Middle East Journal of Applied Sciences
ISSN 2077-4613
Volume : 06 | Issue :03 | July-Sept.| 2016
Pages: 594-605

Roman Coloured Glass Objects Excavated from Tripoli, Libya: a Chemico-Physical Characterization Study

[1]**Abdel Rahim, Nagwa S.**

Department of Conservation, Faculty of Archaeology, Fayoum University, Egypt

Received: 10 August 2016 / Accepted: 11 Sept. 2016 / Publication date: 20 Sept. 2016

ABSTRACT

The finding of considerable collections of coloured glass artifacts, together with considerable lumps of glass chunks, fuel ash slag and kiln fragments related to glass processing strongly suggests a local secondary production (working) of glass at the archaeological site in northern Tripoli, Libya from the Roman period. The main objectives of the research are to understand the production technology and provide some insights into their probable provenance. In addition, corrosion and decay processes were also assessed to determine the influence of the cremation ritual within the fragments structure. The materials used for the manufacture of the glass were revealed using optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDS) and X- ray fluorescence (XRF). According to the microscopic examination, it can also be observed that mould-blowing was the main technique used for forming glass. The resulting data suggest that both soda-lime-silicate and, probably, aluminum-silicate glasses were produced in the making of these glassy materials, using some transition metal oxides as chromospheres or coloring agents. The compositional evidence gathered also suggests that glass fragments were the outcome of trade or exchange practices rather than locally produced.

Key words: Roman Period; Glass fragments; Chemical composition; Secondary production; Chemical Analyses

Introduction

As a matter of fact, there are Different types of glass fragments that are well-known in eastern and southern regions of Tripoli during the first millennium AD. These glassy items have been mainly found in burial contexts in which they usually appear along with other offering elements of various materials, such as metal, pottery, bone and so on.

Such glass fragments come from burial contexts and could have reached these territories as a result of trade, exchange practices of the inhabitants and gateway communities of the coast or intermediate peoples located between them (Davison, 2003). The prevailing colours are green, blue and brown, even though some semi-transparent specimens are also present. Taking into account the importance of these remains not only for the study of the Roman period in Libya but also for the extension of the scientific knowledge on ancient glass technology in the Mediterranean, a representative sample set was chemically and micro structurally characterized through different techniques with the aim of shedding new light on their manufacture and providing some insights into their probable provenance. In meeting these objectives, a basic goal of this research was established, which was exploring the glassy nature of the material itself in order to corroborate whether it was a true glass or just a material made from a sort of vitreous paste. Once this matter was clarified, the study also was aimed at determining corrosion and decay processes to assess whether or not devitrification mechanisms were a pro - decade since offerings were usually subjected to fire due to the cremation ritual (Brill,1999).

Archaeological background

It is known that the area of North Africa, which has been known as Libya. It was under Roman domination between 146 BC and 670 AD. The Latin name Libya at that time referred to the continent of Africa in general. The ancient town of Tripoli is located in the north of Lybia, it was the capital, it is now coastal Libya and was known as Tripolitania and Pent polis. It was divided between the Africa province in the west and Created Cyrenaica in the east. In 296 AD, the Emperor Diocletian separated the supervision

Corresponding Author: Abdel Rahim, Nagwa S., Department of Conservation, Faculty of Archaeology, Fayoum University, Egypt
E-mail: nsa00@fayoum.edu.eg

of Crete from Cyrenaica, and later on, formed the new provinces of "Upper Libya" and "Lower Libya", using the term Libya as a political State for the first time in history. Fig. 1. reflects the location of Tripoli. Because of its historical prominence, the site has seen several periods of excavation, which have unearthed almost half of the ancient Imperial Roman town and small relating extensions (https://en.wikipedia.org/wiki/Roman_Libya).

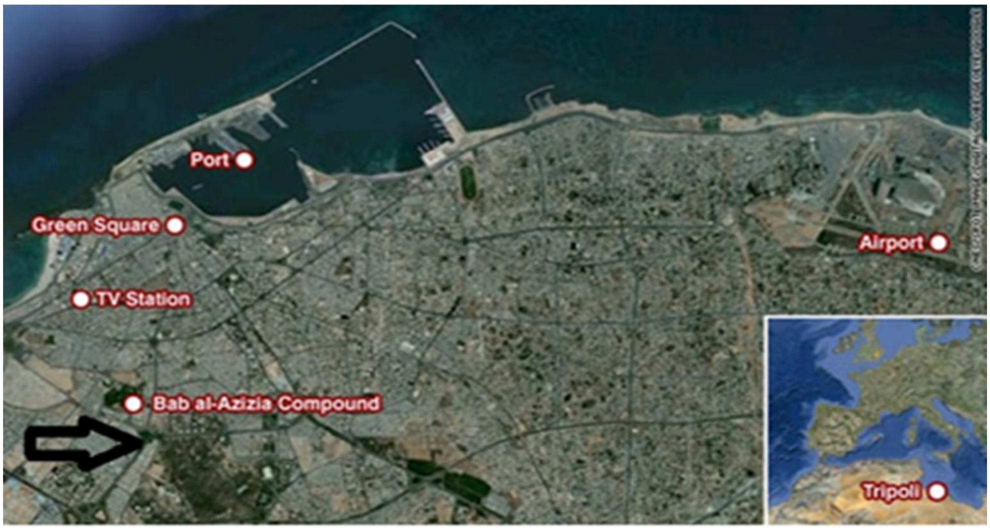

Figure (1) Shows . the map of the excavation the area in Tripoli.

The Roman Empire

At its height, the Roman Empire included the countries which are now the United Kingdom (except Northern Ireland), France, Spain, Portugal, parts of the Netherlands, Germany, Belgium, Switzerland, Eastern Europe, Greece, Turkey, the Middle East and North Africa. Thus all the major glassmaking centers came under the domination of Rome. In addition, the art of glassmaking was spread and important centers were established throughout the Empire. However, the glass production remained essentially Roman, with only minor regional variations until the collapse of the Roman Empire in the West soon after AD 400. Thus, glass, starting from the first to the fourth century AD, might be more accurately described as Roman than, for instance, Spanish or Gallic (Tait, 1991; Wedepohl, 1993).

The original materials of the glass

Irrespective of the geographical location and time-span of the original materials, Roman vessel glass from the first century BC to the sixth century AD has the remarkable property that its major composition (soda–lime–silica) is very similar. The glass of the soda–lime type had continued to be made as the glassmakers in Western Europe were still able to obtain either natron from Alexandria or marine plant ash from the Mediterranean countries. Around the tenth century, however, European glassmakers began using ash from bracken and other woodland plants as a source of alkali thus producing green-tinted potash glass. A different forest glass composition (high lime/low alkali) became prominent (Tait, 1991), it is suggested that an increase in zinc content might indicate the use of ash prepared from bracken and reeds, as an alternative fuel to beech wood(Picon *et al.,* 2003; Newton ,1978).

Glass ceased to be exclusively a luxury product, the styles became largely simple and functional, and in fact glass became more widely used for domestic purposes during the Roman period than at any subsequent time or place. Glass containers were particularly valued as shipping and storage containers because they were light, transparent, reusable and did not impart a taste of their contents(Davison, 2003; Jackson *et al.,* 1999a).

Manufacturing glass vessels.

Manufacturing glass vessels dated fourteen hundred years before the invention of glass-blowing. There were four very different techniques that were already in use for the production of glass artifacts:

core-forming; moulding; cutting or abrading (cold glass); and mosaic. Cold, solid glass could be shaped and decorated by cold working, i.e. by glyptic techniques such as cutting and engraving. However, having the property of becoming molten when heated to sufficiently high temperatures means that practically all ancient (and modern) techniques of manufacture use glass in that condition. Since glass can possess a remarkably wide range of viscosities (and thereby working ranges) depending on its composition and temperature, glass artifacts can be made in an almost infinite variety of shapes. No other material has these properties or permits such a varied manufacture to be undertaken. With the invention of glassblowing, new techniques of producing glass artifacts were developed, and along with them the methods of discoloration. These techniques have, thus, been in use for about two millennia (Davison, 2003; Lucas *et al.,* 1962).

Gradually, the shapes quickly grew more composite and within a few centuries glassware stood on the tables of ordinary citizens. In many roman cities such as Karanis in Egypt bowls, conical lamps, drinking cups, jars, flasks and jugs, as shown in fig.2.

Besides, the utilitarian glassware, mould-blown bottles were widely made, in fanciful shapes such as animals, human heads, fruit, sea-shells and as souvenirs of gladiatorial contests. Some glassmakers incorporated their names in their moulds (Davison, 2003).

Figure 2..shows ,some forms of the most commonly Roman glass pots ifound in the International museum

Materials and Methods

Since the excavations, these glasses are stored in uncontrolled condition storage at the National Museum of Tripoli. The choice of an ancient sample was made for two different reasons: in the early glasses there were no stabilizer elements, and Ca2+ is often contained in variable concentration with an uncontrolled Na/Ca ratio, so they are more sensitive to water-solution aggressiveness (Pollard *et al.,* 1996).

Due to curatorship and conservation constraints and the high archaeological and contextual value of the glass fragments, sample selection was carried out according to the criterion of minimum affectation of the pieces. Consequently, those broken and fragments were preferentially selected when possible. That is the principal reason why it is only a small-scale sample set. Nevertheless, selected samples encompassed ranges of colour and decoration shown by the entire ensemble of glass fragments .

The invention of glass-blowing techniques brought about a complete revolution in the manufacture of glass artifacts. Glass ceased to be a luxury material for scores of vessels could be blown in a day in, contrast with the use of the laborious core-forming process. Another great advantage was the possibility of making articles thinner and lighter and thus more acceptable for domestic purposes than was generally possible using the earlier glassmaking processes (Davison, 2003; Jackson *et al.,* 1999 b).

In addition, Handles and ornamentation have the appearance of having been trailed on quickly. Speed of production gave early blown glass a pace and spontaneity which had previously been unknown .

Glass archaeological materials

Small fragments of glass of about 1 mm were cut from the excavated fragments and embedded in an acrylic resin. Samples were taken only from broken vessels .Fig. 3 shows some samples such as; A- dark green; B- brawn semitransparent; C-blue ; D- blue; E- blue.

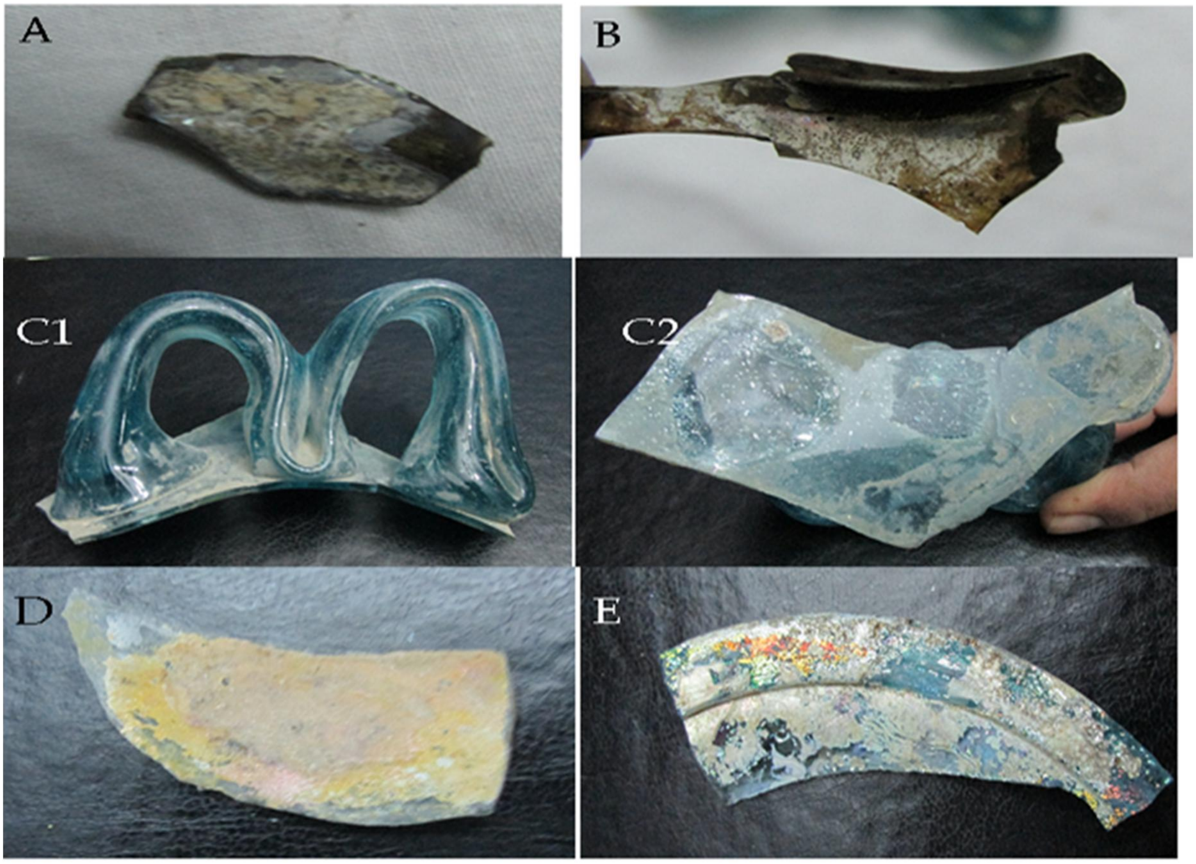

Figure 3 Shows the samples : A, a blown triple-bodied flask square, ; B mould- the edge of blown bottle; C1,C2, The hand of a jar to save the remains of bones a mould-blown, D,a barrelshaped jug, E,the edge of the pot semitransparent . All made in workshops: they were found at the excavated from Tripoli, Libya, probably third–fourth century AD.

Table1: Shows the description of the glasses selected for the analytical study

Sample	Colour	the shape	Deterioration
A	Deep Opaque green	Base fragment of round vessel	Semi corroded
B	Brownish	Rim fragment of small bottle	Semi corroded
C	Light blue	Handel and fragment of thin-walled vessel	Durable
D	blue	Rim fragment of small ask	Semi stable
E	blue	Rim fragment of large bottle	Corroded and pitted

The samples were characterized using the following complementary techniques:

Light microscopy

Paint cross-sections were studied using a NIKON ECLIPSE ME 600 microscope equipped with an Olympus e-410 digital camera. The magnification varied from x100 to x400 depending on the size of the samples. Microscopic examinations in transmitting light were made on thin sections, cut across the thickness of the tiles, using a Leica Zoom 2000 microscope equipped with an Olympus e-410 digital camera in order to determine different typologies of the glass .

Scanning electron microscopy- Energy dispersive X-ray spectroscopy (SEM-EDX)

The SEM-EDX was used to determine micro textural and micro chemical features of both the body and glaze coatings. Polished cross-sections were gold coated, and the SEM-EDX were performed with JEOL 5410 scanning electron microscope equipped with an Oxford (England) EDX microanalysis system (25 kV, 0.28 nA, ~1 µm beam diameter, 60 s counting time). Elemental analysis was obtained using the Oxford INCA-Energy software.

X- ray fluorescence (XRF).

X-Ray Fluorescence was used to identify the elements in certain pigment fillers. There was a dispersive wavelength X-ray fluorescence spectrometer (WDXRF) with a Bench top spectrometer sequential type, wavelength dispersive. The system is equipped with 3 crystals Analyses (exchange automated): LIF (200) for heavy elements (Ti–U), PET and RX 25 for light elements (O–Mg and Al–Sc), X- ray tube of Pd 200W power (voltage. 50KV, ext. 4mA), and detection limit: 1 ppm – 10 ppb; Accuracy <0.1–0.5%. This method was the most accurate method available for determining the elemental composition and the concentration of elements in the sample. This technique was the favourite as it only required a small amount of the samples.

Sample preparation for the XRF measurements:

The samples were prepared as fine powder, then compressed as disks and fused to identify their compositions and the main raw materials used. It should be noted that the weathering products or crusts were mechanically removed from the areas in which the glass samples were taken. These products have a completely different chemical composition of glass. Therefore, any contamination of these products with the selected samples would have affected the accuracy of the results of chemical analyses. Furthermore, many glass fragments were prepared for microscopic examination to characterize their manufacturing technology (Nabil *et al.,* 2015).

Results and Discussion

There is no doubt that the fragments were made of glass. Either the green sample with a less altered surface, or that with an advanced external weathering layer showed the typical amorphous background of glasses in which no crystalline phase is present. This fact could also indicate that no devitrification mechanisms were induced by the funeral pyre. Blue specimens showed, likewise, the same pattern (Freestone *et al.,* 2008b) .

Light microscopy

As a matter of fact, the eye-naked inspection and the microscopic examination of the glass vessels from Tripoli revealed that they are examples of thin-walled glass of fairly good quality. Most of them exhibit blowing marks. This aspect, in addition to the fabric, shape and curvature, indicates that these glasses were made by the mould blowing technique (Silvestre *et al.,* 2006; Turner, 1956).
Stylistically, these glasses resemble very closely a collection of Roman mould-blowing glasses excavated from other Roman sites in Tripoli, Lybia, as well as Roman glass from Egypt, Syria and Palestine. It was already established that blown glass was first invented or appeared early in the Roman period (Al-Ahmed *et al.,* 1995). Pasting or cake-past was the method used for the production. Fig 4. reflects optical microscope images of the thin sections of glass bodies showing the mineral phases surrounded by glassy matrix; samples; A- dark green; B- brawn semitransparent; C-blue ; D- blue; E- blue semitransparent .

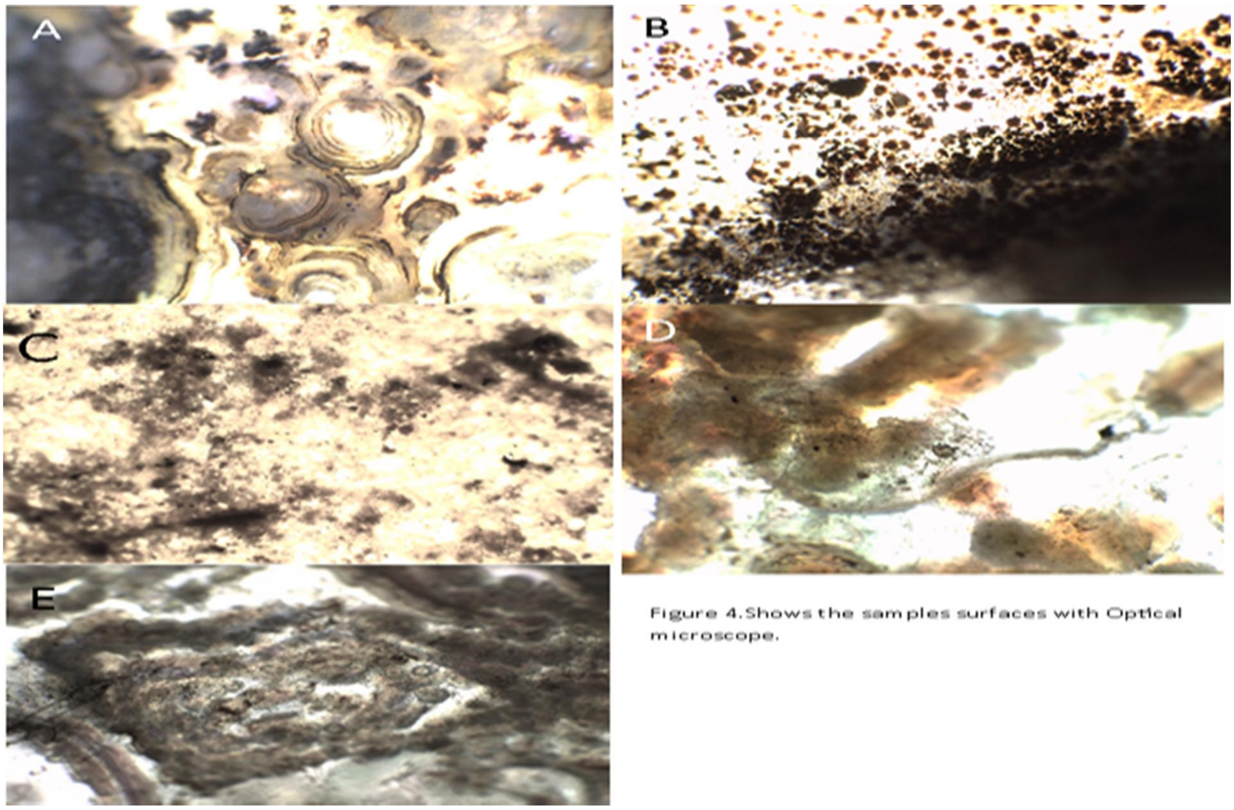

Figure 4.Shows the sam ples surfaces with Optical microscope.

Scanning electron microscopy- Energy dispersive X-ray spectroscopy (SEM-EDX).

Regularly, the Roman glass producing process involved melting a siliceous constituent (e.g., quartz sand, crushed quartz pebbles) with a fluxing agent (e.g., potassium or sodium, rich vegetable ashes) and with additional calcium-rich material (such as limestone, seashells or marble8). Moreover, a lead source and small amounts of colorant, opacifier or decolorant materials were added to the melt. For some time now the composition of glass objects found in the European region and the near East has been known to be very similar to the period of the Roman Empire (Jackson *et al.,* 1991a) . The components of these glasses are basically sodium and silica. Small amounts of alumina (generally between 3.5 and 14wt. %) And calcium oxide (between 7 and 11%) is characteristically present in these glasses as well. Low magnesia and potash contents (~1.5%) distinguish these from other sodic glass types. The lack of magnesia and potash impurities (-between 1and 2 wt. % in most cases) in Greek and Roman glass indicates that the source of Na was mineral and not plant ash as stated by Pliny the Elder10. In the Antique to the post-Roman period, glass was made with Natron as fluxing agent, a mixture of NaHCO3, Na2CO3 and other Na-salts. This resulted in a durable Na-rich glass which could be worked into a variety of shapes. This may indicate that transition in the use of traditional methods and of the same sources of raw materials for glass-making occurred, with obvious modifications, from natron to plant ash and from calcium-rich sand to calcium -free sand at this site(Abd-Allah, 2010 b).

The stability is due to the presence of CaO, increasing the coupling of the vibrational modes of the silica nonbridging oxygen modifier bonds to the bridging of the Si–O–Si network. It would be expected that the replacement of one Ca2+ ion by two protons (H+) would have the same effect as replacing two ions from the network, but in the latter case a much more porous layer is formed. If the lime content is increased above 15 mol per cent, the resistance to deterioration starts drastically to reduce. Lime was not specified as a constituent of pre seventeenth-century glasses, and hence stable (durable) glasses were prepared more or less accidentally either from calcareous sands (in ancient times) or from high-lime wood ash (in medieval times); thus it is not surprising that there was a period when the addition of extra lime was regarded as being positively harmful (Davison, 2003; Abdel-Rahim, 2003).

In case, Cu, homogeneously added to white glass, it can produce a pale green color. The green glass color caused by the presence of Mn using of more than oxide to get the green color, and most important of these oxides cupric oxide, which has been used to get the green copper ore and Alstoc CuWollasnite (Ca,Cu)3 Si3O9. It has been found that both green and stained glass in green is one of the Chrysocolla

(CuSi3.nH2O) and have found that cupric oxide when he entered in the networked installation as a developer, it gives a green color that may be graded to blue, depending on the impurities present as well as the ratio of sodium oxide, as green turned to blue in case of increasing Na_2O. It also found that when Cu enters the silica in the form of single valence copper ions, Cu, in this case, the resulting color green (Clark *et al.,*1979; Hartmann *et al.,*1997), as shown in Fig. 3 .

According to the glasses studied, the major element analysis indicates that the major glass forming elements (Na, Mg, Al, Si, K, Ca, Mn, Fe) are very constant in composition. The glass body contains several elements such as Si, Al, Na, Fe, Mn, Cu, Cr ,for dark green , Si, Al, Na, Fe, Mn for brown , and Co for dark blue colors. It is noticed that for transparent glass, the concentration of K_2O is similar to CaO, it is the first proof for the Venetian receipt of glass bleaching, by glass treating with MnO. This has been observed in other studies. Elements of minor abundance used as coloring agents;(Henderson, 2000b) ,(transition metals for the most part such as Cr, Cu, Co) were seen to vary in the samples. However, it is assumed here that such coloring agents would have been added during the step of glass forming. These agents would not have been part of the base composition supplied to the ateliers of the glass makers. Analysis of the other heavier minor element indicated that most were very constant in abundance but two seemed to vary simultaneously (Henderson *et al.,*1981a; Bettembourg, 1976).

At the early stages of glass corrosion, isolated pits appear , those further grow and connect with each other forming craters, which increasingly become deeper and more abundant. In turn, the craters grow and become interconnected in such a way that they form a continuous altered, opaque corrosion crust ;(Bettembourg, 1976; Abdel-Rahim, 2003).

In Table 2, we can notice that sample D1,D2, SiO2 was decreased from 74.97% to 56.69%, while Na_2O was decreased from 1.38% to 0.58% , moreover, CO2 increased from 6.38% to 14.62% in blue oxide cobalt glass. EDAX analysis of the sample D1 indicated the decreases in the contents of Na_2O, Al_2O_3, K_2O, CaO, CoO and Fe_2O_3 (Table 2). Furthermore the glass corrosion was clearly seen and sample E,E1 there are changes in the ratio of SiO_2 was decreased from 78.09% to 55.72%, while Na_2O was decreased from 1.88% to 0.58% , CO2 increased from 3.90% to 20.05% in blue oxide cobalt glass. increment of sulphur oxide on its surface could be also related to this fact.

Table 2: Shows chemical composition of the samples with EDX analysis

Elements	A-wt%	B -wt%	C-wt%	D1 -wt%	D2- WT%	E1-wt%	E2 -wt%
Al_2O_3	14.37	9.15	3.92	9. 85	4.56	7.78	5.93
SiO_2	57.14	59.94	36.89	74.97	56.69	78.09	55.72
MgO	0.52	1.61	1.73	1.88	1.55	1.45	1.22
SO_3	0.38	0.95	2.23	-	0.62	0.44	0.28
Cl_2O	0. 08	0.36	1.63	-	7.51	1.08	0.24
K_2O	2.05	0.84	1.26	1.99	1.81	0.58	0.50
CaO	7.27	11.20	11.58	9.07	7.04	6.43	5.97
Cr_2O_3	0.47	0.24	0.29	1.29	1.10	0.14	0.09
Fe_2O_3	2.31	0.81	1.63	8.56	7.02	8.33	4.20
CuO	0.89	0.46	0.17	0.56	1.10	0.57	0.29
MnO	8.88	0.34	0.17	0.97	0.73	1.87	0.48
CO_2	4.91	9.15	36.77	6.38	14.62	3.90	20.05
Na_2O	0. 32	10.78	1.43	1.38	0.58	1.05	1.01
CoO	0.43	0.34	0.13	0.18	6.24	0.42	0.20

EDAX analysis of the sample E2 indicated the decreases in the contents of Na_2O, Al_2O_3, K2O, CaO, CoO and Fe_2O_3. Alkaline attacks the glass surface, thereby producing a feedback corrosion mechanism .The high SiO_2 contents suggest that a protecting thin silica gel layer could be present in the surface of the less altered glass. Such a layer could be originated as a result of hydration and acid attack during burial and could explain as well the loss by leaching of NaC and KC ions from the surface, according to the corrosion stages explained above. On the contrary, the increase in SiO_2 was not detected in the sample with a more advanced alteration, even though in this case a higher decrease of Na_2O is readily appreciated. A feasible explanation for this phenomenon could be that this glass was exposed to a stronger chemical attack due to its less stable composition (Garcı´ *et al.,* 2005). As corrosion proceeded following second and third stages, the firstly formed silica gel layer would be then be destroyed, thereby producing a more intense dealkalinisation.(Ferna´ndez *et al.,* 2003). In addition, extreme proportions of Fe_2O_3 and CuO were also detected on the surface of this piece. Since iron or copper usually occur as chromophores or impurities and taking into account that these elements do not form part of the basic composition of glass (Ferna´ndez *et al.,* 2003) , they could be induced by the burial environment or, most probably, deposited by the cremation ritual. In this regard, it is important to emphasize that the great majority of offerings in the necropolis of Tripoli is composed of iron weapons and bronze adornment objects such as swords, rings, daggers, fibulae, etc. (Ernsberger, 1980). The noticeable from SEM observation of the glass samples covered with coherent deposits and encrustations, it can be seen that all the glass surfaces seem to be inhomogeneous pitted, curviplanar, surface planar and highly fractured forms (Figs. 5, 6, and 7). Large areas of the weathering crusts were destroyed and rich in dissolution voids and micro-cracks. In addition, other aspects of sugar-like surface, flaking, and highly fissured nature of decayed crusts were also observed (Figs. 8 and 9). Furthermore, Figs. 8 and 9 show secondary electron images of magnified sections through corroded crusts from glass samples D and E, showing deterioration proceeding from the surface to the interior. On the other hand, dirty layers, soil deposits and encrustations on the glass surface appeared to be inhomogeneous, differ in their thickness and strongly adhered to the glass surface and pitted areas. Figures 5, 6, 7, 8, 9 show samples A,B,C,D,E, (a) SEM image (b) EDX spectrum.

In Fig. 8, a secondary electron image of glass sample (E) showing the aspects cracking and pitting. The compositions of 5 glass fragments from the Roman site as provided by the aid of XRF are shown in Table 3. The results of the analyses indicate that the major components of the glass samples are: silica (SiO2 Avg. 69.65%), soda (Na_2O Avg. 14.63%), lime (CaO Avg. 8.76%) and alumina (Al2O3) Avg. (2.95%). They were also characterized by low contents of potash (K2O Avg. 0.71%) nature. Figure. 10Shows chemical composition of the samples A, B, C, D and E obtained by X-ray

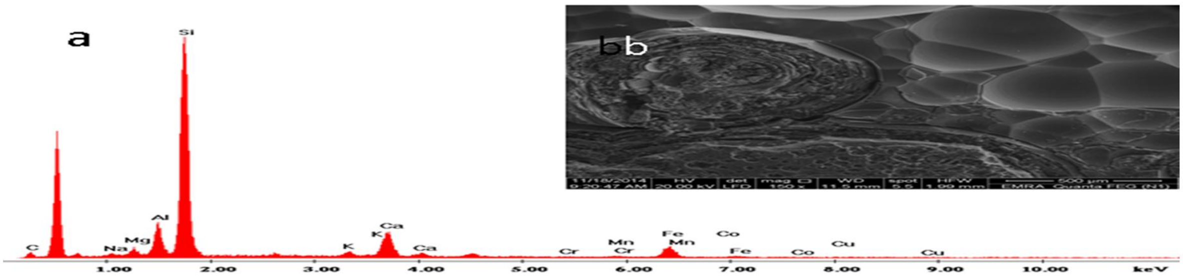

Figure 5 shows sample A (a)ERD spectrum ,(b)SEM image.

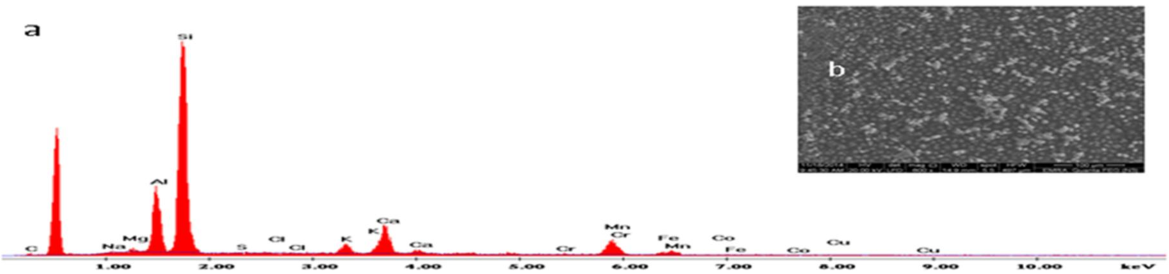

Figure 6 Shows sample B, (a) EDX spectrum ,(b) SEM image

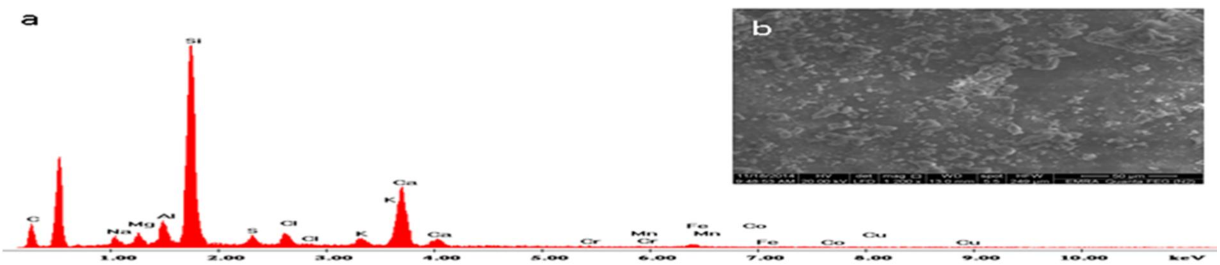

Figure 7 Shows sample C, (a) EDX spectrum ,(b) SEM image

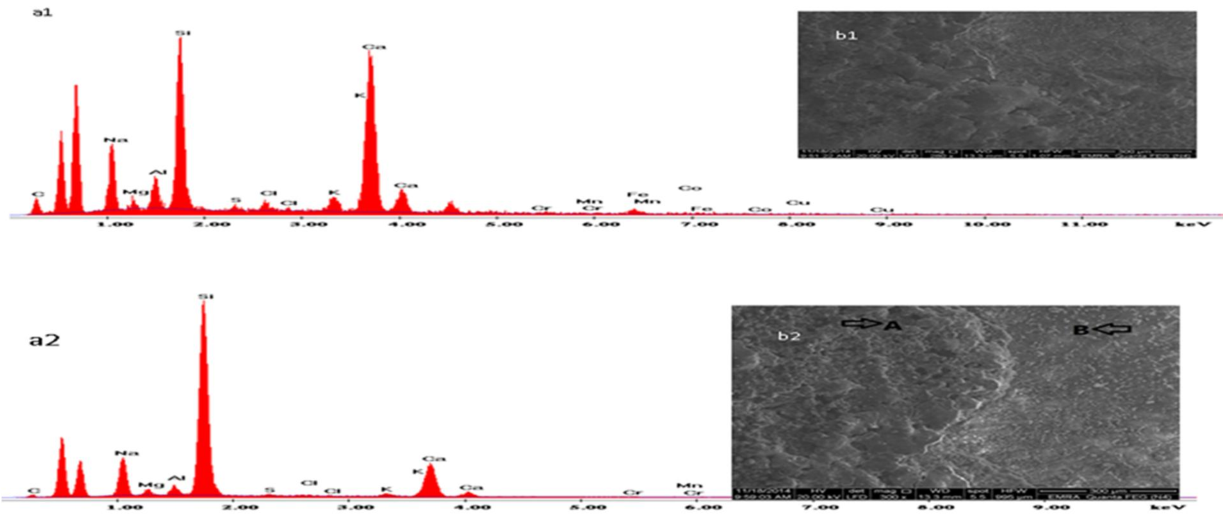

Figure 8Shows sample D (a1) EDX spectrum (b1)SEM image for the original glass ,(a2) EDX spectrum for the corrosion layer (b2)SEM image for the original glass and the corrosion layer .

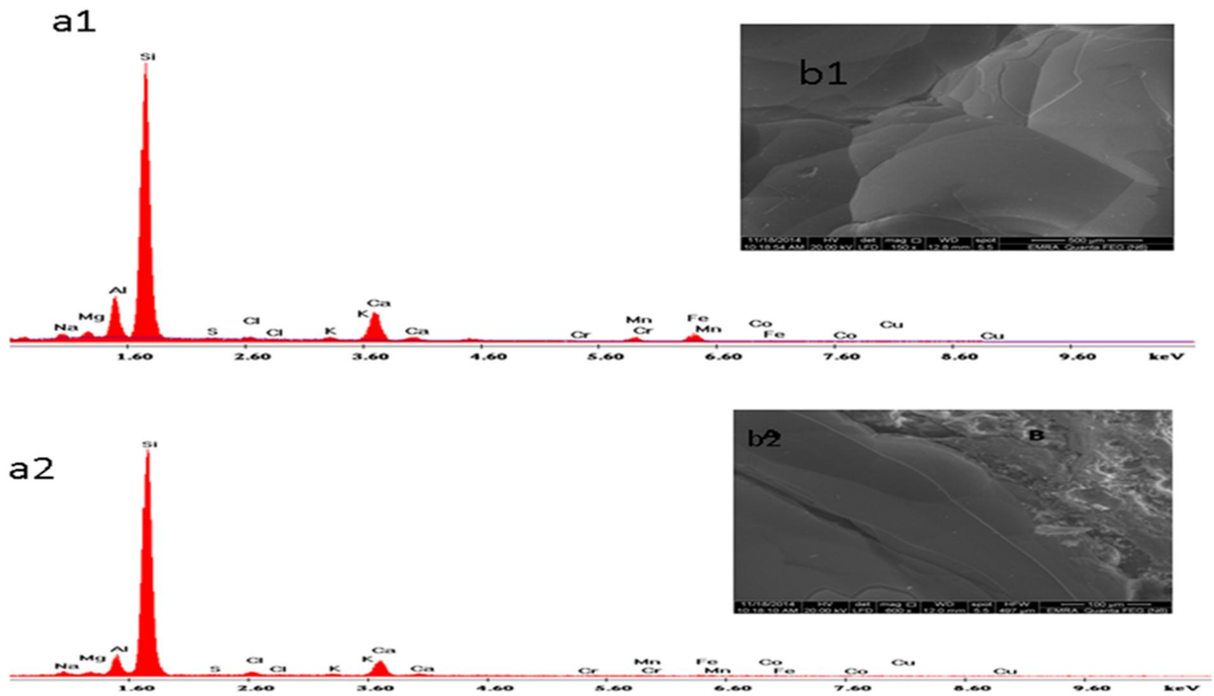

Figure 9 Shows sample E, (a1) EDX spectrum (b1)SEM image for the original glass ,(a2) EDX spectrum for the corrosion layer (b2)SEM image for the original glass and the corrosion layer .

The fluorescence spectroscopy (XRF).

The main component is SiO_2, the glass network-forming oxide, these glasses can be classified as soda–lime–silica (Na_2O–CaO–SiO_2) glass, the common type of ancient glass for more than 3000 years(Ferna´ndez *et al.,* 2003; Scholze *et al.*, 1975) . This composition revealed that the main raw materials from which these glasses were manufactured were sand as a source of silica, natron (from Wadi Natrun in Egypt) as a source of alkali soda, and lime (which is already present as impurity or shell fragments in the sands) as a source of calcium (Clark *et al.,*1979) . However, no evidence for a local primary production of raw glass at these sites has been found to date. It was stated that glass production in the first millennium AD was divided between a relatively small number of workshops that made raw glass and a large number of secondary workshops that fabricated vessels (Hartmann *et al.*, 1997).The XRF data reflect the typical composition of a soda-lime-silicate glass (Table 3).

Table 3: Shows chemical composition of the samples obtained by X-ray fluorescence spectroscopy (XRF).

Elements	A-wt%	B -wt%	C-wt%	D -wt%	E-wt%
Al_2O_3	10.97	10.25	3. 29	10. 15	6.28
SiO_2	54.14	61.24	43.89	70.58	73.99
MgO	0.52	2.11	1.43	1.88	1.65
SO_3	0.38	1.25	1.45	0.52	0.44
Cl_2O	0. 08	1.06	1.43	0.89	1.08
K_2O	2.25	1.64	3.26	2.69	1.28
CaO	10.17	12.20	13.68	12.57	9.93
Cr_2O_3	0.42	0.29	0.32	1.49	0.24
Fe_2O_3	3.13	1.21	1.63	9.21	6.23
CuO	0.89	0.46	0.87	0.56	0.57
MnO	10.28	1.14	0.87	1.37	1.47
Na_2O	0. 32	10.78	2.54	1.38	1.05

During the Roman and later periods, glass was produced from its raw materials in massive tank furnaces in a limited number of glass production centers (potentially in the Levantine area). The unformed chunks of raw glass originating from these furnaces were, then, re-melted to produce glass vessels at a larger number of glass working centers (Freestone, 2008b ; Tite *et al.,* 2006) .
Fig. 10 shows samples A, B, C, D and E analysis by XRF.

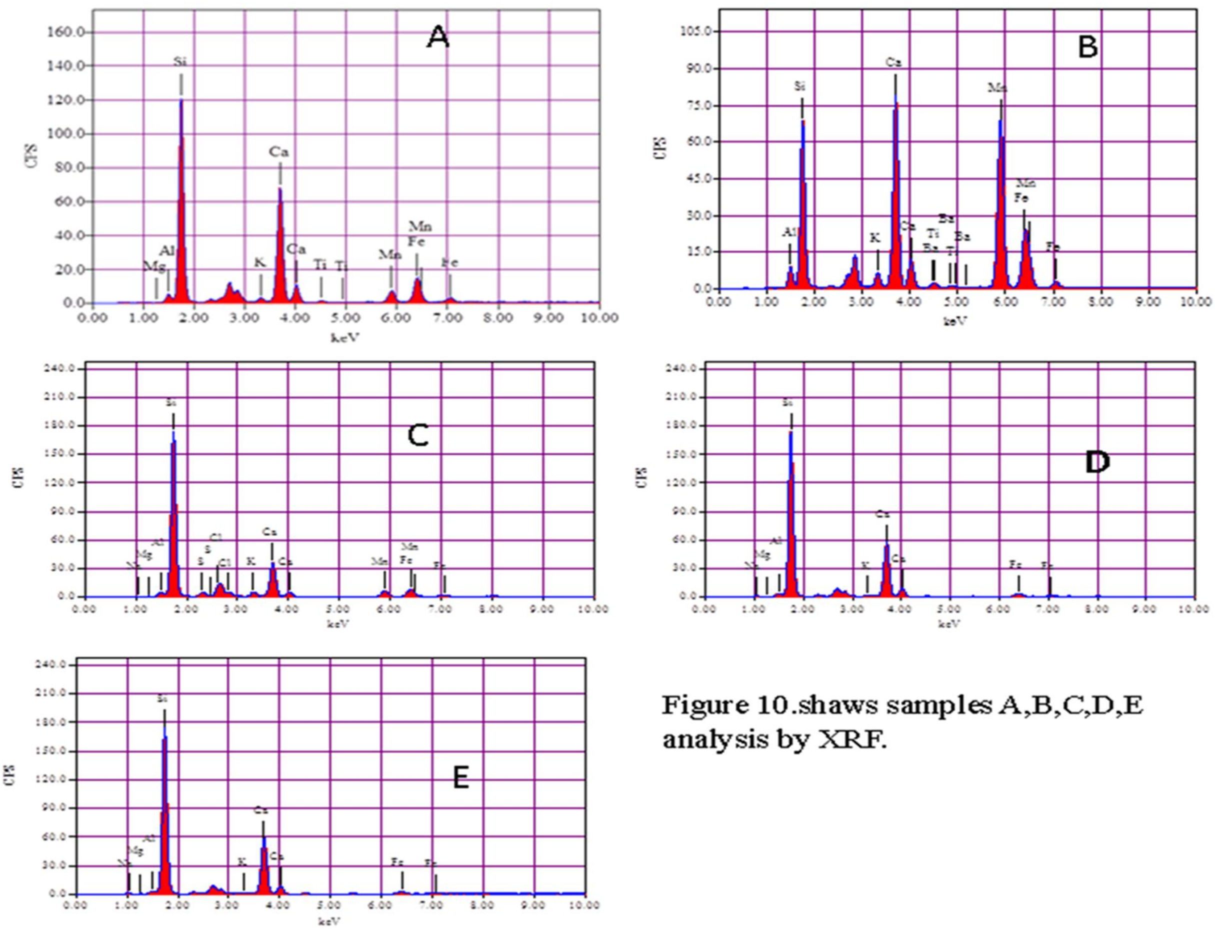

Figure 10.shaws samples A,B,C,D,E analysis by XRF.

The resulting data suggest that both soda-lime-silicate and, alumina-silicate glasses were produced in the making of these glassy materials, using some transition metal oxides as chromophores or colouring agents. The compositional evidence gathered also suggests that glass was the outcome of trade or exchange practices rather than locally produced (Davison, 2003). Potash glasses have about half the durability of soda glasses because the potassium ions are larger than those of sodium ions, and take up more space in the glass network. Thus, when potassium ions are leached out of the glass, they allow a greater number of water molecules in. The resulting reduction in volume of the leached layer causes shrinkage to occur, and further shrinkage takes place if a hydrated alkali-deficient (hence silica-rich) layer then loses water, e.g. upon excavation. Thus, dehydration of glass often thought of as a cause of deterioration, merely highlights the deterioration which has already occurred. The decrease in volume can lead to micro porosity of the surface layer, and this may be the cause of the many-layered effects found in the surface crusts of some medieval glasses (Abd-Allah, 2007a).

Conclusion

The site of Tripoli, Libya was very important, therefore, the inhabitants of Tripoli might purchase their glass objects, which played as market center or trade station, mainly during the Roman period. The samples were examined by using optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray Microanalysis (EDX), and X- ray fluorescence (XRF).

The eyes naked inspection and the microscopic examination and technical observation, exhibit blowing marks on the glass objects, which indicate that mould-blowing was the main technique used for forming glass from the Roman period at Tripoli. Moulding technique was also used in manufacturing Roman glass. However, comparing the chemical composition of glass collections from Tripoli highlights the changing pattern of glass production. The results show that there are significant changes in glass composition in the Roman period. The former sample (B) of glass related to soda-lime-silica glass, with Natron used as a flux, meanwhile the samples (A, C, D, and E) glass related to calcium– rich plant ash soda.

The above chemical composition results supported the archaeological data with respect to technological aspects of glass production and technological change of production. On the synchronic scale of glass production, the analysis of glass collection from Tripoli, Libya show that the Roman glass vessel manufacture was consistent with other Roman sites in North Africa and around the Mediterranean countries. The resulting data showed that the types of analysed samples are examples of soda-lime-silica glass, with Natron used as flux for Roma glass vessels. Furthermore, The Roman fragments were characterized by using multi colours as decorative elements. At the economic scale, the excavation at Tripoli did not uncover any installation or feature associated with glass production. The absence of such features highlights the possibility of trade network between Tripoli and other production or trade locations during the Roman and Islamic period. That is, the mechanism of import or exchange of glass objects to Tripoli might be related to indirect trade type. Major element analysis indicates that the major glass forming elements (Na, Mg, Al, Si, K, Ca, Mn, Fe) is very constant in composition in the glasses studied. This has been observed in other studies. Elements of minor abundance used as colouring agents; (transition metals for the most part such as Cr, Cu, Co) were seen to vary in the samples. However, it is assumed here that such colouring agents would have been added during the step of glass forming. These agents would not have been part of the base composition supplied to the ateliers of the glass makers. Analysis of other, the heavier minor element indicated that most were very constant in abundance, but two seemed to vary simultaneously. Conclusion section must be included and should indicate clearly the advantages, limitations, and possible applications of the paper. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

References

Abd-Allah, R., 2007a. Stabilization and treatment of corroded glass objects displayed in the museum of Jordanian heritage, Mediterranean Archaeology and Archaeometry, 7 : 2, 19–28.

Abd-Allah, R., 2010 b. Chemical characterization and manufacturing technology of late Roman to early Byzantine glass from BeitRas/Capitolias, northern Jordan, Journal of Archaeological Science 37,8.

Abdel-Rahim, N. S., 2003. A Scientific Study on Treatment And Conservation of Manufactured Materials used in Archaeological Ornaments in Ancient Egypt during the new Kingdom and late period , PhD, conservation dept., Faculty of Archaeology, Cairo Univ., Egypt ,

Al-Ahmed, Z., and Z. A. Al-Muheisen, 1995. Chemical and technological study of Roman glasses excavated from Yasileh archaeological site, Jordan. Mu'tah Journal 11 (2), 5-28.

Bettembourg, J.M., 1976. Actes du IXeColloque International du Corpus Vitrearum Medii Aevi, Verres et Réfractaires, 30, p. 36.

Brill, R.H., 1999. Chemical analyses of early glasses, vols 1 and 2, Corning Museum of Glass, New York.

Clark, D.E., C.G. Pantano and L.L. Hench, 1979 .Corrosion of Glass. Books for Industry, New York.

Davison, S., 2003. Conservation and restoration of glass, 2nd edition, Butterworth Heinemann, Oxford Ox28Dp, UK.

Ernsberger, F. M., 1980. The role of molecular water in the diffusive transport of protons in glass. In Phys. Chem. Glasses, 21, 146–9.

Ferna´ndez, J.M., 2003. Navarro, El Vidrio. Constitucio´n, Fabricacio´n, Propiedades, third ed., CSIC, Madrid.

Freestone, I., 2006a, Glass production in Late Antiquity and the Early Islamic period: a geochemical perspective, Geomaterials, in: M. Maggetti, B. Messiga (Eds.), Cultural Heritage, 257, Geological Society of London Special Publication, pp. 201–216.

Freestone, I., 2008b. Ian Charles, Pliny on Roman glassmaking, In: Martinón-Torres, Marcos; Rehren, Thilo (eds), Archaeology, History and Science: Integrating approaches to Ancient Materials, Left Coast Press, Walnut Creek, 218 pg., ISBN 978-1-59-874340-1; p. 77-100.

Garcı´a -Heras, M., J. M. Rinco´n, A. Jimeno, M.A. Villegas, 2005. Pre-Roman coloured glass beads from the Iberian Peninsula: a chemico-physical characterisation study, Journal of Archaeological Science 32, pp. 727,738.

Hartmann, G., I. Kappel, K. Grote and B. Arndt, 1997. Chemistry and technology of prehistoric glass from Lower Saxony and Hesse, Journal of Archaeological Science 24, , 547e559.

Henderson, J. and E. Warren,1981a, X-ray fluorescence analyses of Iron Age glass: beads from Meare and Glastonbury lake villages, Archaeo- metry 23 : 83-94.

Henderson, J., 2000b. The science and archaeology of materials. An investigation of inorganic materials, Routledge, London.

https://en.wikipedia.org/wiki/Roman_Libya .

Jackson, C.M., J. R. Hunter, S.E Warren and H.E.M. Cool, 1991a. The analysis of blue-green glass and glassy waste from two Romano- British glass working sites, in: E. Pernicka, G.A. Wagner (Eds.), Archaeometry 90, International Symposium on Archaeometry (Heidelberg 1990), Birkhauser Verlag, Berlin, 295,304

Jackson , C.M and J.W. Smedley, 1999 b. Raw materials and glass recipes – glassmaking in Staffordshire in the 14th–16th centuries. In Proceedings of Current Research on the History of Glass through Scientific Analysis. London.

Lucas, A. and J. R. Harris, 1962, Ancient Egyptian materials and industries, Edward Arnold, London,.

Nabil, A. and R. Abd-Allah, 2015, The Authentication and Characterization Of Glass Objects Excavated From Tell Es-Sukhnah, Jordan, Mediterranean Archaeology and Archaeometry, Vol. 15, No 1, 39-50.

Newton , R.G.,1978 . Colouring agents used by medieval glassmakers. Glass Technol., 19, pp,59–60

Picon, M., and Vichy, M., D'Orient , 2003. Occident: l'origine du verre à l'époque romaine et durant le haut Moyen Âge, in Échanges et commerce du verre dans le monde antique, Actes du colloque de l'Association Française pour l'Archéologie du Verre, Aix-en-Provence et Marseille, 7–9 juin 2001 (eds. D. Foy and M. D. Nenna), 17–31, Éditions Monique Mergoil, Montagnac.

Pollard, M., C. Heron, 1996. Archaeological chemistry, The Royal Society of Chemistry, Cambridge.

Scholze, H., D. Helmreich, and I. Bakardjiev, 1975. Untersuchungen über des Verhalten von Kalk–Natron Gläsern in verdunten Säuren. Glastech. Berlin, 48, 237–46.

Silvestre, I.L., G. Molin and G. Salvilo and R. Schieveninsand, 2006. Analytical Plan for Roman Glass Production : An Experimental and Philological Study On Source Of Supply , Archaeometry ,48, 3 , 415–432. Printed in Singapore.

Tait, M, 1991a. Five Thousand Years of Glass. BMP, London.

Tite, M., A. Shortland, Y. Maniatis, D. Kavoussanaki and S. Harris, 2006. The composition of the soda-rich and mixed alkali plant ashes used in the production of glass, Journal of Archaeological Science 33 , 1284–1292.

Turner, W.E.S. 1956. Studies in ancient glasses and glass-making processes. Part III. The chronology of the glassmaking constituents. Trans. J. Soc. Glass Technol. 40, 39–52.

Wedepohl, K.H., 1993. Herstellung mittelalterlicher und antiker Gläser. Abh. Akad. Wissenschaften Lit. Mainz, Germany.