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Realgar and Light

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Abstract

Light, necessary for viewing a work of art, as it involves the transmission of energy, it can damage the artwork. Nowadays, the most common methods for controlling light are based on the control of the overall lighting intensity. In particular, museum lighting guidelines recommend to limit the time of illumination or to remove wavelengths of light to which human eyes are insensitive. This research aims at determining how lighting systems can be standardized and developed, by studying the interaction between light and the materials constituting cultural heritage. An interesting case-study was considered as starting point: the arsenic sulphides photo-oxidation induced by visible light. In particular, among arsenic sulphides, realgar photo-degradation was studied, as this pigment was used since antiquity. Light transforms realgar (red mineral, As_4S_4) in arsenolite (white as powder, As_2O_3) and pararealgar (yellow, As_4S_4). The process is not completely clarified so far. This study deepens the comprehension of the realgar degradation process and determines the ability of different halogen lamps and a LED lamp, used in museum exhibitions, to induce photodegradation of pigments The study was carried out by means of FT-IR, micro-Raman spectroscopy, XRD and spectra colorimeter analysis.

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Keywords: realagr, degradation, lighting, infrared spectrometry, micro-Raman spectroscopy, perception

1. Introduction

In a museum, all objects are subjected to decay caused by many contributing factors: temperature, humidity, pollutants [1]. Each factor does not act individually, and its effect can be enhanced or accelerated by the presence

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of other ones. Among the environmental risks, light remains unique because it can neither be eliminated nor completely controlled. Light is necessary to see a work of art, but it transmits energy producing different effects, such as colour alteration, colour fading, mechanical damage, embrittlement, and so on. Optimal solutions for lighting cultural heritage goods do not exist. Therefore the solution of two contrasting problems is needed: from one side, the necessity of exhibiting all objects which constitute the historical and artistic patrimony of every country by high quality in luminance, uniformity, contrast and color reproduction and on the other hand the necessity to minimize the interaction of the artistic production with the electromagnetic radiation in order to ensure its adequate conservation [2]. Two major requirements should be satisfied: to minimize the damage and to obtain a good color reproduction. For solving this complex problem, the most common methods for controlling light are based on the spectral characterictics of the sources and on the control of the overall lighting intensity. In particular, museum lighting guidelines recommend to limit the time of illumination or to remove wavelengths of light to which human eyes are insensitive. The most important parameters are illuminance and time of exposure. According to CIE 157:2004 [3], cultural heritage objects are classified according to their sensitivity to light exposure in no sensitivity, low, medium and high sensitivity, but no guidelines directly consider the photo-chemical interaction between artwork and light.

To fulfill the most up-to-date guidelines on preventive conservation, in recent years several scientific projects supported by the EC were aimed at developing innovative tools that could improve the standard methods for environmental monitoring in museums [4]. The current trend is to combine studies based on commercially available instruments (luxmeters and radiometers) with researches focused on the differentiability of the effects caused by various types of lighting sources, characterized by equal illuminance, to produce photochemical effects on a cultural heritage. For a correct conservation policy, it is important not only to monitor the single physical or chemical parameter, but also to evaluate the impact of the whole environment by measuring temperature/relative humidity, light, powders, selected pollutants, etc..–The available devices allow these measurements separately, but they are not suitable for assessing the overall effects of these factors.

A way of monitoring, coming from Textiles Factory, is to use a sacrificial simulation material such as the Blue Wool Standards on which the effect of light can be studied [5]. In this system, strands of wool dyed with a fugitive (i.e. very sensitive to light fading) blue dye are placed in proximity to objects at risk of light damage. Any fading of the dyed strand is compared to a standard, and this can indicate that light damage is occurring to the objects. It is felt that a more sensitive, standardized system is needed. The benefits coming from new generation sensors based on sacrificial materials consists in the possibility of evaluating the cooperative effects of environmental agents. This approach is based on the observation that the work of art materials, their surface and their structure, which record all the alterations induced by the environment, could be viewed as an environmental sensor [4]. This point of view could be considered the starting point for a novel concept in monitoring devices, that exploits the deterioration effect in order to assess the environmental aggressiveness.

This paper is aimed at determining how lighting systems can be standardized and developed using the materials present in the artworks, considering both the conservative and visual perception aspects. To develop this research the arsenic sulphides photo-oxidation induced by visible light was studied. In particular, among arsenic sulphides, realgar photo-degradation was studied, because this pigment was used since antiquity [6]. Light (wavelength between 500 and 670 nm [7]) transforms realgar (red mineral, As_4S_4) in arsenolite (white ~~if~~ powder, As_2O_3) and pararealgar (yellow, As_4S_4)[8], a compound with the same formula of realgar but characterized by a different structural arrangement of sulphur and arsenic atoms The reaction of realgar with oxygen and light yields a meta phase, the χ-phase (As_4S_5) and arsenolite. In As_4S_5 a sulphur atom is inserted between the As atoms in realgar molecules, because the As-As bonds are weaker than the As-S bond [9]. Pararealgar can then form by the release of a sulphur atom which can be re-attracted ~~to~~ by other realgar molecules. At the end of the process some molecules of As_4S_5 co-exist with pararealgar and the pigment from red-orange turns to yellow.

We propose the use of this compound as marker to determine the optimum lighting system for cultural heritage to prevent degradation effects induced by different halogen lamps and a LED lamp in museum exhibitions.

2. Materials and Methods

2.1. Lighting

In order to quantitatively compare the damage and the "Quality" produced by different illuminants it is important that all of them have the same colour-rendering index (CRI) and colour temperature (CCT). Today, a great variety of lighting systems are used in museums; all of them must be characterized by a defined spectrum, in any case without IR and UV radiations. The halogen lamp is now the benchmark for light quality but shortcomings which include relatively poor energy consumption and lifetime performance has pushed to use Light Emitting Diodes (LED) [9]. Advantages of these systems are very well known: live time, size, compactness, variation of output flux, energy saving and the possibility to obtain an optimized spectral source. [12].

In this study, photo alteration of realgar was induced at various times using the following lamps:

Table I_ Lamps used to induce light-degradation of realgar

	Lamp power	Color temperature	luminous flux 1lm = 1cd·sr	CRI
Eco Classic Philips	100 watt	3000 ˚K	1500 lm	100
Philips masterline ES	45 watt	3000 ˚K	1300 cd	<90
Osram decostar	35 watt	3000 ˚K	920 lm/1000 cd	100
Osram halostar	50 watt	3000 ˚K	1180 lm	100
Osram duluxstar	11 watt≈51w	2500 ˚K	600 lm	80-89
Osram Sylvania LED	13 watt≈75w	2700 ˚K	1100 lm	83

2.2 Realgar degradation

2.2.1 Conservative aspect

In order to reproduce the alteration observed on artworks, degradation lighting was performed on different samples realized mixing realgar powder (Kremer Pigmente, Germany (number: 10800) with various binders: Arabic gum (10% wt+10ml of deionized water), linseed oil (300 mg of realgar in 5ml of oil) and egg (Realgar:deionized water:yolk= 300 mg:5ml:5ml + one tablespoon of white wine). The degradation process was studied using XRD, micro Raman and FTIR spectroscopy. Light fading of samples was effected by placing them on a specific degradation cell realized by Krens Enregia Srl. The cell was open at the top to insert the lamp for the degradation. To operate in uniform condition of temperature and humidity, the lamp was ventilated by air generated by a self-produced system of fans and dehumidified by filtration in a tube filled with silica gel. Further, to induce the degradation of pigment and binder at the same time, the samples were exposed to sunlight for 24 hours (used CPS – Suntest,UV component included)

2.2.2 Perceptive aspect

The Pantone Color Matching System was choosen as a reference. This system was used to standardize colors in the CMYK process that is a method of printing color by using four inks: cyan, magenta, yellow and black. The choice was due to the use-friendly of system. Some Pantone colour spots, close to the realgar colour, were exposed to different lamps to induce degradation. For each lamp, three groups of 15 people, of different age and education, were asked to identify the Pantone colors on a Pantone used as a reference. Realgar mixed with different binders such as linseed oil, rubber and egg, were spread on a wooden support with plaster primer. Some plugs were covered with copal (copal oil varnish, Manufacturer: Winsor & Newton) to simulate the presence of a protective layer. People were asked to indicate on the Pantone plugs color observed at a distance of 40 cm. The plugs were degraded by SunTest for a time 24 hours and again subjected to observation by the people groups to monitor the ability to perceive the color change induced by degradation. The colors selected on the Pantone system and the different plugs were characterized by spettrocolorimetric measurements to determine the parameters L * a * b * using the Minolta 2600d.

3. Results

3.1 Conservative aspect

Before degradation no phases other than realgar were detected by Raman, FTIR and XRD analyses (Figure 1, 2 and 3, time=0), At first, realgar degradation was induced with halogen ECO Classic Philips lamp for various exposition times. The progress of degradation allows to appreciate some spectral variations in the Raman spectra. The most striking spectral change consists in the disappearance of the band at 356 cm^{-1} assigned to the As-S stretching mode (A_1) (Fig. 1) suggesting the formation of pararealgar deriving from the breaking of the As-S bond. In FTIR spectra no-additional peaks were detected but the coalescence of the bands at 374, 366 and 358 cm^{-1}, Fig. 2. The XRD spectra at different times of degradation confirm the results obtained by the other techniques. In particular, realgar degradation after few hours of exposure. After 9 hours of irradiation realgar transforms the into the χ-phase (As_4S_5), the precursor of pararealgar, to pararealgar and arsenolite, Fig. 3. After 72 hrs was characterized by the total absence of realgar and χ-phase and showed only peaks of pararealgar and of arsenolite.

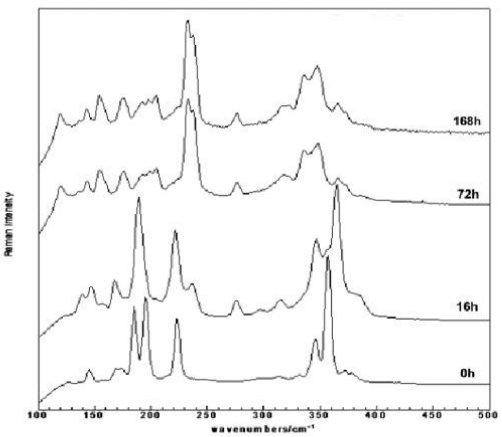

Fig. 1. Raman Spectra obtained on realgar at different exposition times

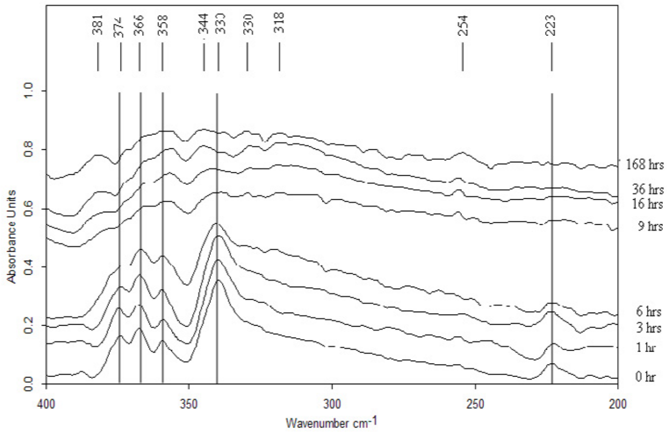

Fig 2. FTIR Spectra obtained on realgar at different exposition times

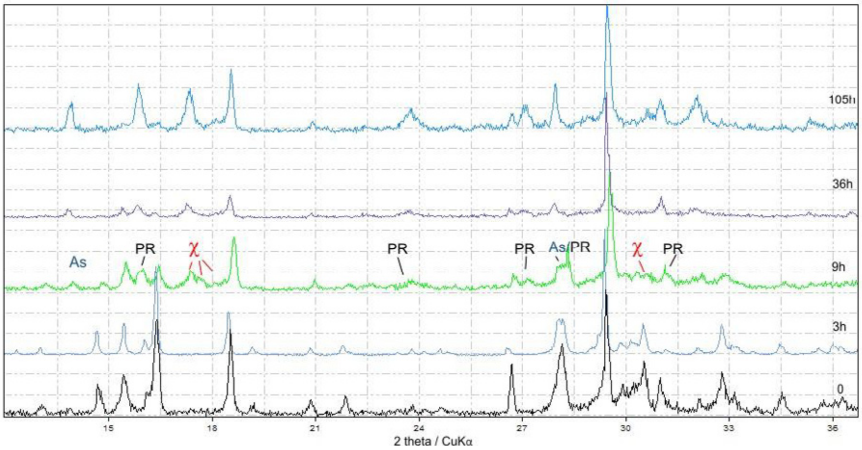

Fig 3. XRD spectra of realgar at different exposition times. As, arsenolite; PR, pararealgar; χ-phase (As_4S_5).

The dispersion of in painting media did not involve any modification both on the reaction kinetics and on the degradation products. Degradation was induced by SUNTEST CPS (illuminant: D65 , temp=30°C, RH=60%, exposition, 24 hrs) to promote at the same time the degradation of realgar and of the binders, Fig. 4.

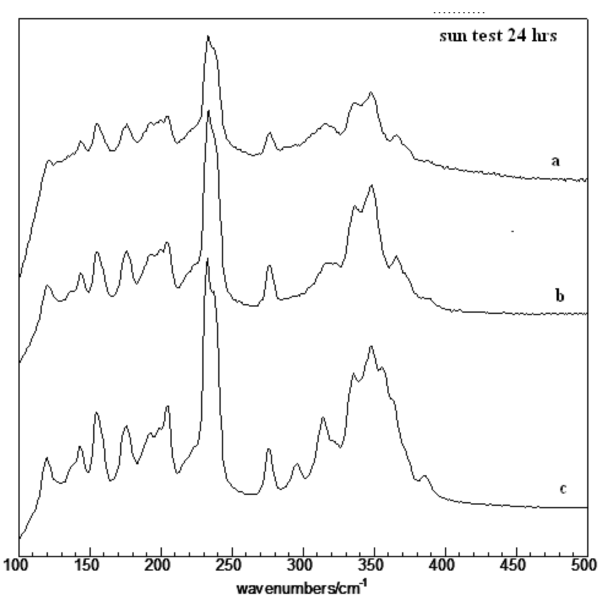

Fig 1. Raman Spectra obtained on realgar dispersed in painting media: linseed oil (a), rubber (b), egg (c) and degraded by Suntest

The degradation induced by Eco Classic Philips on realgar was used to determine the ability of other lamps to produce degradation. The IR and Raman spectra, Fig. 5, show that the LED lamp produces a kinetic of degradation slower than that induced by a 100 watt halogen. After 46 hours, the spectrum is still characterized by the presence of realgar, while after one week, the LED spectrum matches that of 100w halogen.

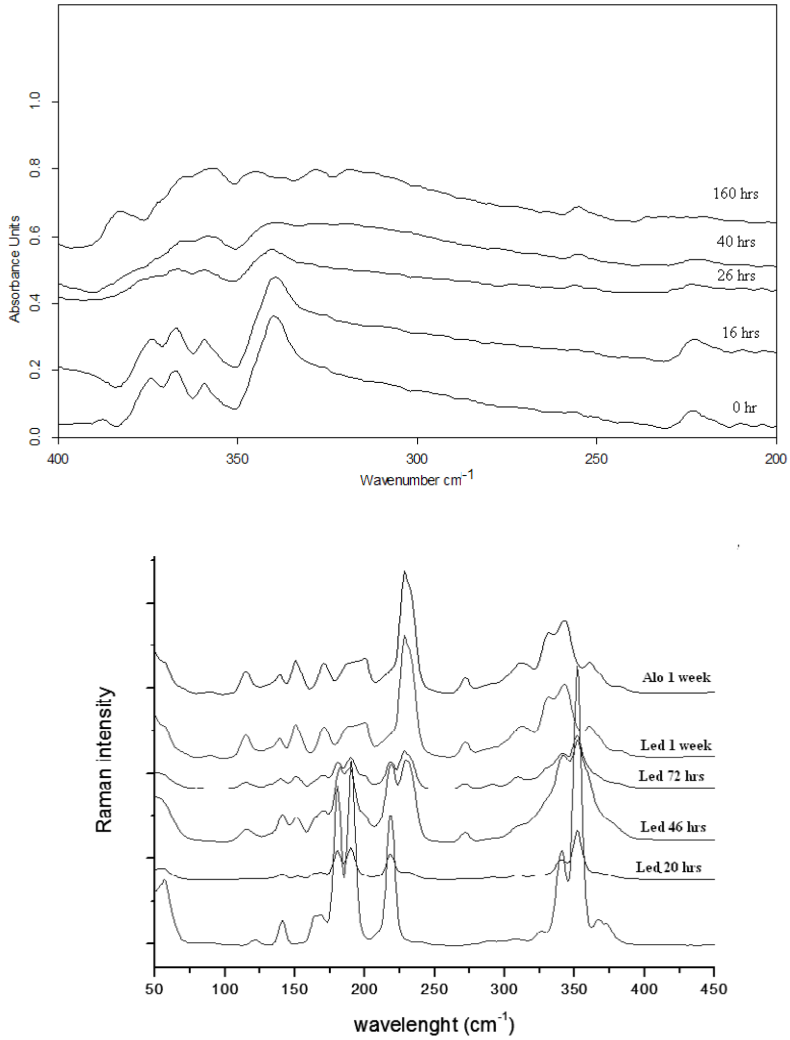

Fig 5. Raman (left) and FTIR (right) spectra of realgar after irradiation with LED

Compared to the halogen lamp, the LED lamp has a main spectral component in the blue region. This characteristic should nfluence~~s~~ the kinetics of degradation of realgar, while reasonably should not lead to the formation of different degradation products. In experiments with halogen lamp, the Raman spectra detected ~~the~~ degradation effects already after 9 hrs of irradiation. Conversely no spectral changes were observed when exposing the sample to LED for 9 hrs. Only after 40 hour the spectra show the effect of degradation. Compared to ECO Classic Philips 100 W, the various halogen lamps differ for luminous flux or luminous power, a measure of the perceived power of light. The Raman spectra shown in Fig. 6 clearly indicate that the Masterline and Decostar lamps transformed realgar in pararealgar and arsenolite, while the Duluxstar and Halostar lamps produced a minor degradation as revealed by the presence realgar together with pararealgar and arsenolite. The result obtained using for the DULUXSTAR lamp, a compact fluorescent lamp, can be ascribed to its emission spectrum. The minor degradation induced by halogen Halostar can be due to the different geometry of this lamp which is not equipped with a reflector.

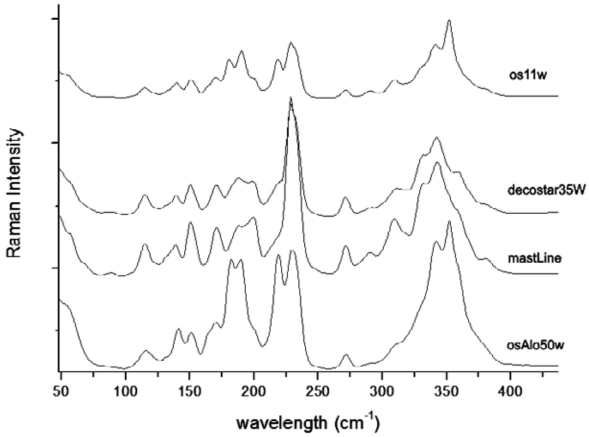

Fig 6 Raman spectra of realgar after irradiation for 72 hrs with different lamps. Decostar35W: Osram Decostar; osAlo50w: Osram halostar; os11w: Osram duluxstar; mastLine: Philips masterline ES

3.2 Perceptive aspect

The perception of a color depends on the system used to lighting. First, it was defined as the Pantone colour spots were perceived by various groups if illuminated by different lamps. The selected spots are reported in table II:

Tab. II Pantone selected spots and related CIE-L*a*b* parameters

	138C	**141U**	**145C**	**142c**	**155c**	**134c**	**136c**	**142c**	**144c**	**124c**	**156c**	**137c**	**141c**	**135c**	**143c**	**152C**	**1**
L*(D65)	72.77	81.69	60.85	77.26	83.49	85.21	80	77.04	65.84	69.98	83.04	72.86	83.54	81.22	72.79	60.72	7
a*(D65)	31.74	8.45	22	11.49	3.59	6.68	18.01	15.41	30.39	16.72	7.73	31.64	4.23	14.67	14.17	36.18	2
b*(D65)	70.21	44.14	51.65	58.33	22.22	44.14	55.44	47.4	59.94	65.78	30.37	69.31	44.78	61.03	58.71	52.18	5

The table III present the percentage of persons who have identified in Pantone system the correct colour of spots, lighted by the different lamps

Tab. III_ Percentage of persons who have perceptive the correct color of spots

Eco Classic Philips	Philips masterline ES	Osram decostar	Osram halostar	Osram duluxstar	Osram Sylvania LED
89%	84%	73%	68%	66%	81%

Eco Classic, Osram Sylvania LED and Masterline allow to perceive the correct color of spot. The high percentage of right observations allows to extend the experiment about the perception of realgar degradation. Different plugs of realgar mixed with various binders were realized and their color measured in the system CIE L * a * b *. The different binders did not affect the uniformity of the plugs.

Table IV. Plugs variability depending on binders

	L*	Std L*	a*	Std a*	b*	Std b*
Lineseed	84,95	±2,33	8,14	±0,99	24,99	±2,39
Rubber	60,37	±1,33	32,89	±1,52	50,48	±3,21
Egg	83,55	±1,91	10,7	±1,24	24,97	±2,88

The plugs, illuminated by the lamps, have been observed by the groups in the same operating conditions of distance and dark background. For all lamps, the observer can distinguish the colors between degraded and not degraded plugs. The plugs have been degraded by Suntest and characterized by spettrocolorimeter. The color changes relative to plugs are reported in table IV as the difference between the colorimetry parameters before and after the degradation expressed in ΔE. The results show~~s~~ that the variation induced by degradation is visible to naked eye ($\Delta E \geq 1$) and is homogeneous for the different binders. The use of a protection layer seems to induce a lower degradation revealed by a less marked color change. The plugs~~,~~ with copal illuminated by the different lamps and without degradation induced by Suntest, have a uniform color identified in Pantone system as 138. However, for the 100W halogen and Halostar lamp a perceptive uniformity among the different groups of observers has been obtained with an average color ~~is~~ near to 138 in the reference system. The degradation plugs showed patchy color depending on the type of binder. The predominant color is 124u. The plugs, protected by copal, show a higher variability of perception color which is reduced in the degraded plugs. The lower perception uniformity is obtained using Eco Classic lamp. The lamps that allow a more homogeneous description of the plugs are the Osram Sylvania LED and Philips MASTERLine ES, while the Halostar and EcoClassic lamps show the differences also in the same binder.

4. Conclusions

Realgar is a good marker to record the alterations induced by lighting in an environment: a) it reacts in a short time; b) light induces surface color change from orange to yellow, making this pigment a sensor ~~to be~~ eas~~il~~y to use~~d~~; c) the degradation reaction is not reversible.

Furthermore, the degradation of realgar to pararealgar is dependent on the type of lamp used. The obtained Raman and FTIR spectra confirm that the degradation process starts with exposition of the pigment to lamp. Light induced structural changes transforming quickly the realgar to χ-phase (As_4S_5), the precursor of pararealgar, and to pararealgar and arsenolite; latter only parearelagar and arseonlite are present. The LED lamp produces a minor degradation compared to other lamps. Among halogen lamps, only Osram halostar produced a minor degradation due to its geometry. Osram duluxstar, being a compact fluorescent lamp, also induced a minor degradation. The color change could be related to perception visual aspect that cannot be underestimated when the light question in the field of cultural heritage is tackled.

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