed green Paint layer, (b) is detail of the previous image (c) showing Uneven surface and surface corrosion and Cu- grains(arrow) (d) is detail of the previous image detioration all layers and Cu- grains (arrow)

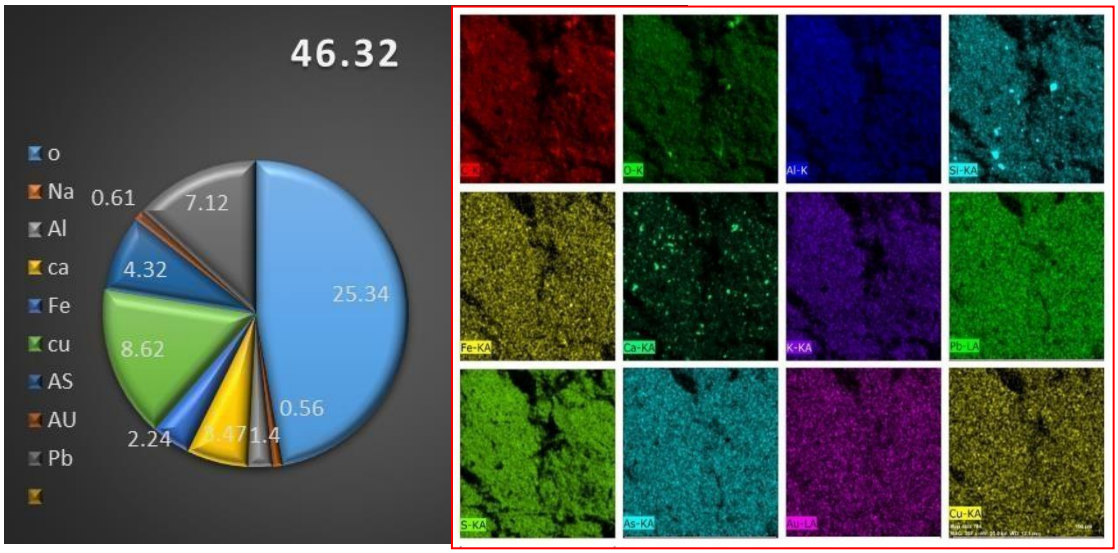
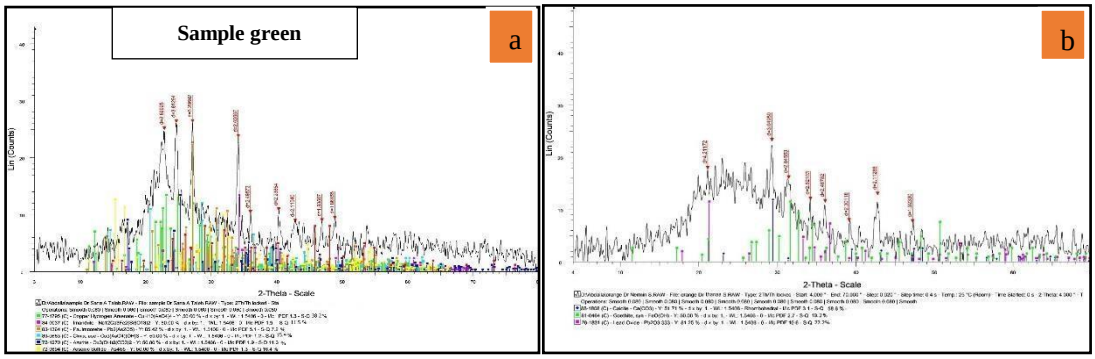


Fig.(7) Elemental maps of green sample showing element Al, Fe, Ca, k. Pb, S, AS,Cu .

3.5. - X-ray diffraction analysis:

The XRD analysis of the green sample showed as Fig. (8-a, b) the presence of different mineral forms of arsenic compounds Fig. (8-a) as, copper hydrogen arsorite$AsCuHO_3$, was found percentage38.2%.accompanying the lead arsenic $Pb_2As_2O_5$ a percentage of 7.2%, Clinoclasee $Cu_3ASO_4(OH)_3$ a percentage of 15.4%,azurite$Cu_3(CO_3)_2(OH)_2$ a percentage11.3 %, Imandrite $Na_{12}Ca_3Fe_2Si_{12}O_{36}$a percentage 11.5% and arsenic sulfideAs_2S_3a percentage 16.4%., XRD analysis of the ground sample as the fig. (8-b) the presence of calcite $CaCO_3$ percentage 58.6%, Goethite (α-FeOOH)percentage 19.2%, and lead oxide PbO percentage 22.2%,



Figs. (8- a , b) XRD analysis shows different mineral forms of arsenic compounds (a) the green sample (b) the ground layer sample.

3.6. –FTIR Analysis:

The analysis FTIR as fig (9 –a ,b)showed for the green sample that the medium used is the linseed oil which showed as in Fig.[9 -a] for the presence of the O-H stretching band absorption groups at the wavelength 3416.125 $cm^{-1}$and the aliphatic CH_2 (asymmetric groups) at the wavelength 2922.441cm^{-1} and the carbonyl absorption groups C = O at the wavelength 1743.773 cm^{-1}, also the presence of the ester

absorption group (C-O) and the absorption group (CH_2)at the wavelength 1175.682 cm $^{-1}$, The presence of a metal carboxyl absorption group (COO) at wavelengths 1554.559 cm $^{-1}$, 3416.125 cm^{-1}, an strong absorption group(As-O) at a wavelength of 647.847 cm $^{-1}$, an absorption group (As-O) medium at a wavelength of 769.182 cm $^{-1}$and the group OH at the wavelength 1461.175 cm^{-1}and the group to absorb alcohol into the oil at the wavelength 1175.682 cm $^{-1}$, as a result of degradation [18] Calcite with a small participation of quartz were found [19] at the wavelength of 1074.299 cm^{-1}and the absorption group $CaCO_3$ at the wavelength 1743.773cm^{-1} which proves that the ground is calcium carbonate ,the carboxylate group appears at the wavelength of 1697.403 cm^{-1} and the sulfate absorption group at the wavelength of 647.847 cm^{-1}, the adhesive on the ground is rabbit skin glue [20] due to the presence of the amide 11 group(CN stretching and NH bending) at wavelength 1554.559 cm^{-1} and the presence of the group (Amide I, C-O stretch), at wavelength 1697.403cm^{-1},the presence of an absorption group of copper-green color [21] at wavelengths1073.299, 1545.559 and 1461.157cm $^{-1}$,Cerussite appears at the wavelength 2040.125 cm $^{-1}$, the analysis showed as in Fig.[9 -b]the presence of goethite v (Fe-OH) and (-O-Si-) at the wavelength of 771.647 cm^{-1},the absorption group of silica and clay (Si-O-Si) at wavelength of 730. 1074 cm $^{-1}$[22] and the presence of the quartz absorption group at a wavelength of 771.647 cm $^{-1}$, The presence of the iron oxide absorption group at a wavelength of 754.332 cm $^{-1}$ and the presence of a group of copper acetate (Cu (CH_3COO) $_2$. H_2O) [23] at Wavelengths 1074 cm $^{-1}$,1337.023cm $^{-1}$, .630 1458 cm $^{-1}$ and 1652.219 cm $^{-1}$.The presence of a strong absorption group for calcium oxalate(C = O asymmetrical stretching)[24]at the wavelength 771.647 cm^{-1} and a strong absorption group (C – C symmetrical stretching) at the wavelength 1337.023cm^{-1}and a strong absorption group (OC = O asymmetrical stretching) at the wavelength 1604.64 cm $^{-1}$, The presence of the absorption group of calcium carbonate and lead at the wavelength 874.222 cm^{-1} and the presence of the absorption group of carbonate at wavelength1458.630cm^{-1}[25],The presence of the absorption of $PbCO_3$ and hydrocerussite (2PbCO. 3Pb (OH) $_2$), at wavelength 2412.542 cm^{-1}[26] Varnish analysis from mastic showed the presence of the OH absorber group at the wavelength 3429.199 cm^{-1} and the absorption group CH(CH_3) at the wavelength 2922.330 cm^{-1} and the absorption group C-H at the wavelength 2872.45 cm^{-1} and the OH absorber group at the wavelength 2513.070 cm $^{-1}$ and the group Absorption C = O str at wavelength 1743.340 cm^{-1} and CH bend absorber at wavelength 1458.630 cm^{-1}.

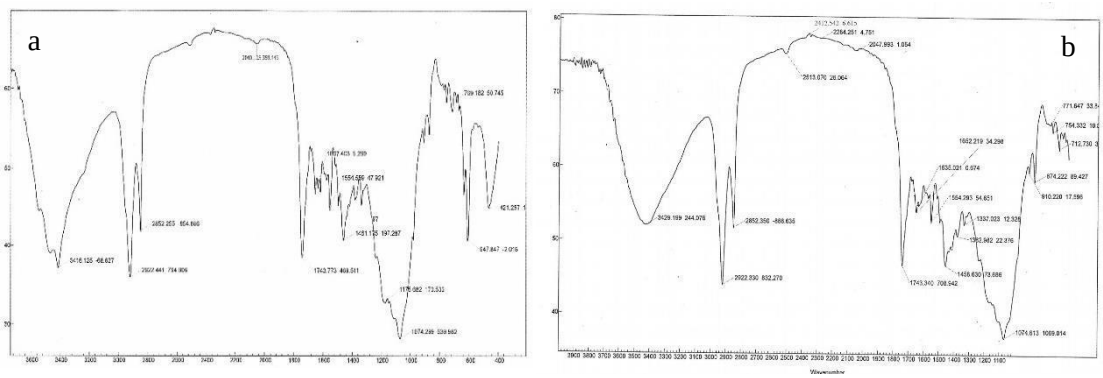


Fig. (9- a ,b) FTIR spectrum (a) showing characteristic vibrations of Emerald green (b) showing characteristic vibrations of ground

Discussions:

The results of examinations of the antique painting, showed cracks due to the shrinkage of the ground layer that contains white lead, which, it is suggested that it is not completely dry before applying the paint and because the application of the color layers is thick (Impasto) without completely dry, Surface examination showed by cross section The artist Montessori was using layers of not dry colors on over of each other and could contain up to three different colors. The color layers are affected by changes in temperature and relative humidity so the color decomposes and weakens the adhesion between the color layers between them and the ground ,The examination showed the color change of the green to the dark color in the trees area from top side to the left and showed white masses of different sizes and other large circular visible and transparent bubbles in the color layer are observed ,as a result of exposure to inappropriate environmental conditions such as high relative humidity and lightinduced decomposition processes [27].

The results of the X-ray diffraction analysis showed that the green sample consists of AsCuHO3 copper arsenic with a percentage of 38.2% that causes bluish green color and is accompanied by lead arsenic $Pb_2As_2O_5$ Paulmooreite which is probably to be present as products of secondary degradation products resulting from the interaction of transitional arsenic ions of color with lead in the ground layer and was formed copper arsenic compound contains copper and lead, which stimulates the formation of dark copper and lead sulfate types. it is accompanied by compounds as Clinoclase Cu_3ASO_4 $(OH)_3$, a percentage 15.4% which is probably to form in the color due to the high relative humidity and light-induced decomposition processes and the presence of water in crystalline structures that lead to color decomposition and over time it turns The dark green color is also accompanied by a compound of Arsine sulfide Percentage 16.4%, and it is likely that it is due to the effect of fluctuating relative humidity and direct light, which causes decomposition of the green color of arsenic, then the structural arrangement is re-launched and the sulfur atoms released from the structure interact, which may lead to the formation of hydrogen sulfide, [28] and it interaction with arseine and formed of arsenic sulfide , It will also be associated with Azurite a percentage 11.3 %, and it is likely that it was used with green to give the shades of trees.

XRD analysis of the ground layer showed that that it contain a mixture of calcium carbonate with lead oxide and the yellow Goethite , and it is probable that the artist used a white ground mixed with yellow oxide in landscape painting and this method lead to Color change[29]which result of the decomposition of the ground layer, the release of iron and lead ions, and their interaction with the products of decomposition of the green color, The analysis EDX confirmed the presence of elements of the damage products that were shown by the analysis with XRD, which also leads to support the explanations for the damage products, so the analysis (EDX) showed the appearance of arsenic and copper, which indicates the use of green color and is accompanied by both oxides of lead, sulfur and carbon SO_4^{-2} and Pb^{+2} It is probable, that as a result of exposure to inappropriate environmental conditions such as high relative humidity and light-induced decomposition processes, the arsenic oxidation of As_2S_3 occurs in green and sulfur ions are released from the color.[30]and released Pb^{+2} ions , Ca^{+2} ions , Fe^{+3} ions ,from the ground layer it is possible, it can be considered nature elements in the materials of ground layer. The FTIR analysis of

the green sample showed the presence of a group of mineral carboxylate (COO) Of copper oxalate [31], and the presence of mineral soap, and it is probable that when the relative humidity increases, it affects the medium (oily), so the percentage of free fatty acids increases [32]. The interaction between fatty acids and metal ions is done in both colors and ground, formed mineral soap that leads to polar changes of the color layer leads to the instability of particles of emerald green and its deterioration, then Copper ions are released, which reduce the bonding of medium molecules. [33] ,The analysis showed the presence of calcium oxalate salts $C_2H_2CaO_5$ which are formed by the interaction of calcium ions with Oxalate ions, calcium oxalate salts resulting from increased relative humidity, and thus lost contact between the grains of the paint[34] and the ground layer, That can move and migrate through layers of colors, lead to be bloom [35] on the surface The analysis showed the presence of the arsenic group (Aso), which is resulted from the color decomposition occur under the influence of light [36] , The arsenic ions are released and sulfur atoms will be released formation of As-As bonds, Arsenic is probable to oxidize in green to AS2O3 because arsenic oxides easily migrate because of their water solubility from the original green to the surface or to the colors surrounding them[37].

Conclusions: -

The green color turns to brown in paintings over time, especially with lead white. Sometimes the mediator is not the only cause of the color layer damage, but it is one of the reasons, there are factors that play an auxiliary role with the mediator for the damage of the plate and show that the green color mixed with linseed oil changed it to dark because the linseed oil may work to extract copper ions (II) from copper acetate (II), and be Black copper oxide and exposure to UV rays cause optical change due to photochemical phenomena causes the color surface to fade so the Emerald green should be preserved by not subjecting to inappropriate environmental conditions, especially strong light, sudden change in relative humidity, and not using water-based cleaning agents to reduce arsenic migration and turned brown or black due to the reactions between the components of the painting layer in inappropriate conditions

Contributions:

The entire database achieved by the authors which read and agree to the manuscript.

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