From Decolorization to Solarization of Historical Glass: A review
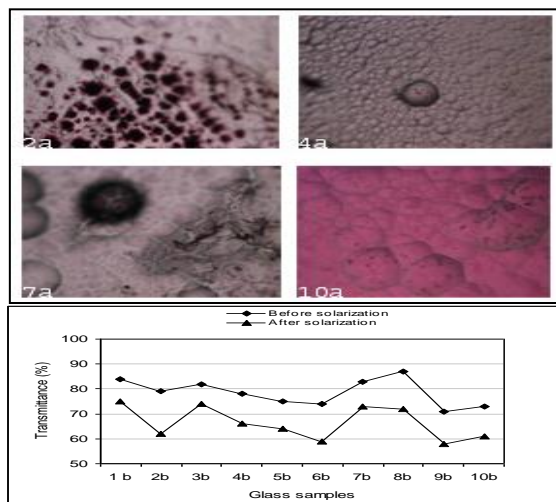
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HIGHLIGHTS

- Decolorization is the colour correction technique known since ancient times.
- Antimony and manganese decolorize glass by oxidizing the iron oxides.
- The influence of visible and UV radiation (less than 380 nm wavelength) on glass is called solarization.
- Solarization may permanently degrade a material's physical or mechanical properties.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Colour from raw material impurities is one of the main concerns for glassware production. Since ancient times until now, decolorizing glass, or making it clear, was a goal that had varying degrees of success from the 7th century BCE to the 1st century CE in the Mediterranean. A method for making glass clear was eventually systematized in Alexandria, under the Roman Empire, around 100 CE and spread through the empire. On the other hand Solarization refers to a phenomenon in physics where a material undergoes a temporary change in colour 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 colours when subjected to X-radiation, and glass may turn

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blue after long term solar exposure in the desert. This paper aims to shed light on the studies and scientific literature of the decolorization and solarization phenomena of archaeological glass that until now has been recorded, but not extensively studied from the archaeometrical side.

1. Introduction

For most glass scientists, contaminants, especially metallic contaminants were the bane of producing a crystal clear product. Great care was taken to ensure the purity of each ingredient at each step of the glass making process. The greatest threat of all was iron. Even small amounts will impart a green tint and for Renaissance era glassmakers, nemesis iron was everywhere. It is a common impurity in quartz, the main ingredient of glass, which appears as yellow "rust stains" both in sand and stones. It is present in the plant salts used for glass flux as a trace-element and in the manufacturing tools. Iron was in the mortars and pestles, in the pots and kettles, in the frit rakes, in the ladles, the stirring rods and in the blowpipes. A mistake at any step could easily tint the batch, even at the final stages [1, 2].

The colour from raw material impurity is one of the main concerns for glassware production. Since ancient times until now the glass manufacturers avoided impurities especially iron oxide (Fe_2O_3) as much as possible. However, the glassware would still contain about 0.03 wt% of iron oxide. The iron oxide is the major impurity in glass, and most of iron oxide comes from sand. [2, 3]. Glass production can avoid this effect by using high purity sand. Nevertheless, the price of high purity sand is very high. It is possible to control the colour of iron oxide in glass by using decolorizing agents. This method can overcome the low quality sand to produce glass, and reduce the production cost. There are several materials that can be used as decolorizing agents, however, they have some disadvantages such as selenium (Se) which is very volatile in the furnace, arsenic oxide (As_2O_5) and antimony oxide (Sb_2O_5) which are both toxic and manganese dioxide (MnO_2) [1, 3,4]. Moreover,, certain types of historical colourless, transparent glasses which contain reduced decolorizers such as manganese, when exposed to sunlight or other radiations for extended periods develop a pink or pale purplish colour depending on glass composition and duration of exposure to radiations. Bottles, insulators, and other objects having this colour are often called *desert glass*, but the scientist prefers the term *solarized glass* [5].

This study aims to:

- Explain the definition of both decolorization and solarization phenomena of historical glass.
- Carry out a survey on the scientific and historical literatures on both phenomena.
- Focus on the mechanism and causes of both phenomena.
- Explain the effect of both phenomena on degrading historical glass.

2. Glass Decolorization
2.1. What is glass decolorization?

Decolorization of glass is an example of a technique that was developed through experimentation without deep understanding of the physics involved. Theories of light and colour and the way they are perceived by the human eye came much later. In fact, manganese itself was not isolated as a metal until 1774, yet it was used skillfully by glass artisans three or four hundred years earlier. This colour correction technique was known as early as the late 14th century. Manganese oxide was known as a pigment in antiquity; the Magnesia region in Thessaly, central Greece was an ancient source for the black mineral. Around the year 1450, a clear crystal-like glass suitable for working into thin elaborate forms was developed in Venice [6, 7].

Removing the green tint of iron contamination with manganese is a clever trick. The manganese imparts a magenta tint to glass. As the complementary colour to green, it effectively "cancels out" the green tint. The trade-off is that the glass is slightly darkened, even if appearing as a neutral colour to the eye [1]. When light passes through glass tinted by iron, green light is unaffected, which is why it appears green. The other colours that

make up white light, notably red and violet are dampened. In effect, the green is enhanced. Now, adding manganese to the glass dampens only green light and brings the spectrum back into closer balance. The overall effect is that all the colours of light are slightly dampened, but by the same amount. However, minor contamination from iron would produce only a small green tinge and the problem was corrected with a small dose of manganese. The resulting grey would hardly be noticed, especially in the thin, delicate pieces so popular at the time. To the eye of all but the most experienced expert, this decolorized glass had perfect crystal clarity [6].

2.2. Decolorization mechanism and glass Decolorizers

As mentioned before, the major constituent of most historical glasses is silica, which is usually introduced as a raw material in the form of sand. Although silica itself is colourless 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 colour and produce colourless glasses. Such ingredients are known as decolorizers, and one of the most common is manganese dioxide (MnO_2) [8, 9]. In chemical terms, the manganese acts as an oxidizing agent and converts the iron from its reduced state (which is a strong greenish blue colourant) to an oxidized state (which has a yellowish, but much less intense, colour) (Fig. 1). In the course of the chemical reaction, the manganese goes into a chemically reduced state, which is virtually colourless (10, 11].

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

Fig.1: Decolorized and nearly colorless glasses from Roman period [3]

except that it does not neutralize the yellow colour [12, 13]. It was explained by Jackson (2005) [11] 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 [14, 15]. The relative amount of either oxidizing agent will depend upon the concentration of iron in the glassmaking raw materials and equilibrium between the two (or more) elements [16, 17].

Manganese is derived from minerals. The purest commonly found manganese-containing mineral is pyrolosite (MnO_2). Manganese has been recorded in soils and sands from Egypt, and at levels approaching 0.5% in sands from the River Volturno, a source noted by Pliny for the production of colourless glass. 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 [18,19]. 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_2 towards the end of the Roman period. Later

work by Sayer (1963) [20] and Sayer and Smith (1967) [21] 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 [5].

The role of manganese in coloration, decoloration and solarization of glass is widely explained. Goffer (1980) [22] affirmed that mixture of pure silica, soda, potash, and lime yield glasses that are essentially colourless. The colour of glass is determined by the presence – whether intentional or otherwise – of various metallic oxides, usually in small amounts. Manganese oxide was added as a colouring agent, yielding an amethyst colour under certain conditions. Manganese (Mn^{3+}) ion colours the glass black or violet. Whereas, manganese (MnO^{2+}) ion does not form any colours in glass, but acts as a decolorizer or a neutralizer of a yellowish or greenish colours , 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 colour the glass blue, and ferric (Fe^{3+}) ions, which colour 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 [13]. According to Pollard (1996)[23] the production of colours 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, 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:

a) $Fe^{2+} \leftrightarrow Fe^{3+} + e-$
b) $Mn^{3+} + e^- \leftrightarrow Mn^{2+}$
c) $Fe^{2+} + Mn^{3+} \leftrightarrow Fe^{3+} + Mn^{2+}$

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 colour 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 yellow from the iron [22, 23].

It should be noticed that, the relationship between the iron, manganese and other compounds in the glass is a complex one. Newton (1989) [10] 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 colour 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) [24] 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) [25] and Silvestri *et al.* (2008) [26, 27] 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) [10] 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 1% of carbon and sulphur is sufficient to give glass a distinct amber or brown hue.

Hadley *et al* (1998) [28] 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 colour 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 (FeSx), 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 colour (light transmittance).

3. Glass Solarization
3.1. What is solarization?
It was stated that solarization refers to a phenomenon in physics where a material undergoes a temporary change in colour after being subjected to high energy electromagnetic radiation, such as ultraviolet light or X-rays.

3.2. Why glass is being solarized?
It is believed that glass solarization is caused by the formation of internal defects, called colour 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. 2, 3).

Brill (1988) [5] 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 contain reduced manganese, when exposed to sunlight or other radiations for extended periods develop a pink or pale purplish colour depending on glass composition and duration of exposure to radiations. Bottles, insulators, and other objects having this colour 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 sun

Fig. 2. Solarized Amethyst glass at UC Davis Department of Anthropology Museum. [2]

Fig. 3. A natural purpled or desert glass. [3]

light 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.

Pitts *et al*. (1998) [29] stated that clear glass and many plastics will turn amber, green or other colours 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 .

3.3. Glass Solarization Mechanism

According to Pollard (1996)[23] 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 sharp colours if they are present in concentrations 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 [10]. More generally, Bamford (1977) [15] gives the following table (Table 1) 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 [15].

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

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 [15]. Furthermore, Newton (1989) [10] 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 thou-

sand parts of sand is present in the glass. Ferric oxide (Fe^{3+}) can be colourless instead of yellow when fluorine (F) and phosphorous (P) are also present, whereas ferrous oxide (Fe^{2+}) produces a green colour 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 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 coordination of the transition metal ions, and by redox reactions between the various ions present, and redox potential in the furnace [23, 26].

As previously mentioned, behavior and mechanism of solarization phenomenon can be easily explained. Overall, this phenomenon intensively occurs to glass fragments which are widespread on the surface of archaeological sites and ruins. Brill (1968) [30] and Glebov (2001) [31] 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. This 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 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 [32].

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 ef-

fect of electron trapping. The colour can be removed by heating to 350 ^{0}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 [10].

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* [10]. 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 [32].

However, it was assumed that solarization may also permanently degrade a material's physical or mechanical properties, and cause 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. In detailed studies of the process of absorption and ionization of silicate glasses, Glebov [31, 32] stated that coloration by visible light of borosilicate glasses represents an interesting example of nonlinear ionization at extreme 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 is increased within exposure [31, 32].

3.4. The Impact of glass composition on its solarization process

According to Abd-Allah (2009) [33] the chemical composition of both solarized and decolorized glasses from Levant was determined and indicate that the glass is identified as soda-lime-silica (Na_2O-CaO-SiO_2) glass (Fig.4). 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%) [34]. This composition may also indicate 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) [35] who found that the increase in the total amount of alkaline-earth oxides at the expense of CaO + MgO decreases solarization of glass of (SiO_2-Na_2O-K_2O- CaO- MgO) system (Table 2).
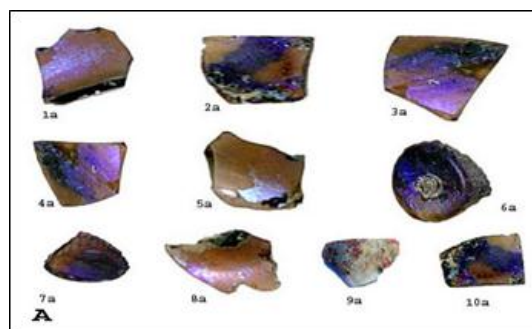

Fig. 4. Solarized or purpled archaeological glasses from Levant [33].

Table 2. The main elemental composition of colorized, decolorized and solarized glasses from Levant obtained by AAS analysis [36].

Item	S.ID.	Fe_2O_3 Wt. %	MnO Wt. %	TiO_2 Wt. %	CaO Wt. %	K_2O Wt. %	P_2O_5 Wt. %	SiO_2 Wt. %	Al_2O_3 Wt. %	MgO Wt. %	Na_2O Wt. %	SO_3 Wt. %	Cl Wt. %	CuO Wt. %	PbO Wt. %	L.O.I Wt. %
1	**L26**	0.53	0.03	0.06	4.39	1.63	0.12	71.60	0.48	0.72	16.90	0.11	0.28	0.10	0.50	2.50
2	**K25**	0.40	0.03	0.05	8.01	0.73	0.13	67.3	2.57	0.79	17.60	0.08	0.17	0.04	-	2.20
3	**Jb23**	0.54	1.48	0.06	8.19	0.66	0.20	69.40	2.52	0.52	15.10	0.05	0.16	0.06	-	1.00
4	**N20**	0.44	0.04	0.06	8.78	0.66	0.15	66.70	2.50	0.57	18.70	0.15	0.33	0.05	-	-
5	**L26**	0.40	0.04	0.05	8.32	0.79	0.16	68.00	2.65	0.51	18.40	0.14	0.34	0.03	-	-
6	**N20**	0.52	1.49	0.06	8.29	0.70	0.30	69.50	2.70	0.56	15.30	0.11	0.26	0.06	-	-
7	**N20**	0.83	0.82	0.11	9.08	1.28	0.27	66.80	2.78	0.72	15.90	0.07	0.31	0.04	0.03	0.20
8	**N19**	0.77	0.73	0.09	8.94	1.22	0.33	66.90	2.90	0.61	16.70	0.16	0.36	0.06	0.05	-
9	**L26**	0.66	1.81	0.10	7.11	1.25	0.14	68.40	3.26	0.57	12.70	0.09	0.19	0.04	-	3.60
10	**K25**	0.72	1.15	0.11	9.84	0.94	0.23	66.50	2.88	0.69	14.20	0.06	0.13	0.04	0.03	2.90
11	**N26**	0.71	0.48	0.08	9.15	1.07	0.23	67.50	2.64	0.50	15.10	0.14	0.20	0.05	0.02	1.50
12	**M20**	0.45	0.03	0.06	8.32	0.97	0.12	68.90	2.49	0.38	17.60	0.16	0.36	0.08	-	-
13	**K24**	0.48	0.29	0.07	8.10	0.81	0.16	69.20	2.70	0.42	16.00	0.04	0.30	0.03	-	0.70
14	**K24**	0.54	0.02	0.05	8.45	0.87	0.08	68.70	2.81	0.78	17.30	0.06	0.11	0.07	-	-
15	**N19**	0.55	0.28	0.07	8.20	0.80	0.19	70.40	2.53	0.47	16.00	0.06	0.20	0.04	-	0.20
16	**N19**	0.58	0.30	0.08	8.62	0.96	0.22	69.90	2.61	0.57	15.50	0.05	0.16	0.04	0.02	0.40
17	**L23**	0.75	0.14	0.11	9.31	1.44	0.32	67.50	3.21	0.66	15.10	0.15	0.24	0.07	-	-
18	**M20**	0.58	0.19	0.07	7.78	0.90	0.19	70.00	2.72	0.45	15.70	0.10	0.32	0.06	-	0.20
19	**N19**	0.46	0.06	0.07	7.85	0.90	0.13	69.00	2.75	0.42	16.30	0.09	0.31	0.03	-	1.60
20	**L26**	0.55	1.60	0.06	7.88	0.96	0.29	67.50	2.92	0.56	16.30	0.11	0.17	0.06	-	1.10
Avg. Wt.%%		0.57	0.55	0.07	8.23	0.97	0.19	68.48	2.63	0.57	16.12	0.09	0.24	0.05	0.10	

The solarized glasses are characterized by high manganese content (MnO avg. 0.904%); in this case, manganese is present in the converted or oxidized form (MnO^{3+}) ion, which imparts a pink or purplish colour to glass, even in low concentrations. The low concentrations of antimony (Sb_2O_5 avg. 0.133%) may suggest that it was the result of intentional addition to act as a second or associated decolorizer in most cases, whereas manganese is the primary decolorizer intentionally used. It was stated by Jackson (2005) [11] that when 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 decolourizer used is relative to the amount of iron which is present here in high concentrations (Fe_2O_3 avg. 2.56%), as antimony is a stronger decolorizer than manganese, lower quantities will render the glass colourless [33, 34].

On the other hand, decolorized glasses are characterized by a moderate manganese content (MnO avg. 0.24%); in this case, manganese is present in the primary reduced form (MnO^{2+}) ion, which does not form any colours in glass, but acts as a decolorizer or a neutralizer of yellowish or greenish colours resulting from the presence of iron oxide in glass composition (Fe_2O_3 avg. 2.55%). The very low concentrations of antimony (Sb_2O_5 avg. 0.080%) point out 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 decolourizer intentionally used. This result is agreement with studies carried out by Brill (1999) [30], Jackson (2004) [24], Freestone *et al.* (2005) [11] and Silvestri *et al.* (2008) [27] which suggested that concentrations above 0.2% of 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 [33].

Transition metals and trace elements, such as Zr, Cr, Ti, Ni, Se, Ce, V, Li, Co etc are present at very low concentrations that cannot affect iron-manganese colour interaction in both the solarized and decolorized glasses. However, concentrations of these elements 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 different production areas, as recently demonstrated by Freestone *et al.* (2000) [24] and Silvesri *et al.* (2008) [11]. However, the results of chemical analyses relatively match the results of previous studies on Levantine glass 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 Levantine glass over many centuries [36-38]. On the other hand, in spite of the presence of sulphur oxide in low concentrations less than 0.5 % in all the analyzed glasses (SO_3 avgs. 0.190 % and 0.172%), intensive natural or artificial oxidized conditions render it to be a strong colorizer that colours the glass yellowish brown and can affect iron-manganese colour interaction [39-40].

3.5. The artificial solarization of decolorized glass

According to Abd-Allah (2009) [33] decolourized Byzantine soda-lime-silica (Na_2O-CaO-SiO_2) glass containing reduced manganese excavated from Barsinia archaeological site in Jordan were solarized artificially by using a concentrated Ultraviolet light generated in UV condensation weathering device as 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. The changes in optical properties (transmittance and the variegated colouration of glass surfaces) of the glasses which were exposed to concentrated UV radiation can be investigated by using optical microscopy and optical assessment using a magnifying lens (10 x) as well as using a double

beam spectral photometer. The standard set-up enables to measure within a wavelength region from 250 nm up to 2500 nm. The measurement accuracy over the complete spectrum is about ±0.5%. Within 300 nm to 700 nm the accuracy is ±0.3%. The wavelength can be measured with an accuracy of ±0.2 nm and ±0.8 nm [39-42](Figs. 5, 6).
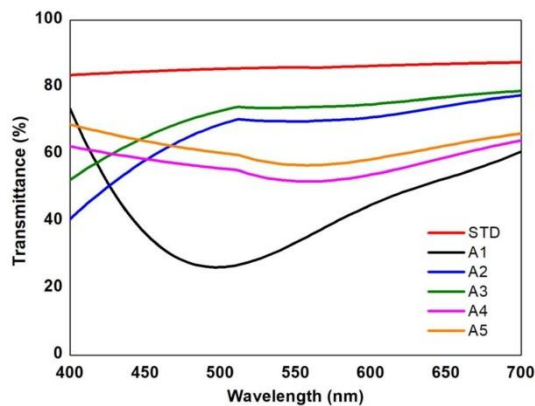

Fig. 5. Visible transmittance spectra of the produced decolorized glass samples [41]
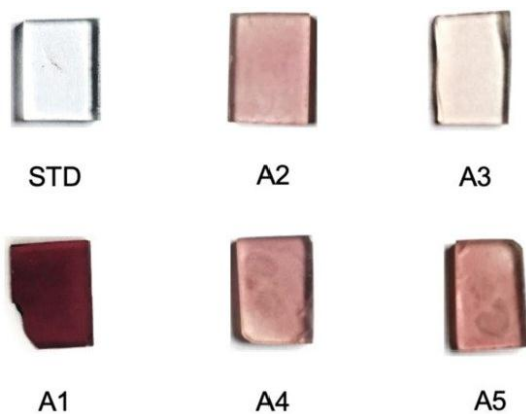

Fig. 6. Display of the fabricated and solarized soda-lime glass samples with RHA. [41]

4. Conclusion

According to literature survey, it can be concluded that:

1. Colour from raw material impurities is one of the main concerns for glassware production. Since ancient times until now the glass manufacturers attempted to avoid impurities especially iron oxide (Fe_2O_3) as much as possible. However, glassware still contains about 0.03 wt% of iron oxide.

2. Iron oxide is the major impurity in glass, and most of iron oxide comes from sand. The glass production can avoid this effect by using high purity sand or adding colour corrections / decolorizes agents to impure sand. The role of manganese in coloration, decoloration and solarization of glass is widely explained but, further studies are required for developing antisolarants, and preventing solarization of significant optical materials such as archaeological glass exhibited in outdoor or indoor area.

3. The increase in the total amount of alkaline-earth oxides at the expense of CaO + MgO decreases solarization of glass of (SiO_2-Na_2O- K_2O- CaO- MgO) system. Likewise, it was found that glass with a high lead content normally has small solarization effects and low transmittance ratio. Moreover, the iron-manganese colour interaction can be affected in the presence of sulphur (S) and various transition metal ions at sufficient concentrations around 0.5% or above.

4. 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 UV radiation generates colour-centers in the glass leading to reduced transmittance. 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.

5. Solarization may also permanently degrade the material's physical or mechanical properties. However, previous research carried out by Jiang *et al.* (2000) and Glebove (2001) assumed that the spectral properties (especially transmittance and colour) of an optical material can be changed by solariza-

tion when it is exposed to short wavelength, near bandgap radiation.

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