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EDXRF and FTIR Analysis of Some Glass Fragments Belong to Ottoman Period, Excavated in Ancient Ainos (Enez) Turkey

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Ancient glass fragments excavated in the archaeological district Enez (Ancient Ainos), Turkey were investigated by combined energy dispersive X-ray fluorescence (EDXRF) and Fourier Transform Infrared (FTIR) spectrometry techniques. Multi-elemental contents of a spirally twisted translucent yellow glass bracelet, fragment of a turquoise blue vessel and its cover and a fragment of a translucent white vase decorated with a surface coating, that belong to Ottoman period were determined by EDXRF method. The concentrations of 23 elements (Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Br, Rb, Sr, Sb, Ba, Ce, U, Pb) which might be present in the samples as flux, stabilizers, colorants or opacifiers and impurities, were examined. The glasses were classified as potassium-limy glass. IR reflection and absorption spectroscopy enable us to determine structural characteristics of the glasses.

Key Words: Ancient glass, Infrared spectrometry, X-ray fluorescence analysis.

INTRODUCTION

Ancient Ainos (Enez), in the Northern Coast of the Aegean sea, has been described as one of the most important archaeological sites in Turkey. The ancient city was established on the calcerous peninsula, belong to mid miocene, which was 25 meters high from the sea level. The city with two well-preserved harbors, was founded at the place where Antic Hebrus (Evros or Meric) river meets the sea, in the junction of seaways and highways that connect Balkans to Aegean and Anatolia. The river Hebrus (Meric) is the second largest river in the Balkans after the Danube. Until the 19th century, the river functioned as the major transportation artery between the north Aegean sea and regional cities like Edirne and Plovdiv. The ongoing excavations has demonstrated that Enez is a site of great antiquity and strategic importance. As mentioned in the Homer's Iliad, the city was flourished in the 5th and 4th centuries BC. The excavations in Enez have been going on for the last 40 years[1].

Glass is a non-crystalline material. The primary constituent making up the chemical composition of glass is silica. Alkalis were utilized in ancient times as flux. Glass production has been known from antiquity (3000 BC in Syria-Palestine area and 1500 BC in Egypt). Over a long period of time, the glass composition was varied with the purpose of improvement of its quality. In the ancient world, it was manufactured by melting a combination of an alkali (potash or soda) and silica (raw materials such as sand). Compositional and structural analyses in the study of ancient and historical glass are important in solving problems connected with the manufacturing technology, raw materials and origin of these objects[2-4]. In this study fragments of a spirally twisted translucent yellow

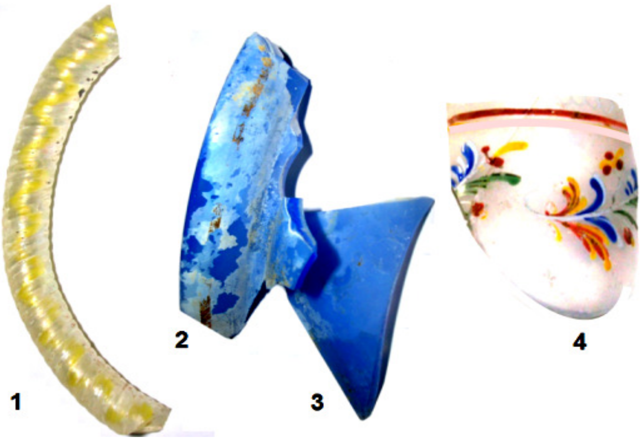

Fig 1. Photographs of investigated glass fragments that belong to Ottoman period, excavated in Ainos (Turkey). Sample No 1 is twisted translucent yellow glass bracelet; samples No 2 and 3 are the fragments of turquoise blue bowl lid, and bowl; sample No 4 is a fragment of a translucent white vase decorated with a "surface coating

glass bracelet, a blue vessel and its cover and a translucent white vase decorated with a surface coating, that belong to Ottoman period, were investigated (Fig. 1). The aims of this study are to obtain chemical and structural information on ancient glasses belong to Ottoman period.

EXPERIMENTAL

X-ray fluorescence analysis was performed with an SPECTRO IQ II model energy dispersive spectrometer. The samples were analyzed for 300 s using an air cooled low power Pd end window X-ray tube (25-50 kV) combined with HOPG crystal for monochromatization and polarization of the primary tube spectrum. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the silicon drift detector was better than 175 eV (for MnK_α at an input count rate of 10,000 cps). During the measurement the excitation area was flushed with helium gas. Analytical processes were performed by its software. Due to varying surface structures and inhomogeneities in the surface composition of the artefacts, analysis was performed on both sides of the objects and a mean value was calculated. The accuracy for EDXRF measurements is between 5 % and 10 % for major and minor components and better than 20 % for traces.

The infrared analyses of the samples were carried out by both using the IR transmittance and reflectance techniques. After washing with distilled water and drying at room temperature, for IR transmission spectra, small parts from each glass fragments were taken and were ground to fine powder in an agate mortar. About 1 mg of the glass powder was mixed with 100 mg of KBr and pressed into a pellet under 10 tons. The IR transmission spectra were recorded with a Bruker Tensor 27 FTIR spectrometer, using KBr pellets, in the 4000-400 cm^{-1} region. 16 background and 200 sample scans were accumulated, with a resolution of 0.5 cm^{-1}. For IR reflection spectra, whole fragments were used. By using Bruker alpha spectrometer, with a DRIFT attachment, 16 background and 100 sample scans were accumulated with a resolution of 2 cm^{-1}.

Spectral manipulations such as baseline adjustment, smoothing, obtaining the second derivative and band fitting procedures, were performed using GRAMS/AI 7.02 (Thermo Electron Corporation) software package. Band fitting was done using Gaussian function and fitting was undertaken until reproducible and converged results were obtained with squared correlations better than r^2-0.99999. The second derivative profile gives valuable information about the position of the bands and band widths. Thus for the band fitting procedure (to locate the position of the peaks), the second derivative of the absorption spectrum was used as a guide.

RESULTS AND DISCUSSION

TABLE-1
EDXRF ANALYSIS RESULTS OF THE GLASS FRAGMENTS*

Sample No	1	2	3	4
Colour	Yellow	T-blue	T-blue	White
Na_2O %	0.7	3.6	3.6	0.5
MgO %	0.6	0.3	0.3	0.4
Al_2O_3 %	1.2	2.0	1.9	1.5
SiO_2 %	66	62	61	67
SO_3 %	0.2	1.5	1.7	0.2
K_2O %	12.7	12.2	12.1	12.0
CaO %	13.2	11.0	11.3	13.0
TiO_2 %	0.3	0.2	0.2	0.2
Fe_2O_3 %	0.05	0.02	0.02	0.03
As %	0.30	0.44	0.42	0.15
Pb %	0.5	2.7	2.7	0.6
Cr	10	32	24	2
Mn	60	50	60	100
Co	100	200	190	-
Cu	50	1700	1500	20
Zn	10	9	8	10
Rb	430	450	450	250
Sr	566	575	590	380
Mo	100	180	220	75
Sb	110	5.0	2.0	3
La	6.0	5.2	6.0	6.0
Ce	15	28	30	12
Au	0.5	0.4	0.5	-
U	50	70	70	40

* The results are in mg kg^{-1}, unless where indicated. T-blue = turquoise blue.

The chemical analyses of the investigated glass fragments are given in Table-1. The concentrations of 24 elements (Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Mo, Sb, La, Ce, Au, U, Pb) which might be present in the samples as flux, stabilizers, colorants or opacifiers and impurities, were determined. The Ottoman glass samples are characterized by elevated potassium but low magnesium oxide levels. They can be classified as potassium-limy glasses with SiO_2 levels vary from 61 to 67 wt. % and Na_2O from 0.5 to 3.6 wt. %. K_2O level is found to be around 12 wt. % and PbO concentrations ranged from 0.5 to 2.7 wt. %. Potassium-limy glass has been invented between 1670 and 1680 AD in glass making works in Bohemia, which is related to Ottoman period. The Al_2O_3 concentrations of the samples were found to be around or below 2 wt. %. The level of Fe was between 0.02 to 0.05 wt. %. The colors exhibited by the glasses are due to the oxidation state and electronic configuration of the metal ions in them, which are known as coloring agents. The coloring agents are usually transition elements or rare earth ions that have absorption frequencies in the visible region due to *d-d* or *f-f* electronic transitions, respectively. The colored effects in ancient glasses were generally produced by the presence of relatively small amounts of the oxides of transition metals such as cobalt, copper, manganese or iron. But the final color of the glass not only depends on the metallic oxides present, but also on the temperature and state of oxidation or reduction in the furnace. Antimony oxide can impart to glass yellow color. Cobalt is a strong blue coloring element. Manganese oxide was used either for discoloration or for coloration of glass to yellow, brown and violet colors. All the samples have Fe_2O_3 concentrations of less than 0.1 %, suggesting the unintentional addition of iron to the glass batch as contaminant. Sample No 1 is a spirally twisted translucent yellow glass bracelet. It has elevated level of Sb (110 mg kg^{-1}). Its coloring agents were probably antimony and manganese (60 mg kg^{-1}) elements. The turquoise blue vessel and its cover (sample numbers 3 and 2, respectively), show elevated levels of Cu (1500-1700 mg kg^{-1}), Co (190-200 mg kg^{-1}) and Cr (24-

32 mg kg^{-1}). Sample No 4 is a translucent white vase decorated with a surface coating. For this glass Mn (100 mg kg^{-1}) was probably used as discoloring element.

The FTIR absorption (KBr) spectra of the glasses are presented in Fig. 2. Confirmation of typical glass structure has been found as Si-O bands around 1300-900, 800 and 500-400 cm^{-1}.The strongest band around 1300-900 cm^{-1} region can be attributed to asymmetric stretching vibrations of the bridging Si-O-Si bonds, where the bridging oxygen atoms move in the direction opposite to their Si neighbors and roughly parallel to the Si-Si lines[5-6]. Besides, the band around 800 cm^{-1} is identified as the bending Si-O-Si vibration in which the oxygens move approximately at right angles to the Si-Si lines and in the Si-O-Si planes and the band around 500-400 cm^{-1} can be attributed to the rocking Si-O-Si vibration. Furthermore, the intensity and the frequency of those bands depend on the concentration of SiO_2 and of the network modifiers (K, Ca, Mg etc.)[7]. The addition of cations reduces the degree of connectivity of the three-dimensional network of SiO_4 groups by the replacement of bridging oxygen bonds by non-bridging silicone oxygen groups[8]. As a result, by increasing the network modifiers (K, Ca, Mg, *etc.*) the Si-O-Si stretching band wavenumber and intensity decreases. Additionally, the Si-O bending vibration decreases and the intensity of the band associated to the Si-O non-bridging groups increases[8]. The [SiO_4] tetrahedron can be bonded with variable non-bridging Si-O- bonds in SiO_4 network. The stretching modes Si-O with one non-bridging oxygen per SiO_4 tetrahedron (Si-O-NBO) can be observed around 975-890 cm^{-1} and Si-O with two non-bridging oxygens per SiO_4 tetrahedron (Si-O-2NBO) around 850 cm^{-1}.

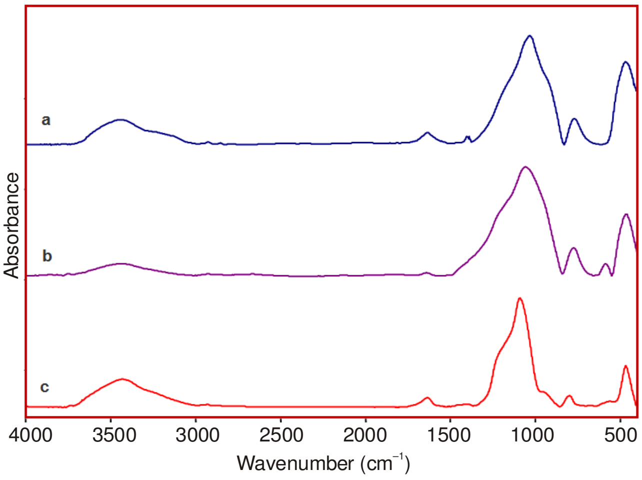

Fig. 2. FT-IR absorption (KBr) spectra of the excavated glasses; Samples No 1 (a), No 4 (b) and No 3 (c)

The wavenumbers correspond to the IR reflection peaks (DRIFT) and the IR absorption peaks (KBr) are slightly different. This situation is partly caused by the difference in techniques[9] and partly caused the difference in the sampling techniques; IR reflection probes the surface layer of the glass, while the IR absorbance probes the entire thickness of the homogeneous powdered sample. In Fig. 3, the IR absorption and reflection (DRIFT) spectra of the sample No 2 (turquoise blue bowl lid) are given. In the DRIFT spectrum the strong reflection band centered at 1091 cm^{-1} (TO$_1$) together with the shoulder around 1236 cm^{-1}(TO$_2$) are assigned to transverse optical modes (TO) of Si-O-Si asymmetric stretching vibration, in agreement with Serra *et al.*[8]. The medium intense reflection band at 768 cm^{-1} and the strong band at 448 cm^{-1} are assigned to Si-O-Si bending and rocking vibrations, respectively, in accord with Aguiar *et al.*[6] and Raffaelly *et al.*[10]. The Si-O-Si bending (775 cm^{-1}) and rocking vibrations (463 cm^{-1}) shift to higher wavenumbers in IR absorption spectra. The 851 cm^{-1} reflection band which is not observed in the absorption spectrum, can be attributed to the Si-O stretching vibration with two non-bridging oxygen per SiO_4 tetrahedron (Si-O-2NBO), also called Q_2 groups, in agreement to Aguiar *et al.*[6] 580 cm^{-1} band, observed both IR absorption and reflection spectra, is attributed to 4 fold rings[6], where four oxygens in a bridging configuration in the tetrahedral network.

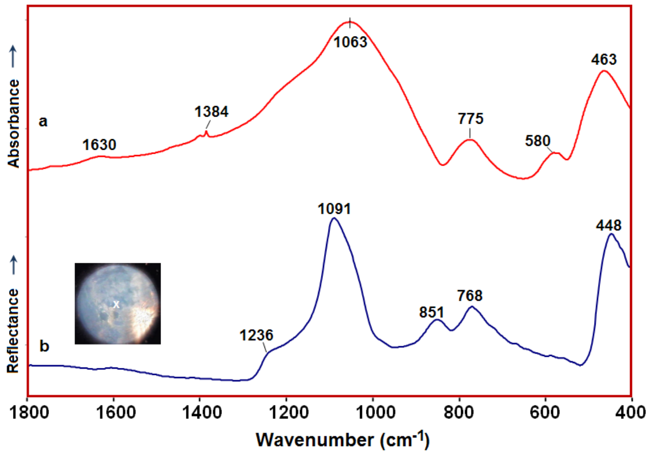

Fig. 3. IR absorption (a) and reflection (DRIFT) (b) spectra of the sample No 2 (turquoise blue bowl lid). The micro-video image of the sample was shown at the lower frame

Fig. 4 represents the DRIFT spectra, taken from the external surface and the cross section part of the bracelet (sample No 1). The wavenumbers and intensity differences observed in Si-O-Si stretching bands from the external surface and inner parts clearly demonstrate the inhomogeneous glassy structure.

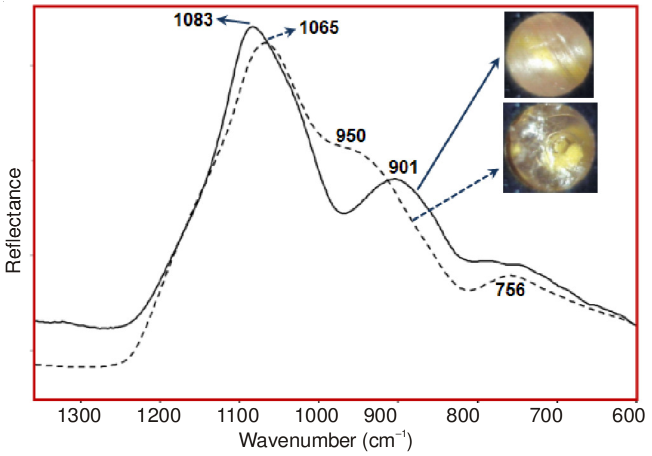

Fig. 4. IR reflectance (DRIFT) spectra of the bracellet (sample No 1). Solid line is taken from the external surface, broken line is the taken from the cross section (inner part). The corresponding micro-video images are shown at the right top

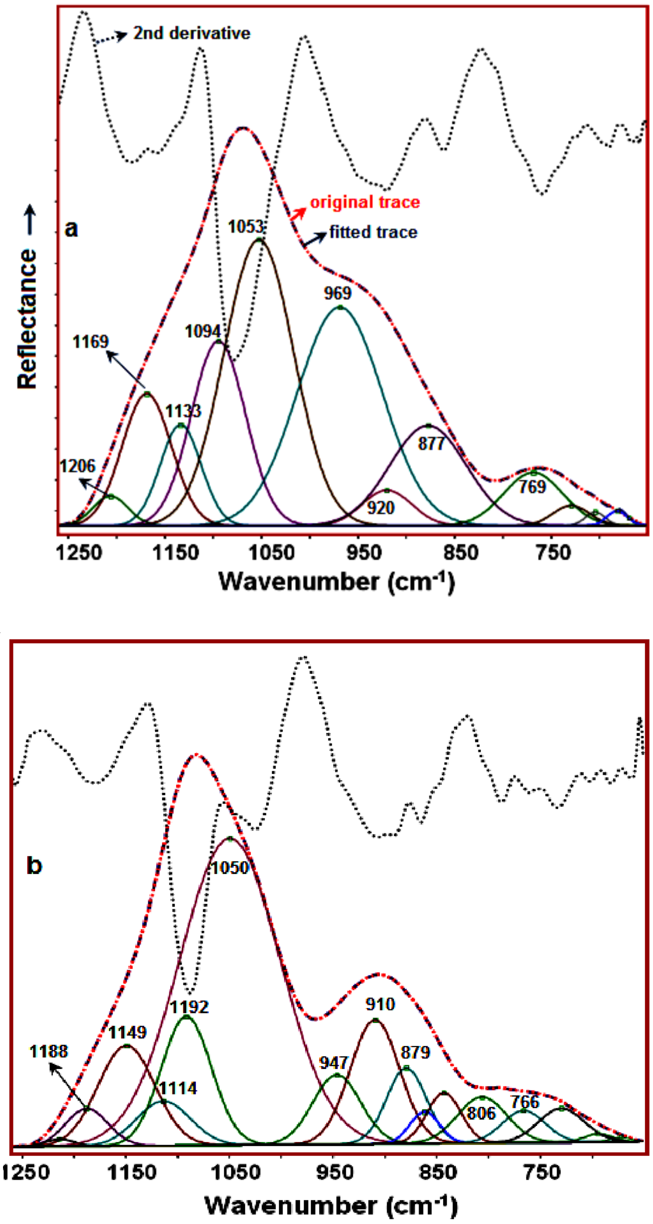

Fig. 5. The band component analyses of the DRIFT spectra taken from the cross section (inner part) (a) and the external surface (b) of the bracellet (sample No 1)

In Fig. 5 the band component analyses of the 1250-650 cm^{-1} region of the DRIFT spectra taken from the cross section part of the bracelet and the external surface of the bracelet (sample No. 1) are given. The bands around 1206-1050 cm^{-1} are assigned to Si-O-Si asymmetric stretching vibrations of the SiO$_4$ tetrahedron, whereas the bands around 969-910 cm^{-1} and 879-842 cm^{-1} can be attributed to Si-O-Si asymmetric stretching vibrations with one non-bridging oxygen per SiO$_4$ tetrahedron (Si-O-NBO) and to Si-O-Si with two non-bridging oxygen per SiO$_4$ tetrahedron (Si-O-2NBO), respectively. The 806-766 cm^{-1} bands are attributed to Si-O-Si bending vibrations.

Conclusion

The data from chemical analyses show that the investigated Ottoman glass fragments excavated in ancient Ainos, can be classified as potassium-limy glasses. Potassium-limy glass has been invented between 1670 and 1680 AD in glass making works in Bohemia, which is related to Ottoman period. The IR absorption and reflection spectra have been revealed very sensitive to the morphological and structural changes in the glass matrix originated by the variations in the glass composition. These changes are related to the textural properties.

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