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EFFECTS OF LIGHT ON SILVER TARNISHING

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ABSTRACT

To date it has generally been thought that metals are not light sensitive. Visible light is known to break down organic coatings and to accelerate the deterioration of showcase materials leading to enhanced off-gassing. Two mechanisms on silver have been studied. The patinas of some silver coins and medals are affected by visible light, with silver chloride converting to fine silver particles. The effect of light, UV light, temperature, RH, ethanoic acid, methanoic acid and methanal concentrations on the reaction have been investigated. In more polluted environments, silver tarnishes in a parabolic manner. The sulfide tarnish is protective to a certain degree. Light exposures above 350 lux have been shown to remove the protective effect of the tarnish.

RÉSUMÉ

Jusqu'à ce jour, on pensait généralement que les métaux n'étaient pas sensibles à la lumière. La lumière visible est connue pour détruire les revêtements organiques et accélérer la dégradation des matériaux d'exposition, conduisant à un dégagement accru. Deux mécanismes sur l'argent ont été étudiés. Les patines de certaines pièces et médailles en argent sont affectées par la lumière visible, le chlorure d'argent se convertissant en fines particules d'argent. Les effets sur la réaction de la lumière, des rayons ultraviolets, de la température, de l'HR, et des concentrations de l'acide acétique, de l'acide formique et du formaldéhyde ont été étudiés. Dans les environnements les plus pollués, l'argent se ternit selon une courbe parabolique. La patine sulfurée est protectrice jusqu'à un certain point. Il a été démontré qu'une exposition lumineuse supérieure à 350 lux supprime l'effet protecteur de la patine.

INTRODUCTION

Visible light has not been reported to have a direct effect on the tarnishing of clean silver, but can have a strong indirect effect by breaking down coatings or accelerating the deterioration of materials in the vicinity, which then emit higher concentrations of a variety of pollutants. In contrast, curatorially significant patinas on coins and medals have been shown to deteriorate under even low light levels where the patinas contain high concentrations of chloride. The sulfidation of silver is often cited as the classic parabolic reaction: the insulating properties of silver sulfide inhibit electron transport and slow the reaction rate. However, silver sulfide is an n-type semiconductor and, if illuminated, its resistance can drop dramatically, removing the protective effect. These two potential light induced changes have been investigated.

LIGHT-SENSITIVITY OF CHLORIDE-RICH PATINAS ON COINS AND MEDALS

A patina (a thin layer of a stable corrosion product) can be very desirable on silver coins and medals. Coin handling removes the patina from, and polishes the silver at, the high points of the decoration. The contrast between the dark patina and polished silver accentuates the design. Chloride and sulfide are the two common, coloured chemically-stable corrosion products of silver which would be expected to be found in patinas of silver objects. The importance of the patina has resulted in differences in conservation treatments between coins and medals and other silver artefacts. In many museums, it is common practice to remove the corrosion or tarnish layer to produce a highly polished surface on three dimensional silver artefacts if possible. Lacquers are often utilised to protect the polished surfaces from tarnishing. However, removal of patina from coins or medals is considered unethical and damaging (Loperfido 1983). Similarly, lacquers have been generally avoided in coin conservation due to concerns about visual appearance.

Over the past two decades, a number of instances of alteration of the appearance of patinas on silver coins and medals on display in The British Museum have been analysed, with earlier observations of changes. The patinas are stable when in dark storage or with the short-term light exposures experienced during curatorial usage or examination by visiting scholars.

RESUMEN

Hasta ahora se solía pensar que los metales no son sensibles a la luz. Se sabe que la luz visible descompone los revestimientos orgánicos y acelera el deterioro de materiales de las vitrinas, lo que provoca una mayor liberación de gases. Se han estudiado dos mecanismos en la plata. Las pátinas de algunas monedas y medallas de plata resultan afectadas por la exposición a luz visible, y el cloruro de plata se convierte en finas partículas de plata. Se ha investigado el efecto de la luz, la luz UV, la temperatura, la HR, el ácido etanoico, el ácido metanoico y las concentraciones de metanal en la reacción. En ambientes más contaminados la plata se corroe de manera parabólica. La corrosión de sulfuro es hasta cierto punto protector. Exposiciones de luz por encima de 350 lux han demostrado eliminar el efecto protector de la corrosión.

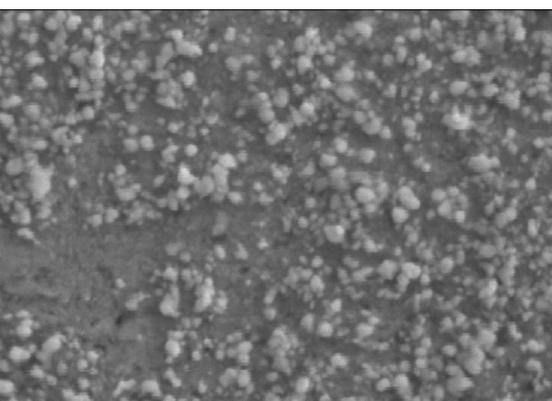


Figure 1

Silver particles on chloride patina surface, width of view is 0.15mm

However, prolonged periods on display have caused alteration to the patina of some silver coins and medals. The alteration manifests itself as a loss of gloss and, in some instances, the black or purple patinas become white, with a totally matt surface. This phenomena was first investigated in 1987 when 5th-century BC Greek coins from a case in the newly refurbished ‘Greeks In Italy Gallery’ were observed to have been affected within three months of the exhibition opening (Bradley 1988).

Over 90 affected coins and medals were examined visually and with a Joel 840 scanning electron microscope (SEM) (Bradley 1988, Thickett 1998). Both sides of each coin or medal were examined and the altered patina was compared to those which were unaltered. The presence of any surface coatings was investigated using Fourier transform infra-red spectroscopy (FTIR). Artefacts were either placed in a diffuse reflectance accessory or, if too large, the surface was wiped with a cotton wool swab dampened with tertiary butyl methyl ether. This was extracted and the spectrum of the extract collected as a potassium bromide disc.

In the vast majority of cases, the alteration was caused by the degradation of a silver chloride patina to produce elemental silver. This silver took the form of small (less than 1 μm diameter) particles on the patina surface. These particles could be readily removed by gentle brushing. A SEM micrograph of a group of such particles is shown in Figure 1.

Scattering of light by the particles causes less light to be specularly reflected from the surface, and hence the loss of gloss. Particles of approximately 1 μm diameter have been shown to cause maximum scattering of visible light when suspended in the atmosphere (Spedding 1974). Light scattering on a surface is a similar process, and it is likely that the silver particles produced are extremely efficient at it. Elemental analysis (Oxford GEM detector EDX with Oxford Link Isis software) confirmed that these particles were silver, although some of the elements from the underlying patina were detected because of penetration of the electron beam and emission of secondary X-rays below the particles. The minimum depth resolution for EDX analysis on SEM is approximately 1 μm and the particles were, in most instances, smaller than this. Analyses of areas of the coin and medal surfaces were undertaken to characterise the composition of the patinas. Results of four such analyses are shown in Table 1. All of the patinas were found to be predominantly chloride based. Sulfur was detected in many of the patinas; however, its concentration was always less than half of the chlorine detected. Several unaffected coins were also analysed and found to have mainly sulfide patinas. Whilst chloride patinas would be expected on coins from a burial context, their high abundance on coins and medals with ‘cabinet’ patinas is surprising. Such patinas accumulate from many years of exposure to the atmosphere and handling, and would be expected to be composed mainly of silver sulfide (Franey 1985, Rice 1980). Sodium, aluminium and silicon were also detected on the patina surfaces. These elements could be associated with dust or dirt deposition or could have originated from burial. The altered patinas had lower chlorine concentrations

than the unaltered patinas retained on the side of coins or medals in contact with the display boards (Table 1). The potential causes of a silver chloride patina are discussed in Table 2. No organic coatings were detected on the surfaces of these coins and medals.

Table 1
EDX analyses of coin and medal patinas

Registration number	description	Side analysed	Percentage Element Present								
			silver	chlorine	sulfur	oxygen	sodium	aluminium	silicon	calcium	copper
M4732	medal of death of James Stewart 1766	displayed	90.7±0.8	2.8±0.2	0.6±0.1	4.6±0.5	BD	0.2±0.1	BD	BD	BD
		reverse	91.3±0.9	4.6±0.2	0.4±0.1	2.5±0.5	0.5±0.2	BD	0.4±0.1	BD	BD
BMC 36	Tetradrachm of Antiochos VI 145–142 BC	displayed	69.2±1.0	1.3±0.1	0.2±0.1	11.5±1.1	BD	BD	BD	BD	BD
		reverse	65.1±0.9	5.2±0.2	1.6±0.1	11.7±1.0	BD	BD	0.5±0.1	BD	BD
1976 6-3 10	Coin of Khusra II 617	displayed	84.2±0.4	2.4±0.1	1.0±0.1	9.8±0.3	0.4±0.1	0.3±0.1	0.5±0.1	0.2±0.1	0.7±0.3
		reverse	77.3±0.7	4.8±0.2	0.9±0.2	12.9±0.6	0.6±0.2	0.4±0.1	0.7±0.1	0.4±0.2	0.7±0.4
		white particle	92.3±0.8	0.9±0.1	1.3±0.1	4.6±0.5	BD	0.3±0.1	BD	BD	BD
SNG 1299	Didrachm of Amastris 306–285 BC	displayed	69.6±0.6	0.2±0.1	BD	15.2±0.5	BD	BD	BD	BD	BD
		reverse	62.4±0.5	1.1±0.1	0.2±0.1	17.2±0.6	BD	BD	BD	0.3±0.1	BD

BD below detection limit
errors quoted are in precision

Table 2
Possible causes of chloride patinas

Cause	Likelihood in this instance
reaction with HCl gas (pos from incinerators) (Robbiola 1995)	low, concentrations have been measured below 0.9 µgm ⁻³ using diffusion tubes, see Table 3
reaction with chloride in dust particles	high, galleries have very high dust levels from high visitor numbers, significant concentrations of dust and chloride analysed inside showcases, see Table 3
reaction with chloride from handling	high, gloves only adopted in last twenty years
reaction from chloride burial	high for archaeological coins, but several coins and medals were never buried
reaction with chloride in conservation or restoration treatments	high, many coins obtained from antiquity market in 19th century

Other causes of altered appearance were observed in the British Museum collections. Four archaic Greek silver coins with altered patinas of similar appearance showed no signs of patina deterioration when examined in the SEM. The patinas were found to be chloride based, but no silver particles were observed. Larger, 3-20 µm diameter particles were observed on their surfaces. In three instances these were composed of magnesium, silicon and oxygen and were probably magnesium silicates. The fourth material was found to be calcium rich and was identified as calcite by FTIR (Lee 1996). French chalk, or talc and chalk are often used as separating agents when impressions are taken of coins or medals. The magnesium silicates and calcite appear to be residues of these materials which were not properly cleaned from the surface. Their presence dulls the surface and, in high concentrations, can colour it white. This generally occurs on both sides of a coin as it is unusual to take an impression of one face only. Similarly,

dust deposition would be expected to matt a coin's surface and this would only occur on the displayed surface of the coin.

One coin exhibited no signs of patina alteration when examined in the SEM and did not have significant amounts of particulate material on its surface. Only the displayed surface was affected and analysis indicated the presence of a wax on the surface (Green 1991). This coin was exhibited in close proximity to a spot light, which generated very high light levels, and caused heating of the coin to over 35°C. These conditions appear to have caused a bloom in the wax coating on the coin.

INFLUENCE OF THE ENVIRONMENT ON THE ALTERATION RATE

The main alteration reaction, the conversion of silver chloride to silver, is almost certainly photochemical in nature and has only occurred when coin or medal patinas are illuminated. The photochemical degradation of silver chloride is well documented (Butts 1967), and the patinas have been unaffected when protected from light exposure, in proximity to a display board. A study of the influence of certain environmental factors on the alteration rate was undertaken to determine if a preventive conservation approach could be used to mitigate the problem (Thickett 1998). The factors investigated were light, relative humidity, temperature and the presence of the pollutant gases, acetic acid and formaldehyde.

All experiments were carried out with coupons cut from commercially obtained silver chloride sheet. This was considered a superior experimental substrate to silver chloride produced by corroding silver. Such a material would better reproduce the patinas, but the commercially purchased sheet had the advantages of homogeneity and a flat surface on which the very early signs of alteration could be readily distinguished in the SEM. The degree of alteration was determined by placing the silver chloride coupon on a standard white ceramic plate and measuring its CIE Lab (CIE 1978, Billmeyer 1981) co-ordinates using a Minolta CR300 chroma-meter. In this arrangement, the light from the chroma-meter passed through the silver chloride coupon, reflected from the white plate and passed back through the coupon into the measuring head. To verify this measurement method, a number of silver chloride coupons were exposed in a Microscal light fastness tester with ML 500W bulb for periods ranging from a few hours to several weeks. This produced a range of surface alterations. The coupons were measured before and after exposure. The coupons were also examined using SEM. The amount of silver particles on the surface was determined by measuring the percentage surface coverage of such particles. The image processing abilities of the Oxford Instruments ISIS software were utilised with the particles being discriminated by atomic number contrast. The particles appeared white, whilst the patina was grey due to its lower atomic number. Images were collected at $\times 4000$ magnification and the percentage surface coverage was determined as the mean of at least five images collected from each coupon. A graph of

change in 'L*' versus the percentage coverage of particles on the surface is shown in Figure 2.

The change in lightness, 'L*', ΔL^* values correlated best with the degree of reaction. The coupons also showed a distinctive browning, which was observed as a sudden increase in the 'a*' value, indicating a shift towards red. This caused a corresponding shift in the ΔE^* values. No such browning was observed on any coins or medals from the British Museum; however, this has been observed on coins from the National Museum of Wales (Hill 1998). Neither ΔE^* or Δa^* gave a good correlation with the number of particles present, and ΔL values have been measured in all following experiments. Although L^* and hence ΔL^* are constrained by a^* and b^* and not independent variables, they only depend on one tristimulus value, 'Y' and in this instance, their use appears to be empirically justified.

The exposure experiments were carried out in a custom-built light bleaching chamber (Daniels 1993). Silver chloride coupons were exposed inside small perspex boxes on a raised polyethylene disc. The light exposure at the coupon surface was measured at 40165 lux with 61 $\mu W/lumen$ of UV. Neutral density and UV filters were placed over the lids of the boxes to examine the effects of different light exposure levels. Atmospheres with different RHs were generated by adding water-glycerol solutions (Miner 1953) to the bottom of the boxes, avoiding any direct contact with the silver chloride coupon. The light bleaching chamber had two fans, normally giving a chamber temperature of 39°C. Using just one fan increased the chamber temperature to 52°C. The effects of temperature were investigated by repeating the 50% RH experiment with just one fan running. Ethanoic (acetic) acid, methanoic (formic) acid and methanal (formaldehyde) atmospheres were generated above 1% solutions in 50% RH producing glycerol solution. The 1% solutions would be expected to generate vapour concentrations in the order of 10,000 $\mu g m^{-3}$ (Donovan 1972), much greater than would be expected in museum display cases (Grzywacz 1993). Results of the accelerated exposure tests are shown in Figures 3 to 5. Raising the temperature had no observable effect and this graph has not been included.

All of the ΔL^* plots rise towards a final plateau value. The greater the initial rate, the higher the plateau and number of silver particles produced. The reaction is strongly influenced by the amount of light energy illuminating the silver chloride. The presence of high UV levels has a marked effect, which is not surprising as silver chloride absorbs strongly in this region of the electromagnetic spectrum (Butts 1967).

Increasing RH and the presence of carboxylic acid and methanal vapours caused small increases in the degree of reaction, in the order of 30%. These results indicated that controlling RH or eliminating carbonyl pollutants from showcases would only have a limited effect and would not significantly extend the lifetime of the patina on coins or medals. Controlling light exposure would seem to be a better option to control the rate of alteration of the patina.

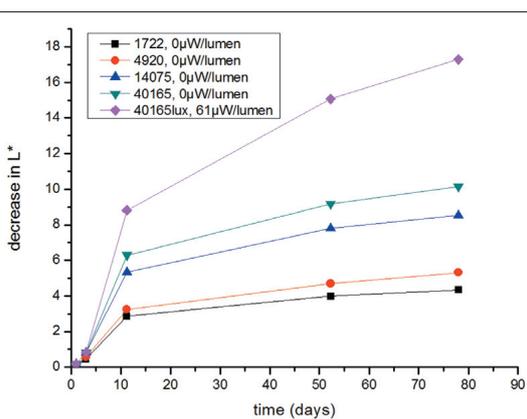
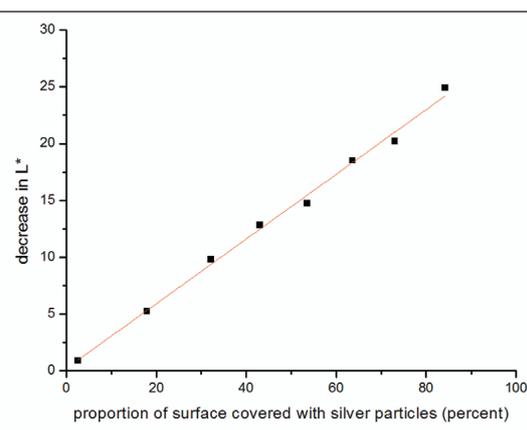


Figure 2

Decrease in L^* determined by colorimetry against the coverage with silver particles determined by SEM and image analysis. Errors are ± 0.3 determined from replicate measurements

Figure 3

Decrease in L^* as a function of light exposure with and without UV present. Errors are ± 0.3 determined from replicate measurements

EFFECT OF LIGHT ON PROTECTIVE EFFECT OF CORROSION LAYERS

The sulfidation of silver is often cited as a classic parabolic reaction. The reaction slows as it progresses, as the insulating properties of silver sulfide inhibit electron transport and the reaction rate is controlled by ‘diffusion’. However, silver sulfide is an n-type semiconductor and, if illuminated, its resistance can drop dramatically, reducing or even totally removing the protective effect. The potential for this to occur with patinas from a number of heritage environments has been assessed.

Silver coated piezo electric quartz crystals (6 MHz Purafill Onguard) were exposed at a range of English Heritage properties presenting very different environments:

- Apsley House – highly polluted urban
- Rangers House – polluted urban
- Brodsworth House – polluted rural
- Audley End House – unpolluted rural
- Walmer Castle – unpolluted maritime

The environments were characterised by monitoring the temperature and relative humidity with Meaco radiotelemetry system (Rotronic Hygroclip RH probes). The nitrogen dioxide, ozone and hydrogen sulfide concentrations were measured with diffusion tubes provided by Gradko International. The dust deposition rate was determined by exposing glass slides. The amount of dust deposited on the slides was determined by microscopy and image analysis (Howell 2002). The dust was extracted from the slides with 18.2 MΩ water and the chloride concentration of the extract analysed with ion chromatography (Dionex 600 with AS14A column with 0.02 M sodium bicarbonate and 0.018 M sodium hydrogen carbonate eluent at a flow rate of 0.5 ml/minute). The environmental conditions are shown in Table 3.

Table 3

Environmental parameters at exposure sites

Site	Amount of time in RH band (%)						NO2 µgm ⁻³	O3 µgm ⁻³	H2S µgm ⁻³	HCl µgm ⁻³	Dust	
	30-40%	40-50%	50-60%	60-70%	70-80%	>80%					% coverage in 30 days	Cl deposition rate µg m ⁻² day ⁻¹
Apsley	1.03	41.73	46.74	9.91	0.53	0.00	31	0.7	0.193	2.17	1.34	9
Rangers	16.04	35.93	29.05	12.55	5.48	0.61	23	1.95	0.175	0.69	0.16	3
Brodsworth	0.00	2.26	18.84	37.51	36.26	5.12	11	2.79	0.043	1.18	0.17	1
Audley End	0.03	3.59	22.70	69.93	3.67	0.00	4	0.98	0.076	<0.52	0.14	7
Walmer	1.27	18.71	31.09	20.83	25.41	2.65	8	6.23	0.130	1.23	1.14	94
British Museum showcase	45.13	51.83	5.90	0.80	0.00	0.00	20	1.5	0.72	0.86	1.74	38

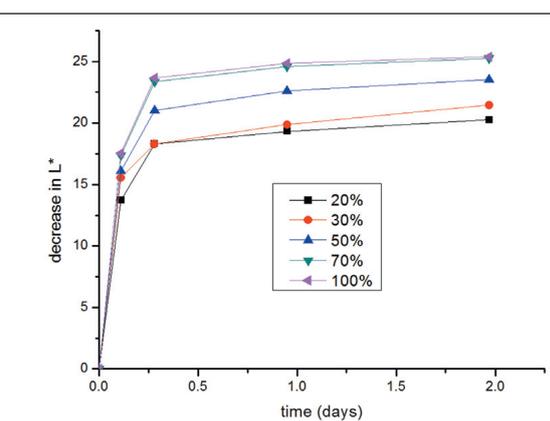


Figure 4

Decrease in L* of silver chloride sheet exposed to different relative humidity levels. Errors are ± 0.3 determined from replicate measurements

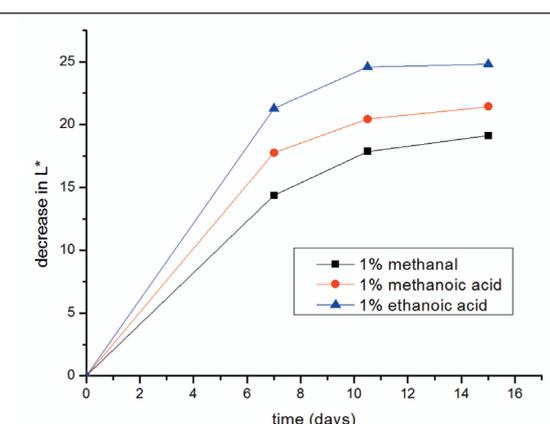


Figure 5

Decrease in L* in the presence of ethanoic acid, methanoic acid and methanal. Errors are ± 0.3 determined from replicate measurements

The increase in mass of the crystals was measured continuously with Onguard 3000 data loggers. Some of the environments produced parabolic tarnish kinetics (Baboian 2005). The crystals were collected after 12 months of exposure. The crystals were attached to an Onguard 3000 data logger with one exposed silver crystal and one new unexposed silver crystal. Each crystal was allowed to settle, then run for 60 minutes in the near darkness. Both crystals were then exposed to 50, 200, 350, 500 and 1000 lux from a tungsten halogen source via fibre optic cables. The silver tarnish rate was measured during all exposures.

Table 4

Tarnish behaviour and effect of light exposure on patinas formed

Site	Tarnish behaviour	Ratio of tarnish rate of exposed crystal to new crystal at					
		0 lux	50 lux	200 lux	350 lux	500 lux	1000 lux
Apsley	Parabolic	0.17	0.21	0.24	0.40	0.98	0.98
Rangers	Parabolic	0.16	0.19	0.22	0.22	0.87	0.86
Brodsworth	Linear	0.54	0.50	0.57	0.53	0.56	0.62
Audley End	Linear	0.47	0.45	0.47	0.48	0.43	0.48
Walmer	Parabolic	0.23	0.26	0.28	0.25	0.97	0.95

The tarnish rates increased to close to those of clean silver for some sites, when illuminated (Apsley House, Rangers House, Walmer Castle). This effect appears to occur between 350 and 500 lux with a slight increase in tarnish rate at 350 lux for one site (Apsley House). This illustrates breakdown of the protective nature for silver sulfide containing tarnish layers when illuminated with visible light.

The temperature compensation circuits on the Onguard system are reported to not fully compensate for increased temperature (Ankerschmit 2004). Increased temperature decreases the oscillation frequency of the quartz crystal and induces an apparent increase in mass. If the lighting was heating the crystals, then the increased tarnish rates may be an effect and not real. This was a particular concern as the albedo of the tarnished layer is much smaller than that of the clean crystal surface. The surface temperature of the crystals was measured with an Infra-red camera just after light exposure. It did not increase above that of the clean crystals within the errors of the camera used (0.1°C). The temperature of the gold leg conductors, which are thermally connected to the deposited silver film, was also measured with high precision Pt100 surface temperature probes. The temperature measurements, on the crystal leg connectors, registered temperature rises below 0.03°C. Comparison of these figures with the temperature calibration reported by Ankerschmit (2004) indicated that these increases in temperature on the tarnished layers are not sufficient to explain the increase in tarnish rate measured when illuminated.

The tarnish layers formed in these environments were characterized by SEM-EDX and electrochemical stripping (Costa 2002). Coupons exposed in these locations for three years, as part of a different project, were analysed. The Onguard monitoring is being continued to determine if the patinas from the less polluted sites become protective with further exposure and then display light sensitivity.

Table 5

Characterisation of patinas formed on three years exposure

	SEM-EDX wt%			Cathodic stripping nm		
	Ag	S	Cl	AgS	AgCl	AgO
Apsley	84.79	0.16	0.23	148	46	160
Rangers	88.35	0.05	0.03	56	12	60
Brodsworth	89.16	0.02	0.01	18	6	64
Audley End	89.79	0.01	0.06	14	20	24
Walmer	72.14	0.12	0.31	61	126	113

The discrepancy in the SEM and stripping analyses is most likely due to the different information depths of these two techniques. The information depth of the EDX is determined by the energy of the characteristic X-rays used to characterise the elements and will be shallowest for sulfur, followed by chlorine, and deepest for silver. For silver it is likely to be in the order of 1 μm . The stripping process will analyse the tarnish through its full depth.

CONCLUSIONS

Relatively low light levels have been shown to bleach the chloride patinas present on many coins and medals. Controlling other environmental parameters has limited potential to slow this deterioration.

Silver sulfide containing patinas formed in relatively polluted museum environments have a significant passivating effect. This is essentially lost when illuminated in excess of 350 lux with light from a tungsten lamp transmitted through fibre optics. Whether patinas from less polluted sites will develop passivating characteristics when exposed for longer time periods is unknown and requires further study.

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