

WHICH LIGHT FOR CULTURAL HERITAGE: COMPARISON OF LIGHT SOURCES WITH RESPECT TO REALGAR PHOTODEGRADATION

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This paper is a part of the wider project aiming at determining how lighting systems can be standardized and developed, by studying the interaction between light and the constituting materials. To develop this research, an interesting case-study was performed as starting point: realgar photo-degradation. Light transforms realgar in arsenolite and pararealgar, a compound with the same formula of realgar but characterized by a different atomic disposition and color. This study deepens our knowledge of realgar degradation and determines the capacity of inducing degradation by different lamps. The survey was carried out by means of FTIR and micro-Raman spectroscopy. The results confirm literature studies on realgar degradation and suggest that the LED lamp produces less degradation, keeping a high quality of lighting.

Keywords: FTIR, micro-Raman spectroscopy, lighting, realgar, degradation, museum.

Introduction. Among environmental risks for cultural heritage exposed in a museum, light remains unique because it is necessary for viewing but involves the transmission of energy and can damage the artwork. In a museum, all objects are subjected to decay caused by many contributing factors: temperature, humidity, pollutants [1]. Each factor does not act individually, but its effect can be enhanced or accelerated by the presence of other factors. Among the environmental risks, light remains unique because it can be neither eliminated nor completely controlled. Light is necessary to see a work of art, but produces different effects, such as color alteration, color fading, mechanical damage, embrittlement and so on. As it involves the transmission of energy, it can damage the artwork. Nowadays, the most common methods for controlling light are based on the spectrum 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 [2], cultural heritage objects are classified according to their sensibility to light exposure in no sensibility, low sensibility, medium sensibility and high sensibility, but no guidelines directly consider the photo-chemical interaction between the 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 [3]. The current trend is to combine the studies based on commercially available instruments (lux meters and radiometers) with researches focused on the coefficient of damage that is the differentiability of the 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. The available devices allow to measure temperature/relative humidity, light, powders, selected pollutants, etc., separately, but they are not suitable for assessing the overall effects of these factors.

A way, coming from Textiles Factory, is to use a sacrificial simulation material on which the effect of light can be studied. This type of monitoring does already exist, with the use of Blue Wool Standards [4]. 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.

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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 still needed. The benefit of using these new generation sensors based on sacrificial materials consists in the possibility to evaluate the cooperative effects of environmental agents. The change in the sensor indirectly indicates the relative strength of the environmental impact of a given agent (or 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 [3]. The study of these materials from this point of view could be considered the starting point for a novel concept in monitoring devices, one that exploits the deterioration effect in order to assess the environmental aggressiveness.

This paper is a part of the wider project aiming at determining how lighting systems can be standardized and developed using the materials present in the artworks. To develop this research, an interesting case study was performed as a starting point: arsenic sulfide photo-oxidation induced by visible light. In particular, among arsenic sulfides, realgar photo-degradation was studied, since this pigment was used since antiquity [5]. Light (wavelength between 500 and 670 nm [6]) transforms realgar (red mineral, As_4S_4) in arsenolite (white if powdered, As_2O_3) and pararealgar (yellow, As_4S_4) [7], a compound with the same formula as that of realgar but characterized by a different disposition of sulfur and arsenic atoms. Light transforms realgar in pararealgar. In this reaction the realgar reacts with oxygen and light to form a metaphase and arsenolite. In the metaphase (As_4S_5), a sulfur atom is added and inserted between the As atoms in realgar molecules, because the As–As bonds are weaker than As–S bond [8]. From the metaphase, pararealgar is obtained. The sulfur atom is released and is reattached to other realgar molecules. At the end, some molecules of As_4S_5 co-exist with pararealgar, and the pigment changes from red-orange to yellow.

This study deepens understanding of the realgar degradation process and proposes to use this compound as a marker to determine the degradation effects induced by different halogen and LED lamps, used in museum exhibitions.

Materials and Methods. *Lighting sources.* Lighting is an integral part of the story-telling process of museums [9]. Today, more than ever, there is a greater variety of lighting systems used in a museum. All must be characterized by the defined spectrum, in any case without IR and UV radiations, and of the specific "quality": color-rendering index (CRI) and color temperature (CCT). Halogen lamps are traditionally used in museums with filters and with fiber optic systems to reduce the damage [9]. The halogen lamp is now the benchmark for light quality but it has shortcomings that include high energy consumption and low lifetime performance. These reasons have led to light emitting diodes (LED) [9]. LEDs allow energy and maintenance saving with respect to halogen lamps for museum lighting. One of the biggest concerns for curators is whether the artwork deterioration is faster when due to the LED than to the halogen lamps now used (there is a little more energy in the blue portion of the spectrum) [10].

In past, "high Color Temperature single phosphor corrected (PC) white LEDs" had shortcomings with gaps in the spectrum affecting an accurate color discrimination while high outputs/spikes in the blue spectra can produce color fading in light-sensitive materials of cultural heritage [11]. Recent improvements in LED technology make LED use applicable in all areas. The LED modules designed for high-quality lighting are on a par with halogen ones, as far as it concerns the quality of lighting in museums. They also offer energy savings of nearly two-thirds and longer-term benefits, which can include greater protection for cultural heritage [12].

In this study, photo-alteration of realgar was induced using a number of lamps (Table 1). The lamps have been chosen with a similar CCT and CRI. Only the Osram Duluxstar and Sylvania LED differ from this rule because the former is a compact fluorescent lamp while the latter is an ultra-high performance omni-directional LED that can rival incandescent and halogen light sources. For all photo-induced experiments the lamps have been positioned at 20 cm from the sample surface, and for each source the illuminance was measured using a mobile luxmeter BABUC/M LSI.

Realgar degradation. In order to reproduce the alteration observed on artworks, degradation lighting was performed on realgar powder samples (Kremer Pigmente, Germany; number 10,800), whose elemental composition was ascertained through SEM EDX measurements: 68.3 ± 1 of As and 32.5 ± 0.8 of S with low weight % of Si and Ca (1.1 ± 0.3). Realgar is a good marker to record the alterations induced by lighting in a definite environment: a) it reacts in a short time; b) the induced light surface color changes, from orange to yellow, makes this pigment a sensor that can be easily used; c) the reaction is not reversible. Furthermore, the color change could be related to visual perception, which cannot be underestimated when the light question in the field of cultural heritage is tackled.

The degradation process was studied using Raman and FTIR spectroscopy. Before the manipulation, Raman and FTIR spectra ascertained the only presence of realgar. The presence of different arsenic sulfide compounds is important because it can influence the process of degradation or the spectra interpretation. The research was focused on light-induced

TABLE 1. Lamps Used to Induce Light-Degradation of Realgar

Lamp	Lamp power, W	Color temperature, K	Luminous flux 1 lm = 1 cd·sr	CRI
Eco Classic Philips	100	3000	1500 lm	100
Philips Masterline ES	45	3000	1300 cd	<90
Osram Decostar	35	3000	920 lm/1000 cd	100
Osram Halostar	50	3000	1180 lm	100
Osram Duluxstar	11 ≈ 51	2500	600 lm	80–89
Osram Sylvania LED	13 ≈ 75	2700	1100 lm	83

realgar degradation at different times: 0, 1, 3, 6, 9, 16, 36, 72, 168 h. Light fading of samples was affected by placing them in a specific degradation cell realized by Krens Energia Srl. The cell was open at the top to insert the lamp for the degradation. To operate under uniform conditions of temperature and humidity, the lamp was ventilated by air generated by a home-made system of fans and dehumidified by filtration in a tube filled with silica gel. The samples were prepared mixing 300 mg of realgar powder dispersed in isopropyl alcohol and put in a Petri dish ($d = 60$ mm).

Micro Raman and FTIR. Raman spectra were measured for realgar powder, untreated or irradiated under controlled conditions, using a confocal Raman microscope (DXR dispersive Raman Microscope, Thermo Scientific) equipped with the 785 nm laser, objective 50× giving a spot of 0.7 μm . An interferometer IFS 113 (Bruker) equipped with Mylar beam splitters was employed for the IR spectroscopic analyses. Transmission spectra were taken in the range of 600–180 cm^{-1} cumulating at least 200 scans with a resolution of 2 cm^{-1} . Untreated or irradiated realgar samples were finely dispersed in Nujol and uniformly spread on a Cs I window transparent in the 4000–180 cm^{-1} interval. The best results were obtained mixing 15 mg of the sample in 5 drops of Nujol. The spectrum of the same amount of pure Nujol on the Cs I window in the same experimental conditions was used as reference.

Results. At first, the realgar degradation was induced with halogen lamps ECO Classic Eco Classic Philips. The measured peaks, obtained in the realgar spectrum at time 0, correspond to the value in the literature (Table 2). The realgar sample has been irradiated with the same lamp to different exposition times to obtain information about the degradation (Fig. 1). The realgar degradation starts with an exposition of the pigment to the lamp. Light induced structural changes indicate a transformation of realgar to the χ -phase (As_4S_5), the precursor of pararealgar, and to pararealgar and arsenolite. After 6 h an important change occurs in the realgar spectra, while the spectrum at 72 h is characterized by the total absence of realgar and χ -phase and shows only peaks of pararealgar and of arsenolite. With increasing exposure time, the pararealgar peaks became weaker while χ -phase peaks decreased.

The most striking spectral change consists in the disappearance of the absorption peak at 356 cm^{-1} assigned to the As–S stretching mode (A_1), suggesting the formation of pararealgar derived from breaking the As–S bond, removing S2 and adding S2b atom in the As–As bond (Fig. 2). The peak at 268 cm^{-1} may be assigned to arsenolite or to the χ -phase As_4S_4 [15]. Complete degradation occurs in 72 h as the Raman spectrum does not change for longer exposures (1 week). The presence of the peak at 268 cm^{-1} in combination with the peak at 276 cm^{-1} unequivocally assigns these peaks to the presence of arsenolite [16].

The FTIR analysis confirms the photodegradation time. The realgar molecule absorbs well in the IR range, and the characteristic peaks are well separated and resolved, as shown in Fig. 3. The progress of the degradation, induced by Eco Classic Philips, at different times allows one to detect some spectral variations already after 6 h of irradiation. Additional peaks are not detected, but the bands at 373.9, 367.3, and 359.3 cm^{-1} coalesce (Fig. 4).

After 9 h of irradiation, the vibrational modes of realgar are no longer distinguishable. The obtained spectrum is less resolved and the observed bands are larger, suggesting increased scattering of the IR radiation, probably due to the degradation process. Furthermore, few peaks of low intensity appear (236, 274, 318, 330, 358 cm^{-1}), confidently attributable to pararealgar (Fig. 5). The peaks present in the 400 to 480 cm^{-1} range are probably due to the presence of arsenolite. With increasing exposition time, the photodegradation allows the detection of absorption peaks at 420, 444, 477 cm^{-1} assigned to arsenolite [16].

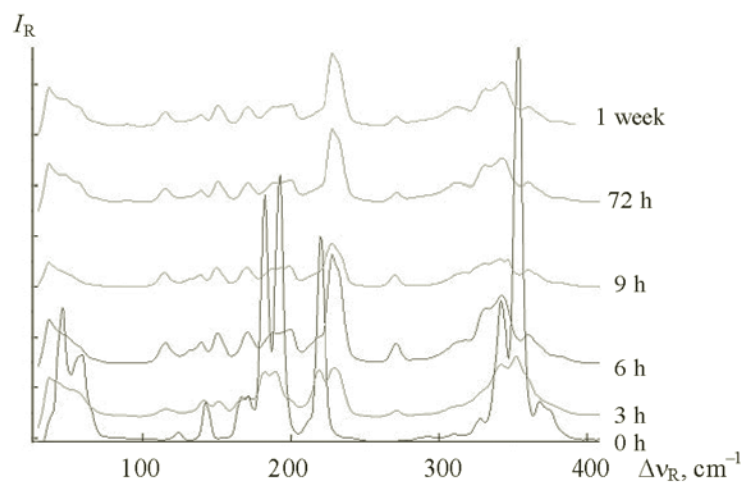


Fig. 1. Raman spectra obtained on realgar for different exposition times.

TABLE 2. Comparison between Realgar Peaks in the Literature and Measured Values

Raman vibrational frequency (cm^{-1}) of mineral As_4S_4 [13, 14]	Measured vibrational frequency (cm^{-1}) of As_4S_4 (this work)	Assignment (D_{2d})
376 m	375 vw	As–S st (<i>E</i>)
370 w	368 vw	As–S st (<i>E</i>)
355 vs	355 vs	As–S st (<i>A1</i>)
345 s	345 m	As–S st (<i>B2</i>)
235 m		
222 vs	223 m	S–As–S b (<i>E</i>)
193 vs	195 m	S–As–S b (<i>B1</i>)
183 vs	184 m	S–As–S b (<i>A1</i>)
172 m		
166 m	168 vw	S–As–S b (<i>E</i>)
143 m	143 m	S–As–S b (<i>B2</i>)

Note. b — bending, st — stretching, s — strong, vs — very strong, m — medium, w — weak, vw — very weak.

The obtained information on the realgar degradation induced by Eco Classic Philips was used to analyze the ability of other lamps to produce realgar degradation. To compare the effective light power delivered to the sample surface, in Table 3 the illuminance (lux) for each lamp is reported.

The IR and Raman spectra show that the LED lamp produces slower degradation than that induced by a 100 W halogen lamp (Fig. 6). At 46 h, the spectrum is still characterized by the presence of realgar, while after one week, the spectra of realgar irradiated with the LED and 100 W halogen lamps are equal.

As compared with the halogen lamp, the LED lamp has a main spectral component in the blue region. This characteristic certainly influences the kinetics of realgar degradation but reasonably should not lead to the formation of different degradation products. In experiments with the halogen lamp, the spectra show degradation already after 9 h of irradiation. In contrast, no spectral changes were observed when exposing the sample with LED during 9 h. Only after 40 h do the spectra show the effect of degradation. Importantly, with respect to ECO Classic Philips 100 W, the other halogen lamps differ by the luminous flux or luminous power, which is a measure of the perceived power of light. The Raman spectra show

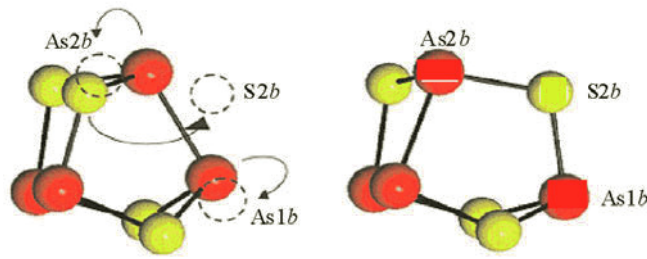


Fig. 2. Light induced transformation from realgar to pararealgar, red sphere — arsenic, yellow sphere — sulfur [7].

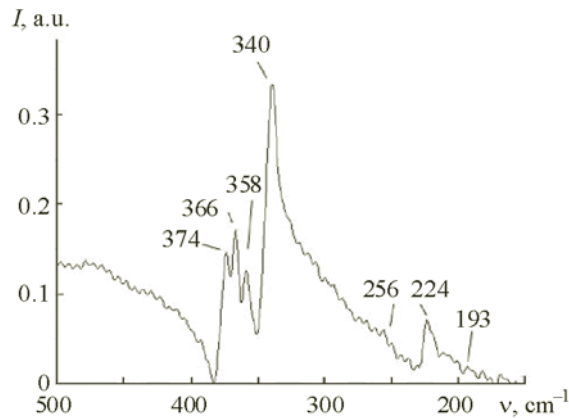


Fig. 3. IR spectrum of realgar.

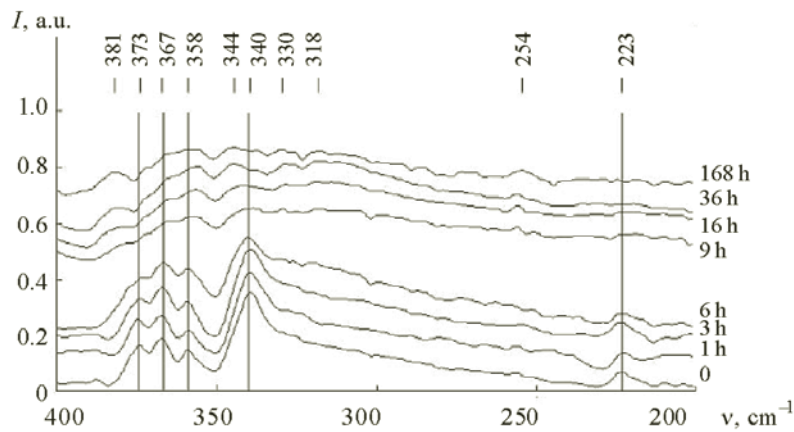


Fig. 4. FTIR spectra of realgar irradiated by a halogen lamp for different lapses of time.

(Fig. 7) that the lamps Masterline and Decostar transform realgar in pararealgar and arsenolite, while the lamps Duluxstar and Halostar produce a minor degradation demonstrated by the presence of realgar together with pararealgar and arsenolite. This result for the lamp Duluxstar is due to its emission spectrum as a compact fluorescent lamp. The minor degradation induced by the halogen lamp Halostar is due to the different geometry of this lamp, which is not equipped with a reflector. Compared to the other halogen lamps, it has no reflector, and for this reason it produces minor illuminance (Table 3) and consequently minor degradation. For clarity, in Fig. 7 the Raman spectra of realgar exposed during 72 h with different sources are compared.

TABLE 3. Effective Illuminance (lux) of the Sample Surface Exposed to Different Lamps

Eco Classic Philips	5700 ± 53
Philips Masterline ES	$26,200 \pm 45$
Osram Decostar	$22,040 \pm 87$
Osram Halostar	1980 ± 87
Osram Duluxstar	2023 ± 59
Osram Sylvania LED	$16,946 \pm 64$

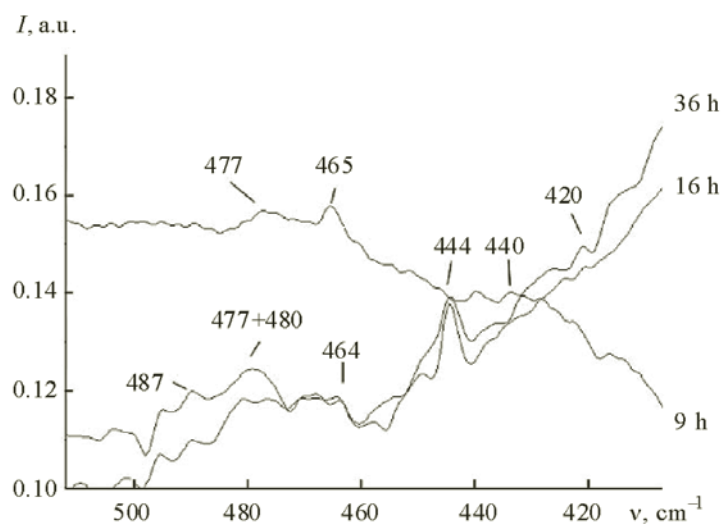


Fig. 5. FTIR spectra of realgar irradiated by a halogen lamp for different exposition times: 9, 16, 36 h.

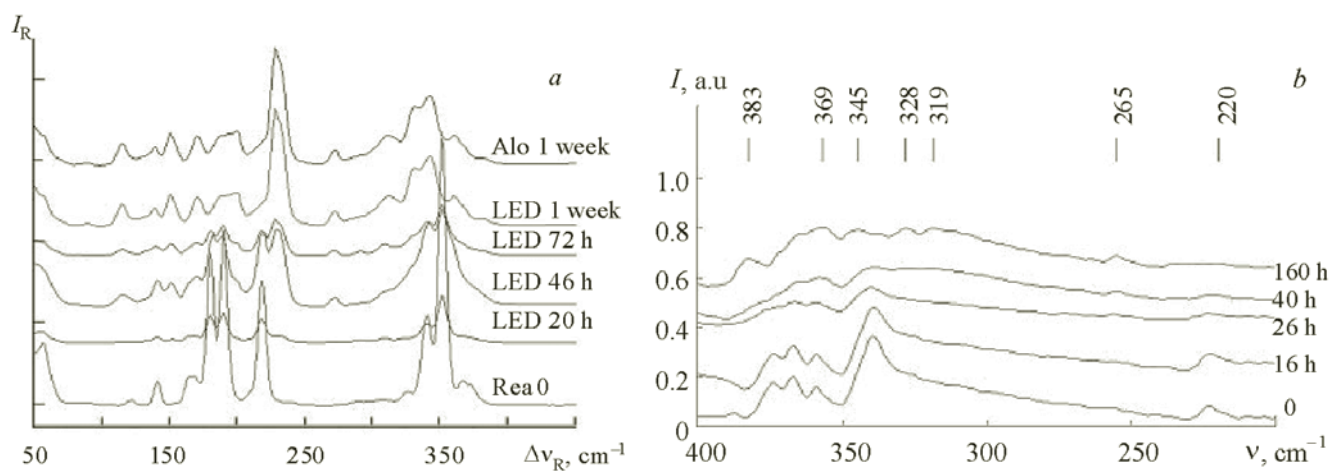


Fig. 6. Raman (a) and FTIR (b) spectra of realgar after irradiation with LED.

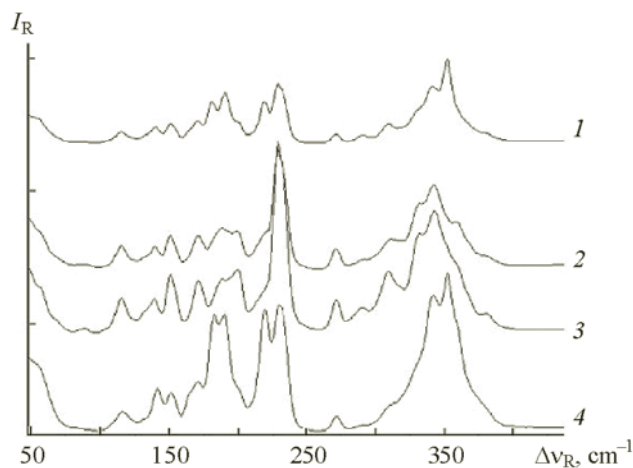


Fig. 7. Raman spectra of realgar after irradiation during 72 h with different lamps: 1 — Osram Duluxstar (Os 11 W), 2 — Osram Decostar (Decostar 35 W), 3 — Masterline (Philips Masterline ES), 4 — Osram Halostar (OsAlo 50 W).

Conclusion. The transformation of realgar to pararealgar depends on the type of lamp used. The obtained Raman and FTIR spectra confirm that the degradation process occurs with an exposition of the pigment to a lamp. Light-induced structural changes quickly transform realgar to the χ -phase (As_4S_5), the precursor of pararealgar, and to pararealgar and arsenolite. The LED lamp studied is characterized by high illuminance and produces minor degradation compared to other lamps. Among the halogen lamps, only Osram Halostar produces minor degradation due to its low illuminance. Osram Duluxstar, being a compact fluorescent lamp, produces an effect similar to that of Halostar lamp. It is, however, necessary to consider not only the conservative properties but also the aspect of perception. Therefore, it is important to take into account the minor lighting and the lower color rendering.

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