



SOLARIZATION BEHAVIOUR OF MANGANESE-CONTAINING GLASS: AN EXPERIMENTAL AND ANALYTICAL STUDY

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Received: 21/4/2008

Accepted: 7/7/2008

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ABSTRACT

This paper is an initiative study of the solarization phenomenon of archaeological glass that until now has been recorded, but not extensively studied. It also aims to reveal the fact concerning this phenomenon as a photochemical process that affects the spectral and optical properties of ancient glass. Many solarized or purpled glasses found at Barsinia archaeological site in Jordan were collected and analyzed using atomic absorption spectroscopy (AAS) technique to identify the elemental composition of these glasses. Furthermore, many pieces of decolorized or colourless glasses containing reduced manganese were exposed to a concentrated ultraviolet (UV) radiation in accelerated weathering chamber for long times. A preliminary examination by light transmission microscopy and using double beam spectral photometers allowed determination of the changes in optical properties (transmittance and colour) of selected glasses. However, it is the goal of this paper to show that solarization becomes more than an aesthetic problem when it occurs on glass components of an optical system. Solarization may also permanently degrade a material's physical or mechanical properties.

KEYWORDS: Solarization; glass; Manganese oxide; chemical composition; UV radiation; Photo-oxidation.

INTRODUCTION

Solarization refers to a phenomenon in physics where a material undergoes a temporary change in color after being subjected to high energy electromagnetic radiation, such as ultraviolet light or X-rays. Clear glass and many plastics will turn amber, green or other colors when subjected to X-radiation, and glass may turn blue after long term solar exposure in the desert. Artificially, this phenomenon can be simulated in a short period of time in laboratory through the accelerated testing by using concentrated natural sunlight at high flux solar furnace and/or exposing the glass to the effect of both β and γ irradiation (Pitts *et al.* 1998). It is believed that solarization is caused by the formation of internal defects, called color centers, which selectively absorb portions of the visible light spectrum. Glass turned purple or violet by the sun used to be called *desert glass*. Now that's reserved for tektites and other glassy meteoric materials. Now, purpled glass is called *irradiated glass* (Figs. 1 and 2).



Fig. 1: A natural purpled or desert glass.

Brill (1988) reported that the influence of visible and UV radiation (less than 380 nm wavelength) on glass is called solarization. Certain types of archaeological colourless, transparent glasses which containing reduced manganese, when

exposed to sunlight or other radiations for extended periods develop a pink or pale purplish color depending on glass composition and duration of exposure to radiations. Bottles, insulators, and other objects having their color are often called *desert glass*, but the scientist prefers the term *solarized glass*. Newton (1989) noticed that some originally colourless glasses have developed a marked tint when exposed to sunlight for long time, a phenomenon known as *solarization*; similar changes can be produced in sensitive glasses by any kind of energetic radiation, from visible light to gamma rays. The effect is particularly noticeable in examples of nineteenth-century house windows which have assumed a marked purple hue in the course of time.



Fig. 2: An artificial purpled or solarized glass.

The major constituent of most archaeological glasses is silica, which is usually introduced as a raw material in the form of sand. Although silica itself is colorless in glass form, most sands contain iron as an impurity (about 0.5- 2%), and this imparts a greenish tint to glass. By adding certain other ingredients to a molten glass, it is possible to offset the greenish color and produce colorless glasses. Such ingredients are known as decolorizers, and one of the most common is manganese dioxide (MnO_2) (Abd-Allah 2006, 2007). In chemical terms, the

manganese acts as an oxidizing agent and converts the iron from its reduced state (which is a strong greenish blue colorant) to an oxidized state (which has a yellowish, but much less intense, color). In the course of the chemical reaction, the manganese goes into a chemically reduced state, which is virtually colourless (Newton 1989 and Jackson 2005).

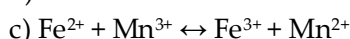
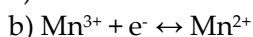
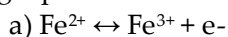
Manganese dioxide is believed to have been first used as a decolorizer as early as about the second century B.C. It was probably introduced as the mineral pyrolusite. From Roman times onward, glasses often contain about 0.5% to 1.0% manganese oxide. Later on, manganese dioxide (MnO_2) was sometimes called "glassmakers' soap". Antimony (Sb_2O_5) is another main oxidizing agent used as a glass decolorizer in ancient periods, which has an analogous effect on the iron except that it does not neutralize the yellow colour (Aerts *et al.* 1999 and Rutten *et al.* 2005). It was explained by Jackson (2005) that an alternative way of making colourless glass is to add a "decolorizer". Antimony and manganese decolorize glass by oxidizing the iron, although the relationship between the iron, manganese and other compounds in the glass is complex one. Antimony, a stronger decolorizer than manganese, also acts as a fining agent in glass by removing dissolved gases, so producing a more brilliant glass (Weyl 1981 and Bamford 1977). The relative amount of either oxidizing agent will depend upon the concentration of iron in the glass-making raw materials and equilibrium between the two (or more) elements (Sanderson and Hutchings 1987).

Manganese is derived from minerals. The purest commonly found manganese-containing mineral is pyrolusite

(MnO_2). Manganese has been recorded in soils and sands from Egypt (Turner 1956) and at levels approaching 0.5% in sands from the River Voltumo, a source noted by Pliny for the production of colourless glass (Brill 1999). Other authors note the presence of manganese in glasses, but suggest that its inclusion was a result of recycling or the use of glassmaker's soap to clarify the glass (Veld and Gendron 1980 and Mirti *et al.* 1993). In 1961, Sayer and Smith proposed a model for the use of colourless glasses. They found that colourless glasses from the Syrian coast are characterized by the increasing use of manganese oxide (MnO_2) rather than antimony oxide (Sb_2O_5), in concentrations in the order of 1% MnO towards the end of the Roman period. Later work by Sayer (1963) and Sayer and Smith (1967) showed that Islamic glasses were generally decolorized with either antimony or antimony/manganese until the end of the 9th century A.D, when an increase in manganese is observed. However, Jackson (2005) confirmed that colourless glass could have been produced in a number of ways relating to the choice of primary raw materials, decolorizers and the production technology.

The role of manganese in coloration, decoloration and solarization of glass is widely explained. Goffer (1980) affirmed that mixture of pure silica, soda, potash, and lime yield glasses that are essentially colorless. The color of glass is determined by the presence – whether intentional or otherwise – of various metallic oxides, usually in small amount. Manganese oxide was added as a coloring agent, yielding an amethyst color under certain conditions. Manganese (Mn^{3+}) ion colors the glass black or violet. Whereas, manganese (MnO^{2+}) ion does not form

any colors in glass, but acts as a decolorizer or a neutralizer of a yellowish or greenish colors resulting due to the presence of iron oxide in glass composition. Iron is usually present in glass as a mixture of ferrous (Fe^{2+}) ions, which color the glass blue, and ferric (Fe^{3+}) ions, which color it yellow; the combination effect of the two ions is the familiar "bottle green". Less than one percent of iron is sufficient to impart glass a distinct green hue (Rutten *et al.* 2005). According to Newton (1989) and Pollard (1996) the production of colors in glass depends not only upon the inclusion of a specific metal oxide (such as iron to produce blue or yellow glass), but also upon the presence of other oxides in the batch, and the temperature and state of oxidation or reduction in the kiln. When iron and manganese ions are present in the glass, equilibrium between the different states of oxidation of the iron and manganese is occur according to the following equations:



Thus when the conditions during melting of the glass are fully reducing (the equilibrium has been forced to the left) the iron contributes a bright blue color due to the Fe^{2+} ions and the manganese is in the colourless form so that a blue glass is obtained. When the conditions are fully oxidizing (the equilibrium has been moved towards the right) the iron contributes a brownish colour and the manganese contributes a purple colour, so that the glass appears brownish-violet. When conditions are intermediate all sorts of colours are obtained, such as green, yellow, pink etc., including a colourless glass when the purple from the manganese just compensates for the yel-

low from the iron (Goffer 1980 and Newton 1989).

It should be noticed that, the relationship between the iron, manganese and other compounds in the glass is a complex one. Newton (1989) explained that manganese acts as a decolorizer, but it has its effect only on the iron and not on the other colouring oxides which were used in ancient glasses. It was also stated that the iron- manganese color interaction can be affected in the presence of other components in glass composition, especially at least sulphur and possibly various transition metal ions. Freestone *et al.* (2005) suggested that the presence of manganese in some high iron-manganese fourth century glasses is to oxidize sulphur (S) and prevent the glass from going black. Shortland (2004) and Silvestri *et al.* (2008) explained that the high amount of sulphur oxide (SO_3) in ancient glasses is due to the use of natron as flux which contains Na_2SO_4 in various proportions as a contaminant. Newton (1989) found that as the result of melting various mixtures of sand and beachwood ash which contain a reasonable content of sulphur oxide, the resultant glass could vary from bluish-green through yellowish- to reddish-violet, depending on the furnace conditions. At this point it should be mentioned that there has been much confusion in the literature when amber (or yellow) glasses have been discussed. These colours are often described as *carbon-sulphur ambers*, whereas nearly the same colour can be obtained, as described above, by using iron and manganese and having the correct state of oxidation. So less than 1percent of carbon and sulphur is sufficient to give glass a distinct amber or brown hue.

Hadley *et al* (1998) suggested that to reduce bubbles in the finished product, "melting and fining aids such as SO_3 " may be added. Such compounds predominantly dissipate during the cooling process; some sulfate, however, remains dissolved in the finished glass. Though generally this has no effect on the color of the glass, strongly oxidized conditions are produced at the interface with the molten tin, which causes the formation of sulfide ions (S^{2-}). These ions combine with ferrous iron to produce iron sulfide (FeS_x), which is yellowish-brown and results in a 0.5% change in the total light transmittance of the glass, as well as a 3 nanometer shift in its color (light transmittance).

According to Pollard (1996) ions of transition metals such as scandium (Sc), titanium (Ti), chromium (Cr), nickel (Ni), vanadium (V) zirconium (Zr) etc. are strong colorizers of glass and impart it sharp colors if they are present in a concentration around 1%. These ions go into solution in the silicate network and form a part of it in the way that other multivalent cations do (Newton 1989). More generally, Bamford (1977) gives the following table to help work out which oxidation states will predominate when any two transition metals are present in melt:

Table 1: Colors of some transition metals according to their oxidation states in the glass

Transition metal	Oxidation state	Resulting colour
Vanadium	$\text{V}^{4+} / \text{V}^{5+}$	green / blue to gray
Titanium	$\text{Ti}^{3+} / \text{Ti}^{2+}$	purple / brown
Chromium	$\text{Cr}^{6+} / \text{Cr}^{3+}$	yellow / green
Nickel	$\text{Ni}^{3+} / \text{Ni}^{2+}$	Purple / yellow
Copper	$\text{Cu}^{2+} / \text{Cu}^+$	blue / colorless to red
Cerium	$\text{Ce}^{4+} / \text{Ce}^{3+}$	yellow / colorless
Arsenic	$\text{As}^{5+} / \text{As}^{3+}$	red / gray
Selenium	$\text{Se}^{4+} / \text{Se}^{2+}$	pink / red
Antimony	$\text{Sb}^{5+} / \text{Sb}^{3+}$	red / colorless

In addition, there can be complications due to the presence of other metal ions. For example, if a pair of transition metals are present (such as Cr and Fe), then the lower of the pair in this table (in this case, iron) will tend to exist as the left hand (oxidized) form of iron (Fe^{3+}) and the upper of the pair will be in the right hand (reduced) state (Cr^{3+}). This tendency is shown by the direction of the arrows. In most ancient glasses iron is present so the iron will always tend to be in the Fe^{3+} state and any other transition metal in its lower oxidation state (Bamford 1977). Furthermore, Newton (1989) affirmed that a brown solarization colour, instead of purple, can be produced when as much as ten parts of arsenic (As) and selenium (Se) per thousand parts of sand is present in the glass. Ferric oxide (Fe^{3+}) can be colourless instead of yellow when fluorides (F) and phosphates (P) are also present, whereas ferrous oxide (Fe^{2+}) produces a green color but when in the presence of zinc oxides they intensify to a blue. This is important not just from the point of the colour, but also because in glasses with a high transition metal content the redox state of these metals can influence glass durability. For example, Fe^{3+} improves the durability, whereas Fe^{2+} reduces it. However, it is clear that the colour of glass is the result of a complex interplay between the co-ordination of the transition metal ions, and by redox reactions between the various ions present, and redox potential in the furnace (Pollard 1996 and Silvestri 2008).

As previously mentioned, behavior and mechanism of solarization phenomenon can be easily explained. Overall, this phenomenon intensively occurs to glass fragments which widespread on the surface of archaeological sites and

ruins. Brill (1968), Newton (1989) and Glebov (2001) stated that if pieces of decolorized glass containing reduced manganese (Mn^{2+}) are exposed to ultraviolet radiation for long periods of time, the manganese may become photo-oxidized. This converts it back into an oxidized form (Mn^{3+}), which, even in rather low concentrations, imparts a pink or purplish colour to glass. The ultraviolet rays of the sun can promote this process over a matter of a few years or decades, thus accounting for the colour of desert glass. The effect has been reproduced in the laboratory conditions. Other chemical elements, which are subject to photo-oxidation, can also undergo colour changes in glasses when exposed to ultraviolet light. Since about the turn of the century, some of these, such as selenium and cerium, were occasionally used as decolorizers and therefore can produce solarization colours, just as manganese does. The colours developed by these two elements are said to range from yellow to amber.

In 1825 Faraday produced a scientific report on the effect of solarization. Since then the phenomenon has been much studied and it has been shown that the darkening of glass by radiation damage is part of a general effect of electron trapping. The colour can be removed by heating to 350 °C. The effect is discussed at length by Weyl (1951) who stated that the first satisfactory explanation of the development of the purple colour was given by Pelouze (in 1867), showing that it was produced by the interaction of Fe_2O_3 and MnO , leading to the formation of Mn_2O_3 and FeO (see equation c). A brown solarization colour, instead of purple, can be produced when as much as ten parts of arsenic and selenium per

thousand parts of sands is present in the glass (Newton 1989).

It was stated that the properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques, or both. In any glass, the mechanical, chemical, optical, and thermal properties cannot occur separately. Instead, any glass represents a combination of properties. And in selecting an individual glass for a product, it is this combination that is important. Usually one property cannot be changed without causing a change in the other properties. When a beam of light falls on a piece of glass, some of the light is reflected from the glass surface, some is absorbed in the glass and some of the light passes through the glass. The measure of the proportion transmitted is the *transmittance* (Scholze 1991 and Shelby 1997). Most glass is transparent, or, to be more accurate, partially transparent. Complete transparency would imply no reflection and no absorption. No glass achieves this uncompromised state but most glass transmits most of the light that lands on it. For this reason it is easy and convenient to classify glass loosely as a transparent material. A number of glasses are selectively *transparent*. They transmit light of one wavelength or colour more efficiently than any other. This selectivity carries over into the ultraviolet and infrared regions (Glebov 1998).

However, it was assumed that solarization may also permanently degrade a material's physical or mechanical properties, and causes obvious changes in optical properties of glass especially transmittance and transparency ratio. The UV radiation generates colour-centers in the glass leading to a reduced transmittance. (Pitts *et al.* 1998 and Jiang

et al. 2000). In detailed studies of the process of absorption and ionization of silicate glasses, Glebov (1998 and 2001) stated that coloration by visible light of borosilicate glasses represents an interesting example of nonlinear ionization at extremely irradiance. In addition, sensitivity to visible radiation occurs only in glasses that were previously exposed to UV radiation and coloration rate is proportional to squared initial concentration of colour centers. Spectral shape of absorption was the same before and after visible irradiation. Coloration rate was proportional to squared irradiance of exciting radiation. Finally, in contradiction with known photoinduced process, coloration are increased within exposure (Glebov 1998 and 2001).

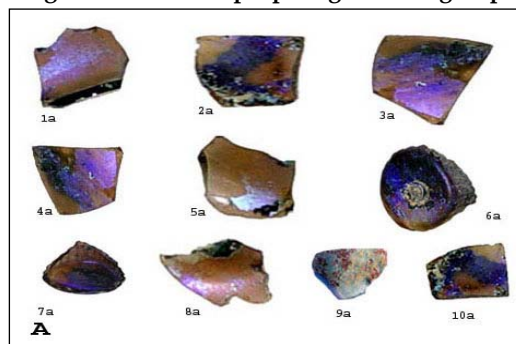
EXPERIMENTAL

Glass samples

Many archaeological glasses of different typology excavated from Barsinia archaeological site in Jordan have been collected, cleaned and prepared for chemical analysis, accelerated testing and microscopic examination. Based on the date determined by archaeologists, these glasses are dated to the Early Islamic period in Jordan. The chemical analyses show that all these glasses are of soda and identified as manganese-containing glass. These glasses were divided into two main groups according to the excavation stratum in which they were found, as well as their characteristic colour. The first group represents unstratified or surface finds was collected from the surface of the site. The preliminary diagnosis indicated that all the glasses of this group are partially or completely solarized and having a pur-

ple and violet hue due to the exposure to sunlight in the site for extended periods of time (Fig. 3).

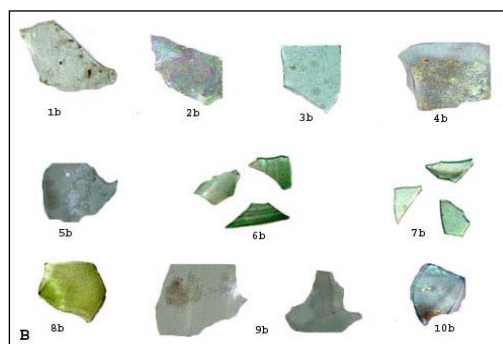
Fig. 3: Solarized or purpled glasses in group



(A).

Whereas glasses of the second group were unearthed from different strata of the site. So they are completely decolorized and/or nearly colourless (Fig. 4).

Fig. 4: Decolorized or nearly colourless glasses



in group (B).

Therefore they were employed for the UV accelerated testing. For the AAS measurements, the glass samples were prepared as solutions, whereas large pieces of glasses were required for the microscopic examination and accelerated solarization testing by using concentrated ultra violet radiation. The description of selected glasses is given in Table 2.

Table2: The visual description of the glass samples selected for analytical and experimental study

Group no.	Sample no.	Square	Description	Colour	
(A)	Solarized glass	1a	A1	Translucent body fragment	Tint violet
		2 a	A1	Translucent body fragment	Deep purple
		3 a	C1	Transparent body fragment	Deep violet
		4 a	C2	Translucent body fragment	Deep violet
		a 5	C1	Translucent body fragment	Tint purple to brown
		a 6	A1	Opaque cylindrical cup	Deep violet
		7a	A9	Opaque base fragment	Deep violet to brown
		a 8	A1	Translucent base fragment	Tint purple
		9a	C2	Translucent rim fragment	Tint brown
		10a	B1	Translucent body fragment	Deep purple to brown
(B)	Decolorized glass	1b	A1	Transparent body fragment	Nearly colourless
		2b	D1	Transparent body fragment	Tint blue
		3b	Tomb1	Translucent body fragment	Tint green
		4b	A1	Transparent circular facets	Tint green
		5b	C1	Translucent neck fragment	Tint blue
		6b	C1	Transparent neck fragment	Nearly colourless
		7b	D1	Transparent pinched fragment	Yellowish green
		8b	B1	Transparent body fragment	Yellowish green
		9b	Tomb1	Translucent body fragment	Nearly colourless
		10b	B1	Transparent body fragment	Tint blue

Analytical technique

To determine the elemental composition of the glass samples, a Perkin-Elmer Atomic Absorption Spectrophotometer (AAS, model 2380) with air-acetylene flam located at Yarmouk University in Jordan was used. There are a number of features that make this particular method well suited for archaeological specimens; among these features are: the method's versatility, in that it is able to detect over 65 different elements, high sensitivity in identifying and determining the percentages of elements concentrated in the sample; accuracy, in determining elements in a sample as small as 10 mg and

intensive to certain elements and each element must be analyzed individually; and finally the method's efficiency, in which concentration readings for a solution is usually carried out in a relatively short time (Sababha, 2000). The chemical elements were determined by two operating modes; the emission mode was used for the determination of sodium and potassium while the absorption mode was used for the determination of the other elements (Al-Ahmed and Al-Muheisen 1996).

Accelerated testing by UV radiation

Using concentrated Ultraviolet light generated in UV condensation weather-

ing device (model Atlas UV2000) located at Faculty of Archaeology and Anthropology, Yarmouk University in Jordan, the second group of glasses was exposed to acceleration factors of up to 300 times the normal outdoor UV exposure dose. The UV2000 is the perfect screening device for testing the effects of the sun's energy on material easily and affordably. Innovative design features improve test reproducibility and lower operating costs. The samples were irradiated with an Atlas UV2000 lamp of 340 nm for one month at a distance of 7 cm at a temperature of 90°C. This accelerated rate allows the exposure of materials such that a year of outdoor exposure can be simulated in about 5 hours. This test aims to investigate the solarization behaviour of ancient colourless or decolorized glasses containing reduced manganese in group (B) by producing the effect in the laboratory.

Examination methodology

To determine the changes in optical properties (transmittance and colour) of selected glasses, especially which exposed to concentrated UV radiation, photomicrographs with different magnifications for each glass sample were taken using the optical microscopy (Nikon model H-III) located at the Department of Earth sciences in the same university. Furthermore, the optical assessment by the critical eye and magnifying lens (10 x) was carried out to investigate the variegated coloration of glass surfaces.

Furthermore, to determine the optical changes of glasses in group (B) that artificially were solarized, the percent transmittance was measured for them before and after solarization process carried out, using a double beam spectral

photometer (model Perkin Elmer with special modifications) located in the Department of Physics in Yarmouk University. The standard setup enables to measure within a wavelength region from 250 nm up to 2500 nm. The measurement accuracy over the complete spectrum is about $\pm 0.5\%$. Within 300 nm to 700 nm the accuracy is $\pm 0.3\%$. The wavelength can be measured with an accuracy of ± 0.2 nm and ± 0.8 nm. As possible the suitable measurement sample thickness used.

RESULTS AND DISCUSSION

AAS determinations

The chemical composition of both the solarized glasses in group (A) and the decolorized glasses in group (B) was determined by (AAS) technique. Analyses results given in Tables 3 and 4 generally indicate that the solarized and decolorized glasses in both groups are identified as soda-lime-silica ($\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$) glass. Although glasses are characterized by their high potassium content (K_2O avgs. 4.94% and 4.27%) soda is the main alkali used (Na_2O avgs. 14.54% and 14.86%). This composition may indicate also that they have been made with mixed alkali rather than only natron salt as a source of alkali. The impact of this high amount of alkali on glass solarization have been explained by Lityushkin *et al.* (1995) who found that the increase in the total amount of alkaline-earth oxides at the expense of $\text{CaO} + \text{MgO}$ decreases solarization of glass of (SiO_2 - Na_2O - K_2O - CaO - MgO) system.

The solarized glasses in group (A) are characterized by high manganese content (MnO avg. 0.904%); in this case, manganese is presents in the converted or oxidized form (MnO^{3+}) ion, which

even in rather low concentrations, imparts a pink or purplish color to glass. The lower levels of antimony (Sb_2O_5 avg. 0.133%) may suggest that it would be the result of intentional addition to act as a second or associated decolorizer in most cases, whereas manganese is the primary decolorizer intentionally used (Fig. 5). It was stated by Jackson (2005) that when the both decolorizers are present in sufficient quantity, it would have the desired effect and, therefore, the presence of both is puzzling. The level of the decolorizer used is relative to the amount of iron which present here in high concentrations (Fe_2O_3 avg. 2.56%), as the antimony is a stronger decolorizer than manganese, lower quantities will render the glass colourless.

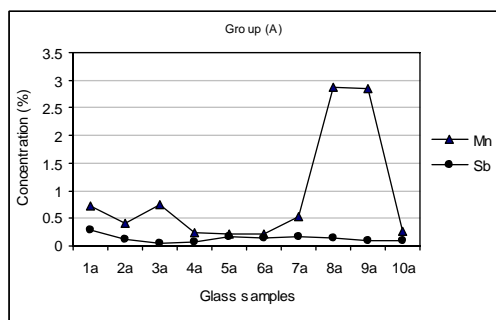


Fig. 5: A comparative pattern of Mn and Sb concentrations of solarized glasses in groups (A).

On the other hand, the decolorized glasses in group (B) are characterized by a moderate manganese content (MnO avg. 0.24%); in this case, manganese is presents in the primary reduced form (MnO^{2+}) ion, which does not form any colors in glass, but acts as a decolorizer or a neutralizer of a yellowish or greenish colors resulting due to the presence of iron oxide in glass composition (Fe_2O_3 avg. 2.55%). The very lower levels of antimony (Sb_2O_5 avg. 0.080%) point that antimony appears to be an impurity in

raw materials rather than deliberately added as a decolorizer in most cases, whereas manganese is the main decolorizer intentionally used (Fig. 6). This result is agreements with studies carried out by Brill (1999), Jackson (2004), Freestone *et al.* (2005) and Silvestri *et al.* (2008), which suggested that levels above 0.2% of the both oxides would be the result of intentional addition. Furthermore, the concentration required to decolorize iron-containing glass would appear to be more than 0.2% of manganese and around 0.5% of antimony.

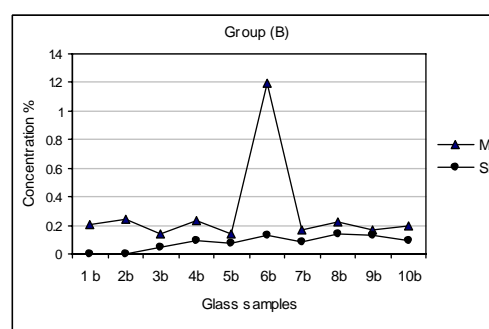


Fig. 6: A comparative pattern of Mn and Sb concentrations of decolorized glasses in groups (B).

Transition metals and trace elements, such as Zr, Cr, Ti, Ni, Se, Ce, V, Li, Co etc are present at very low levels of concentration that can not affect iron-manganese color interaction in both the solarized and decolorized glasses. However, levels of these elements contents are also diagnostic of the raw materials used, the differences in the concentration of these elements in archaeological glass is useful in identifying the possible source of sand, because they are also attributed to the geochemistry of differing production areas, as recently demonstrated by Freestone *et al.* (2000) and Silvesri *et al.* (2008). However, the obtained data of chemical analyses is relatively matches the results of previous

studies of Al-Ahmed and Al-Muheisen (1996) and Sababha (2000), which indicate that the sand at the mouth of river Byblos on the Syrian coast was the main source of sand utilized in the production of Jordanian glass over many centuries. On the other hand, in spite of sulphur oxide also is present in low levels less than 0.5 % in all the analyzed glasses (SO₃ avgs. 0.190 % and 0.172%), inten-

sively natural or artificial oxidized conditions render it to be a strong colorizer that colors the glass yellowish brown and can affect iron-manganese color interaction. This aspect may be observed on the solarized glass samples 5a, 7a and 10a which relatively are yellowish brown to amber hue.

Table 3: The main element composition of solarized glasses in group (A) obtained by AAS analysis

Oxides (wt. %)	Glass samples										Avg. %
	1a	2a	3a	4a	5a	6a	7a	8a	9a	10a	
SiO ₂	69.37	68.67	72.78	73.23	72.29	69.10	70.15	72.00	72.19	76.02	71.58
Na ₂ O	17.03	18.75	14.73	13.56	14.27	13.47	18.11	12.48	11.44	11.57	14.541
K ₂ O	2.471	4.373	3.953	4.571	5.877	6.751	5.473	5.077	5.276	5.609	4.943
CaO	4.763	2.406	3.958	4.095	2.120	5.362	2.071	3.324	3.777	2.248	3.412
MgO	0.0677	1.175	0.6844	0.2484	0.7834	0.6581	0.5556	0.5542	0.7907	0.7393	0.625
MnO	0.7135	0.4153	0.7535	0.2431	0.2099	0.2105	0.5284	2.873	2.838	0.2581	0.904
Al ₂ O ₃	0.7391	0.9042	0.9064	1.134	1.221	1.017	0.7849	0.9584	0.9434	1.060	0.966
Sb ₂ O ₅	0.2998	0.1155	0.0406	0.0694	0.1780	0.1520	0.1620	0.1339	0.0972	0.0909	0.133
PbO	1.904	0.00	0.0038	0.0204	0.0379	0.00	0.00	0.0128	0.0427	0.0489	0.207
SnO ₂	0.0322	0.0031	0.0053	0.0700	0.0055	0.00	0.0626	0.0898	0.0619	0.1120	0.044
Fe ₂ O ₃	2.309	3.148	2.158	2.224	2.974	3.242	2.061	2.453	2.500	2.547	2.561
CuO	0.0128	0.0254	0.0261	0.0254	0.0304	0.0319	0.0342	0.0354	0.0366	0.0377	0.029
SO ₃	0.221	0.253	0.205	0.213	0.191	0.187	0.151	0.201	0.132	0.178	0.190
CoO	n.d.	n.d.	0.014	n.d.	n.d.	0.022	n.d.	n.d.	n.d.	n.d.	0.018
Ce ₂ O	0.02	n.d.	n.d.	0.01	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	0.03
Cr ₂ O ₃	n.d.	0.082	n.d.	n.d.	0.018	0.035	n.d.	n.d.	n.d.	0.012	0.036
TiO ₂	0.101	0.094	0.126	0.103	0.071	0.075	0.134	0.118	0.046	0.090	0.095
NiO	0.020	n.d.	n.d.	0.055	n.d.	n.d.	n.d.	n.d.	0.014	n.d.	0.029
SeO	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	n.d.	0.004
SrO	0.049	0.022	n.d.	0.054	0.037	n.d.	n.d.	n.d.	n.d.	0.026	0.037
Li ₂ O	n.d.	n.d.	n.d.	0.048	n.d.	n.d.	0.029	n.d.	n.d.	n.d.	0.038
B ₂ O ₃	0.053	0.025	0.062	0.010	0.081	0.047	0.063	0.016	0.121	0.034	0.051
ZrO ₂	0.018	0.051	n.d.	n.d.	0.033	0.015	n.d.	n.d.	n.d.	0.042	0.031
V ₂ O ₅	0.051	0.024	n.d.	n.d.	n.d.	n.d.	n.d.	0.013	0.026	n.d.	0.028
Total %	100.24	100.53	100.40	99.98	100.42	100.37	100.42	100.33	100.33	100.72	100.37

Table 4: The main element composition of decolorized glasses in group (B) obtained by AAS analysis

Oxides (wt. %)	Glass samples										Avg. %
	1b	2b	3b	4b	5b	6b	7b	8b	9b	10b	
SiO ₂	67.78	69.44	74.58	68.94	76.54	71.31	71.14	69.20	72.45	78.03	71.94
Na ₂ O	19.61	18.64	12.18	16.03	12.74	15.16	14.71	14.47	14.11	10.99	14.86
K ₂ O	2.585	3.043	3.194	4.815	3.763	4.642	4.639	6.209	5.195	4.634	4.271
CaO	5.637	4.784	4.682	4.866	2.678	2.904	4.592	2.181	4.700	1.677	3.870
MgO	0.7276	0.7206	1.579	0.8928	0.5529	0.9369	0.6647	0.9421	0.8375	0.6005	0.845
MnO	0.2041	0.2433	0.1393	0.2325	0.1371	1.191	0.1699	0.2224	0.1660	0.1925	0.289
Al ₂ O ₃	0.8663	0.9238	0.5423	0.9062	0.9826	0.9381	1.008	1.147	0.0001	0.148	0.846
Sb ₂ O ₅	0.00	0.00	0.0439	0.0932	0.0793	0.1303	0.0829	0.1440	0.1353	0.0915	0.080
PbO	0.0205	0.0422	0.00	0.0005	1.165	0.8562	0.2553	0.00	1.702	0.00	0.404
SnO ₂	0.0603	0.0569	0.0532	0.0607	0.0390	0.0133	0.0565	0.0708	0.0547	0.0704	0.053
Fe ₂ O ₃	2.538	2.373	2.339	3.132	2.149	1.879	2.600	3.407	2.318	2.531	2.526
CuO	0.0135	0.0161	0.0152	0.0218	0.0207	0.0266	0.0224	0.0298	0.0244	0.0274	0.021
SO ₃	0.124	0.101	0.085	0.123	0.54	0.129	0.181	0.230	0.093	0.116	0.172
CoO	0.011	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.011
Ce ₂ O	n.d.	n.d.	0.02	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	0.035
Cr ₂ O ₃	n.d.	n.d.	0.015	n.d.	n.d.	n.d.	n.d.	0.048	n.d.	n.d.	0.031
TiO ₂	0.071	0.114	0.046	0.131	0.066	0.052	0.148	0.143	0.067	0.071	0.090
NiO	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	n.d.	0.006	0.005
SeO	0.006	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0042	n.d.	n.d.	0.005
SrO	n.d.	0.051	n.d.	n.d.	n.d.	0.022	0.043	n.d.	n.d.	n.d.	0.038
Li ₂ O	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.08	n.d.	n.d.	n.d.	0.045
B ₂ O ₃	0.035	0.019	0.113	0.006	0.073	0.023	0.040	0.068	0.091	0.046	0.051
ZrO ₂	n.d.	0.021	n.d.	n.d.	n.d.	0.074	n.d.	n.d.	0.015	n.d.	0.036
V ₂ O ₅	0.060	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.062	n.d.	0.047	0.056
Total %	100.34	100.58	99.62	100.26	100.09	100.33	100.43	98.57	99.95	99.27	100.04

Optical microscopy observations

From optical microscopy observations of the naturally solarized glasses in group (A), it can be seen that the hue of these glasses is varied between the tint violet and deep purple. Figure 7 shows the microscopic images of the most solarized glass samples in this group (1a,

2a, 4a, 5a, 7a, and 10a), from which we can find a nearly homogeneous distribution and sharpness of purple colour in most cases whereas, the violet colour is nearly not. Additions to that, other aspects of sugar-like surface and aciniform or botryoidal air bubbles in different sizes also were observed.

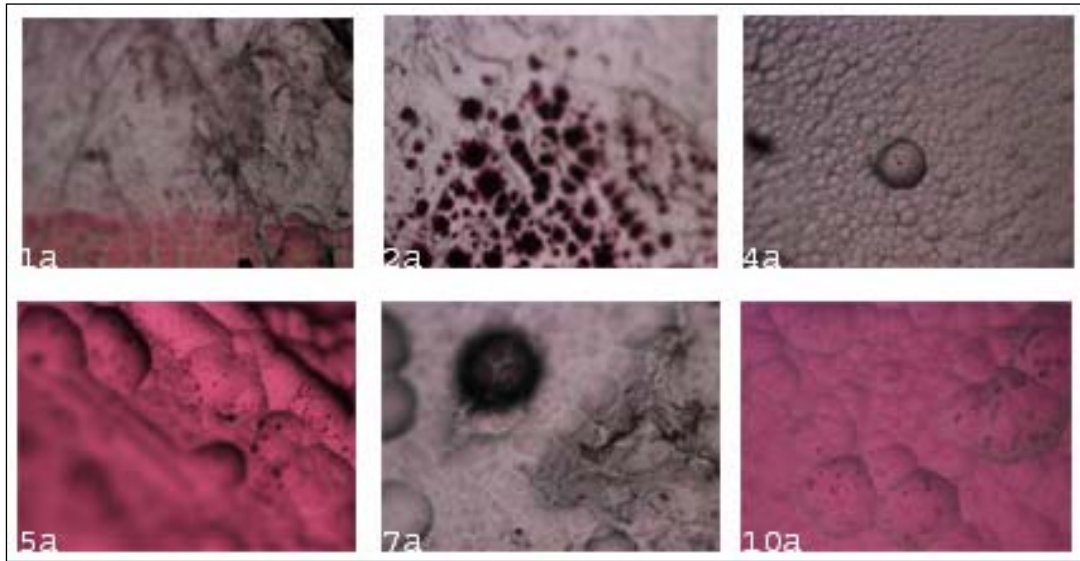


Fig. 7: Microscopic images of the most solarized glasses (1a, 2a, 4a, 5a, 7a, and 10a) in group (A).

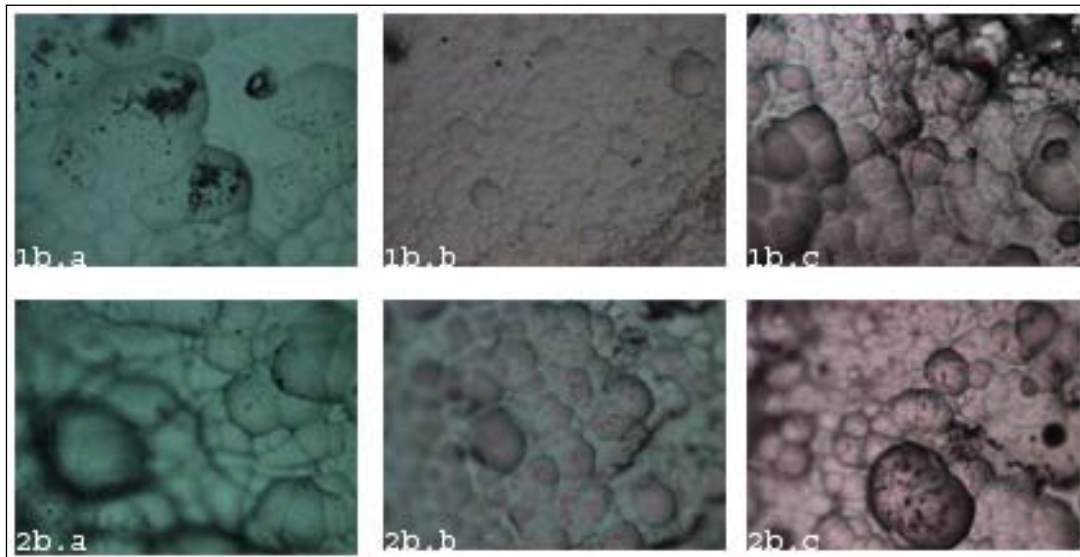


Fig. 8: Microscopic images of the most colourless glasses (1b and 2b) in group (B) before exposure to accelerated solarization test.

On the other hand, Figure 8 shows the microscopic images of the most colourless glasses (1b and 2b) in group (B), which artificially were solarized by using concentrated Ultraviolet light generated in UV condensation weathering device, from which we can see the gradual effect of accelerated test on the formation of violet and purple hues in the

glass samples due to the oxidation reaction of reduced manganese, wherein the (Mn^{+2}) ion is converted to (Mn^{+3}) ion by the UV radiation. (See equation c). The hues are gradually formed by time and cumulative exposure. The solarization of glass containing reduced manganese is rapid, with the process being complete in only a few days of exposure.

Measurement and specification of glass transmittance

Figure 9 comparatively shows the changes of transmittance values of glasses in group (B) as a function of exposure to accelerated solarization at 340 nm of UV radiations. From which, it can be generally concluded that the transmittance of glass is influenced by electromagnetic radiation or solarization. In addition, it can be observed that glass with a high lead content in samples 5b (Pb 1.16%) and 9b (Pb 1.70 %) normally have small solarization effects and low transmittance ratio. This result appears to be of the same opinions of Pitts *et al.* (1998), Jiang *et al.* (2000) and Leonid *et al.* (2001) that the visible, UV, and IR irradiations transmittance characteristic is mostly influenced by heavier elements in the glass composition (like e.g. lead, barium, niobium, titanium, and lanthanum), melting technology and/or residual impurities. These heavier elements are necessary to achieve a high refractive index but decrease the transmittance in the blue region. It was also observed that glasses undergo a rapid 10-20% decrease in transmittance.

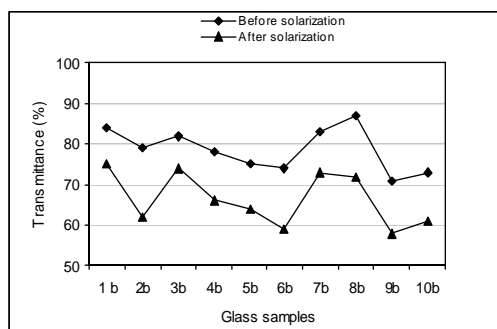


Fig. 9: Transmittance changes of glasses in group (B) as a function of exposure to accelerated solarization by UV radiation.

Furthermore, in Figure 10, a comparison of the effect of natural sunlight solarization of group (A) and artificial or accelerated solarization by UV radiation at 340 nm of group (B) on the transmittance of manganese containing glass is shown. From the data one may also conclude that the solarization rates are obviously different in the two groups, perhaps resulting from differences in the chemical compositions, spectral content, radiation intensity, and duration of normal outdoor exposure to sunlight in the sit or indoor exposure to concentrated UV radiation in the laboratory.

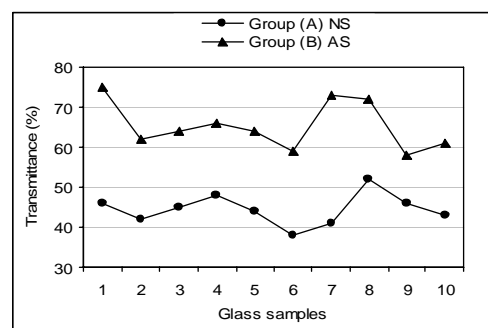


Fig. 10: Transmittance rates of naturally solarized glasses in group (A) in comparison with that of the accelerated solarized glasses in group (B).

CONCLUSIONS

The new results obtained by the qualitative and quantitative technique (AAS) that followed by accelerated solarization testing and microscopic examination of twenty glasses from Barsinia archaeological site in Jordan confirm some of the results previously obtained by other authors, and yield a consistent set of data for comparison with the data obtained on other archaeological glass containing manganese.

It has been demonstrated that solarization or electromagnetic radiation influences the transmittance of a glass de-

pending on glass type, composition and the wavelength of radiation. The increase in the total amount of alkaline-earth oxides at the expense of CaO + MgO decreases solarization of glass of (SiO₂-Na₂O- K₂O- CaO- MgO) system. Likewise it was found that glass with a high lead content in normally have small solarization effects and low transmittance ratio. Also the iron-manganese color interaction can be affected in the presence of sulphur (SO₃) and various transition metal ions at sufficient levels of concentration around 0.5% or above.

It is also shown that the solarization behavior of glass can be effectively investigated in laboratory by irradiation with a UV lamp. It was observed that manganese containing glass undergoes a rapid 10-20% decrease in transmittance at 340 nm of UV radiations. The explanation of this phenomenon is reported by virtually authors that the UV radiation

generates color-centers in the glass leading to a reduced transmittance.

It is important to emphasize that solarization becomes more than an aesthetic problem when it occurs on glass components of an optical system. The solarization causes deterioration of the UV performance and eventual failure of the glass and the system. Solarization may also permanently degrade a material's physical or mechanical properties. However, this study is in agreement with the previous research works carried out by Jiang *et al.* (2000) and Glebove (2001) which assumed that the spectral properties (especially transmittance and colour) of an optical material can be changed by solarization when it exposed to short wavelength, near bandgap radiation. Thus, further studies are required for developing antisolarants, and preventing solarization of significant optical materials such as archaeological glass exhibits in museums.

ACKNOWLEDGEMENTS

The author would hereby like to acknowledge the general directorates of laboratories of AAS, microscopes unit and weathering unit located in Yarmouk University in Jordan. The gratitude is also extended to the two anonymous referees for their critical reviews and suggestions.

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