

RAMAN SPECTROSCOPY FOR NON-DESTRUCTIVE ANALYSIS OF SOME PIGMENTS, GLAZES AND COLOURED GLASSES

*Rodica-Mariana Ion**, *Sofia Teodorescu***, *Mihaela-Lucia Ion****

* ICECHIM, Bucharest, Romania; Valahia University of Targoviste, Materials Engineering Department, Romania; rodica_ion2000@yahoo.co.uk

** Multidisciplinary Scientific and Technologic Research Institute, Valahia University of Targoviste, Romania; sofiateodorescu@yahoo.com

*** Valahia University of Targoviste, History Department, Romania; mihaella_ion@yahoo.com

Rezumat. Examinarea spectroscopică a operelor de artă este de mare importanță pentru conservatori, istorici de artă și colecționari din muzee. Aceste investigații oferă informații utile despre contextul istoric și despre interacțiunile dintre diferite culturi și rutele comerciale ce au contribuit la acestea. În știința conservării, spectroscopie Raman s-a impus ca tehnică analitică nedistructivă, extrem de versatilă, care permite identificarea de particule de până la 1 pm. Această tehnică permite identificarea de pigmenți anorganici / organici, și contribuie la identificarea cu ușurință a noilor pigmenți sintetici obținuți din minerale extrase din sol, precum și a liantului și a lacurilor utilizate. Această metodă a fost deja utilizată pentru a investiga diverse artefacte din sticlă (zona Brașov și zona Histria), iar rezultatele vor fi prezentate în această lucrare completate cu alte tehnici analitice necesare pentru a elucidă structura și componența artefactelor investigate: reflectanța cu absorbție difuză, spectroscopie în infraroșu cu transformată Fourier și spectrometrie de fluorescență cu raze X cu dispersie după lungime de undă (WDXRF). Spectroscopia Raman este de asemenea utilizată pentru a identifica compoziția, structura și impactul factorilor de mediu asupra procedurilor de restaurare.

Cuvinte cheie: Raman, sticlă, artefacte, reflectanța cu absorbție difuză, WDXRF.

1. Introduction

In conservation science, the non-destructive techniques are extremely important. In this context, Raman spectroscopy is one of these techniques, which allows material identification from different artifacts, including panel paintings¹, glass², wall paintings³, and manuscripts⁴. This technique is useful for understanding

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, projects number PNII 222/2012, PNII 261/2014 and PN 09.09.03.07.02.

¹ Ortega-Aviles *et alii*, 2005, p. 164; Vandenabeele *et alii*, 2001, p. 263.

² Robinet *et alii*, 2004, p. 662.

³ Edwards, 2003, p. 271; Vandenabeele *et alii*, 2005, p. 707.

the chemistry and degradation mechanisms of historical materials and pigments, assessing the effectiveness of conservation procedures. Raman spectroscopy is well-suited for this purpose: it enables the identification of inorganic⁵ and organic pigments⁶, as well as binding media and varnishes⁷. As an optical method, Raman spectroscopy offers a great advantage over most other techniques because can be performed without any contact with the studied artifact, both at the laboratory and on-site using portable instruments. In this study, our first goal is the spectroscopic characterization of pigments and colored glasses (Braşov area and Histria area). This technique is completed with Diffuse Reflectance UV-Vis Spectroscopy (DR-UV-Vis), Fourier Transformed Infrared Spectroscopy (FTIR) and Wavelength-Dispersive X-ray Fluorescence (WDXRF).

2. Instrumentation, Materials and Preparations

2.1. Characterization techniques

The samples were analyzed by using the following techniques:

The phases were also characterized by **Fourier transformed infrared spectroscopy** (FT-IR, spectrometer FTIR 6300 with ATR Specac Golden Gate (diamant-safir, windows KRS5, 30 accumulations). The samples of paints, ground, and adhesives from the artwork were analyzed using FTIR in order to identify binding media, pigments, and fillers. Infrared spectra were measured in transmittance mode by the use of KBr pellets. In this case, 2mg of the original samples were mixed with KBr (~2% w/w) and ground to a finely divided powder with the use of an agate mortar and pestle. Spectra were recorded at 1.0 cm⁻¹ resolution, in the range 4000–400 cm⁻¹ as a ratio of 64 single-beam scans of the sample to the same number of background scans from air.

Raman spectra have been obtained with a portable dual wavelength Raman analyzer IR -XANTUS 2 – RIGAKU, with the following parameters: Dual wavelength source 1064nm & 785nm, spectral range (cm⁻¹) 200 – 4000, Spectral Resolution (cm⁻¹) 7 – 10, Laser Output Power (mW) 400 – 490, Laser Output Power (mW) 30 – 490, cooled detectors – CCD and InGaAs. The paint cross sections were analyzed using Raman spectroscopy in order to identify pigments and fillers.

The laser beam was focused on a diameter of about 25.5 and 1.5–2 µm, respectively. Spectra were acquired using 10 sec. of signal collection time and five accumulations.

Absorption spectra studies were performed using a diffuse reflectance in the ultraviolet (UV)–visible–near-IR spectral regions, by using a Carl Zeiss Jena UV-Vis spectrophotometer.

X-Ray Fluorescence was used to identify the elements in certain pigments, fillers. A dispersive wavelength X-ray fluorescence spectrometer (WDXRF) with a Benchtop spectrometer sequential type, wavelength dispersive. The system is

⁴ Gilbert *et alii*, 2003, p. 1213; Doncea, Ion, 2008, p. 53.

⁵ Wehling *et alii*, 1999, p. 253.

⁶ Vandenabeele *et alii*, 2000, p. 509.

⁷ *Ibidem*, p. 261.

equipped with 3 crystals Analysis (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%.

2.2. Glass archaeological materials

Small fragments of glass of about 1 mm² were cut from the excavated fragments and embedded in an acrylic resin. Samples were taken only from broken vessels (Fig. 1).



Fig. 1. The used samples (Braşov samples).

3. Results and Discussion

3.1. Background information

In Europe the glass producing process usually 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, seashells⁸ or marble). Also, 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 for the period of the Roman Empire⁹.

The components of these glasses are basically sodium and silica. Small amounts of alumina (generally near 2.5 wt.%) and calcium oxide (between 6 and 8%) are characteristically present in these glasses also. Low magnesia and potash contents (~1.5%) distinguish these from other sodic glass types. The lack of magnesia and potash impurities (-1 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. In view of its

⁸ Henderson, 1985, p. 267.

⁹ Fleming, 1999.

¹⁰ Cunningham, 2013; Freestone, 2008, p. 77; Degryse, Schneider, 2008, p. 1993.

relatively low Fe content, it could easily be rendered colorless by addition of oxidizing products such as MnO_2 or Sb_2O_5 ¹¹. After the breakdown of the Roman empire and roughly until 1000 AD, knowledge on glass making was no longer available in Europe while also some of the raw materials were no longer available.

Glass could be divided into three groups:

- sodic glass ($\text{Na}_2\text{O} > 6\%$ w/w);
- calco-potassic glass ($\text{K}_2\text{O} + \text{CaO} > 22\%$ w/w);
- lead glass ($\text{PbO} > 15\%$ w/w).

In the literature only a limited number of papers has been published. Michail Alekseevič Bezborodov, in a summary of glass analyses from the literature¹², indicates low titania contents (-0.15%) for glasses of central European find sites in the 1–3rd century period. Maria Carina Calvi reports low titania glasses (-0.1 wt.%) for samples from northern Italy of 1–2nd century AD¹³. In general, glasses produced in the period 100 BC– 300 AD appear to have low TiO contents. The major different glass-making components: fusing agent, silica source, and colour treatments. The low content of magnesia and potash in the glasses studied could be attributed to fusing agent. Elements such as Mn and Sb have often been added as de-colouring agents in the elaboration of the final glass product. Some minerals as magnetite and iron titanates such as ilmenite, or silicates such as zircon. The titania content is very low, normally 0.15 wt.% or less¹⁴.

Although Roman and post-Empire glasses found in Europe are reputed to have a very constant composition and hence source of components, it appears that some 4–5th century and later specimens show evidence of a different source of silica (sand) component. Zirconium, Strontium and titanium are the discriminating elements. Data presented here for different specimens from 1st to 4th century samples indicate a strongly homogeneous Sr and Ti content; while 4–5th century samples show a strong trend of concomitant Ti and Zr increase. The variation of the Ti and Zr content, could very well reflect the results of political instability of the 4–5th century exemplified by the fragmentation of the Roman Empire into two parts.

In Europe, numerous investigations of the 17th and 18th century glasshouses and glass waste have been achieved. The study on the chemistry of late 16th century and early 17th century green container glass, similar to the materials in this study, documents the wide use of high-calcium glasses (CaO 17.9–28.5%) during this period.

3.2. Braşov glass artifacts

The UV-Vis DR absorption spectra for coloured glasses are presented in Fig. 2. White glass shows a strong absorption band in the UV, compatible with SnO_2 absorption in this spectral region. The green glass has two maxima at about 400 and 750 nm. This chromium oxide pigments that exhibit absorption peaks at 455 and 636

¹¹ Velde, Hochuli-Gysel, 1998, p.185.

¹² Bezborodov, 1975.

¹³ Calvi, 1968, p. 288; Jackson *et alii*, 1996, p. 301.

¹⁴ Kennedy *et alii*, 2013, p. 465.

nm, characteristic of Cr³⁺ ions¹⁵. This is also in agreement with the WDXRF data presented in Tables 1 and 2, where in green samples the amount of chromium oxide detected is significant¹⁶. Brown glass absorption curves exhibit a maxima spreading from about 350 nm to about 450 nm with long tails in the visible region of the absorption spectra, while the maxima for the dark brown curves is clearly located in the UV.

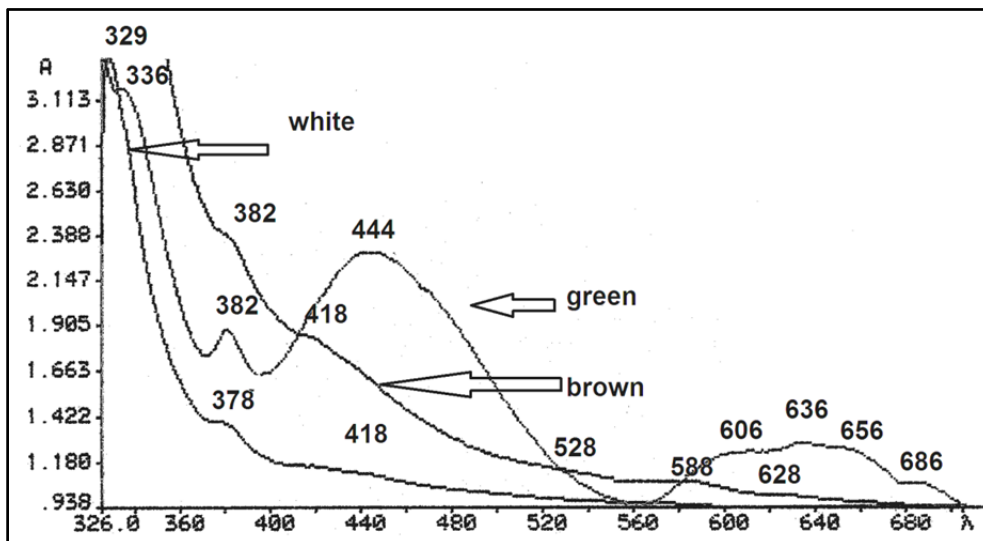


Fig. 2. The UV-Vis DR spectra of glass samples.

Sample color	Brown	Green	White
Na ₂ O	3	5.2	5.4
MgO	0.8	1.6	1.6
Al ₂ O ₃	3.8	6	3.5
SiO ₂	69.4	72.3	59.1
P ₂ O ₅	9.12	0.56	0.93
SO ₃	1	0.71	0.2
Cl	1.73	1.95	2.7
K ₂ O	2.15	0.47	10.5
CaO	7.37	10.4	12.8
MnO	1	0.028	0.563
Fe ₂ O ₃	0.708	0.579	0.816
CuO	–	–	0.035
PbO	–	–	1.8
TiO ₂	0.12	0.11	0.12
ZnO	0.03	–	–

Tab. 1. Chemical composition of medieval glass.

¹⁵ Visinescu *et alii*, 2010, p. 124; Reiche *et alii*, 2009, p. 1025.

¹⁶ Ion *et alii*, 2008, p. 114.

Major element analysis indicates that the major glass forming elements (Na, Mg, Al, Si, K, Ca, Mn, Fe) are 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, V, Zn, 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, heavier minor element indicated that most were very constant in abundance but two seemed to vary simultaneously.

Sample color	White	Green	Brown
Ag	14.4	4.6	4.85
Ti	2032.77	665.21	462.78
Pd	211.15	363.76	211.15
Zr	10636.96	4314.55	2189.27
Tl	231.19	3.09	60.27
Al	125819.13	23423.52	12776.03
Sr	2114.02	434.6	402.00
Ca	28938.4	30448.44	54332.28
Ba	10117.96	6321.9	6084.12
Si	219528.78	591180.23	745005.26
Mn	2638.27	78.4	3617.25
Fe	8716.91	2385.49	3232.39
Cr	33.08	367.6	–
Mg	2782.44	6119.51	8889.59
Na	114809.96	41979.12	31819.14
Sn	31.26	16.51	343.95
Zn	312.58	34.21	181.18
Cu	92.31	23.65	58.03
Li	233.29	21.3	10.07
Re	263.17	1187.69	287.07
K	3361.73	5307.31	3563.62
P	9686.76	–	6343.85

Tab. 2. ICP-AES results for historical glasses¹⁷.

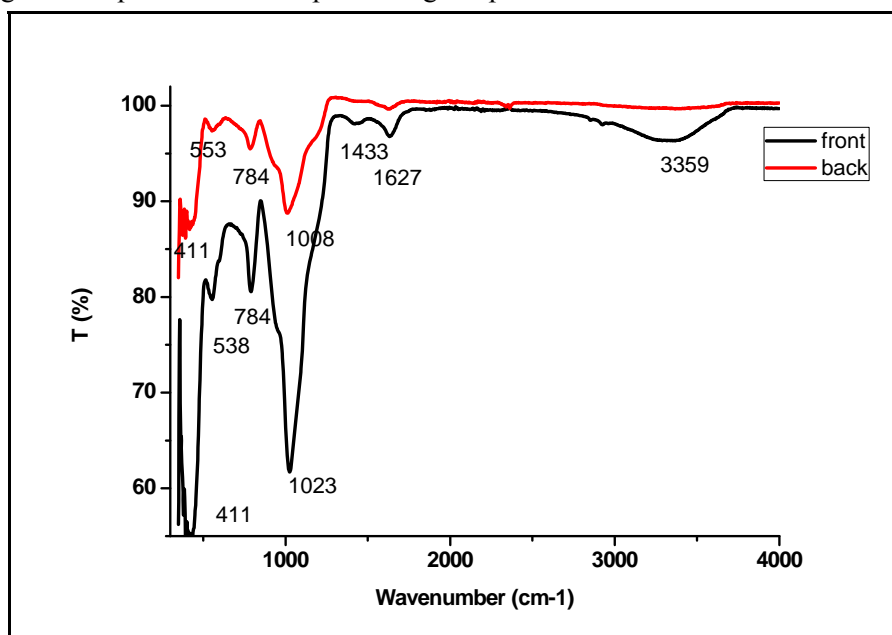
Cu, homogeneously added to white glass, can produce a pale green color. The glass body contains several elements such as Pb, Si, Al, Na, Fe for yellow, Cu for dark green and Co for dark blue colors. The presence of the elements K, Ca and S indicates the formation of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) as main weathering product. Additionally, enrichments of Na and Cl imply the formation also of NaCl

¹⁷ Ion *et alii*, 2006, p. 34.

and of a K-containing compound (e.g. KNO_3), as elements with a low atomic number such as N could also be detected.

All FTIR spectra are dominated by the aluminosilicate network absorption bands at 1057, 797–781 and 465 cm^{-1} , which are characteristic of silica rich matrix: Si–O–Si antisymmetric stretching band, Si–O symmetric stretching and Si–O rocking motion, respectively¹⁸. Also, the 1650 cm^{-1} (H–O–H) and 3400–3500 cm^{-1} (–OH) are present in all pastes (Fig. 3). The characteristic absorptions of calcium carbonate (CaCO_3) is observed¹⁹ at 1440 and 876 cm^{-1} . Also, by FTIR was possible to evaluate the differences between concav and convex faces of glass artifacts, as a proof of dust and other impurities (Fig. 4). Glass objects and glazes are silicate-based materials, built with SiO_4 tetrahedral, which are strong and stable chemical entities. Because strong covalently bonded structures, the Raman spectrum of a silicate consists, in a first approximation, as a significant signature of the M–O covalent network.

Additional, the Raman spectrum of the amorphous phase of a glass consists of two broad bands around 500 and 1000 cm^{-1} . The band at $\sim 500 \text{ cm}^{-1}$ originates from the two bending vibrations of isolated SiO_4 tetrahedra and the one at 1000 cm^{-1} from the Si–O stretching vibrations (Fig. 5). The relationship between the Raman index of polymerization ($I_p = A_{500}/A_{1000}$ with A being the area under the Raman band), the glass composition and the processing temperature is well documented²⁰.

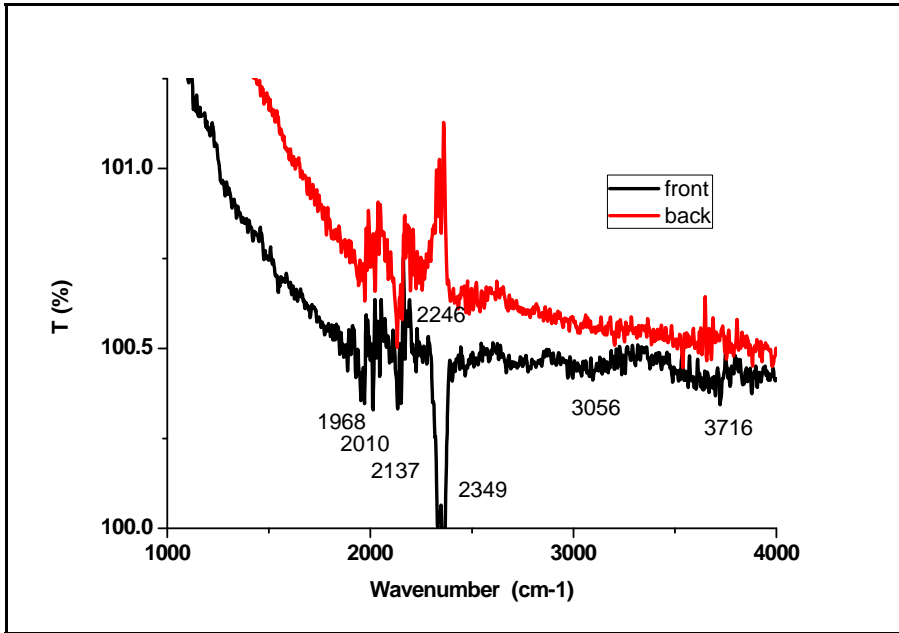


Brown

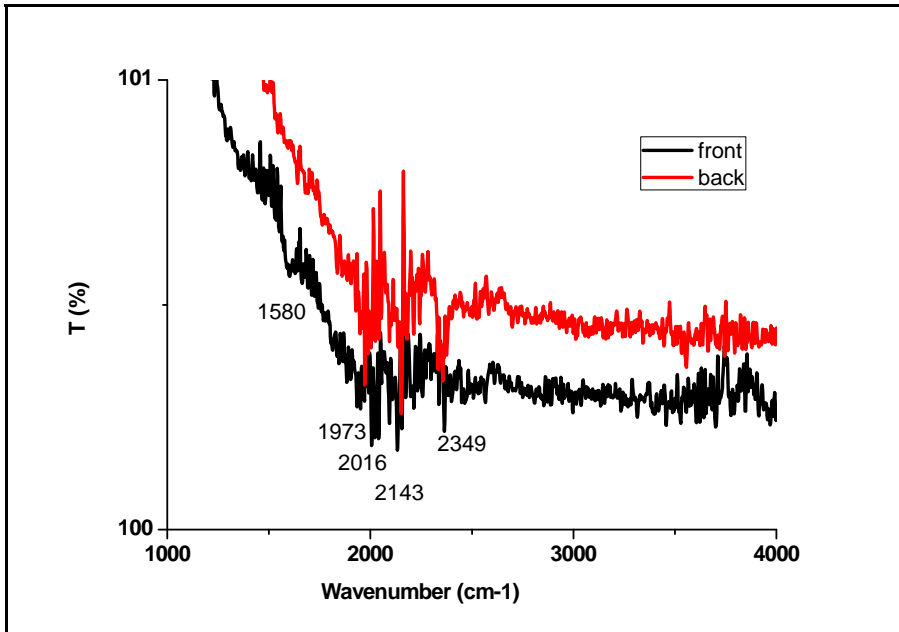
¹⁸ Stoia *et alii*, 2010, p. 49; Jonynaite *et alii*, 2010, p. 158.

¹⁹ de Waal, 2004, p. 646; Colomban, 2008, p. e55.

²⁰ Colomban *et alii*, 2003, p. 205; Colomban, Truong, 2004, p. 195; Colomban *et alii*, 2006, p. 841.



Green



White

Fig. 3. The FTIR spectra of glass spectra.

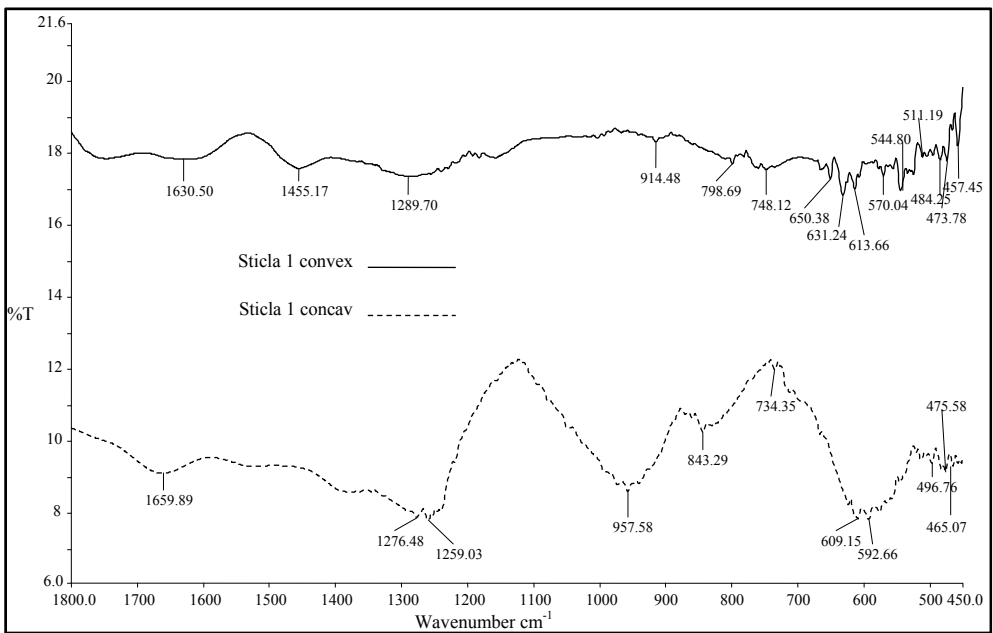
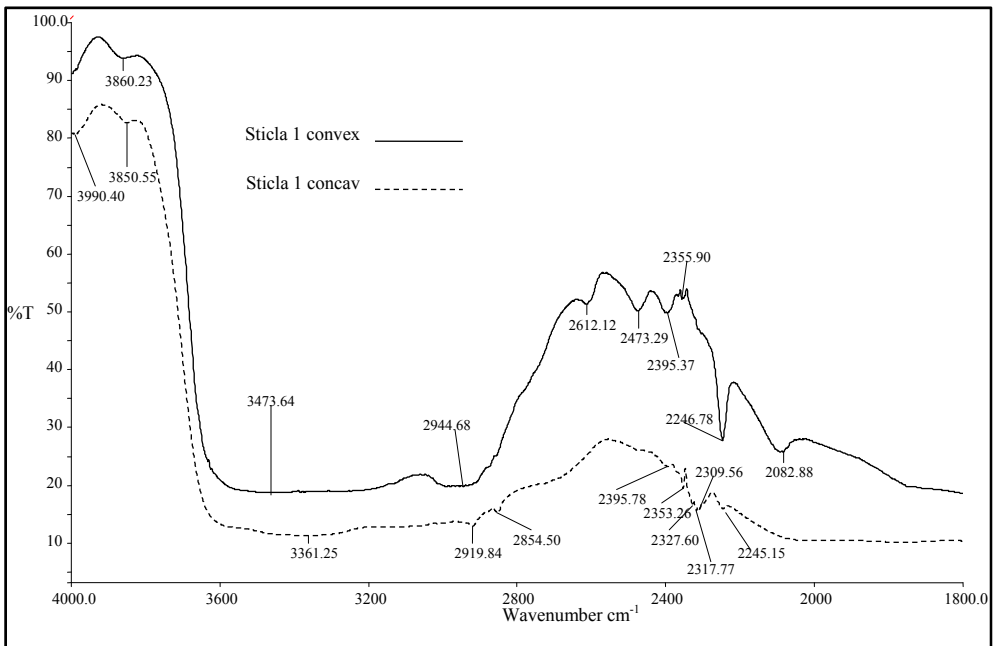
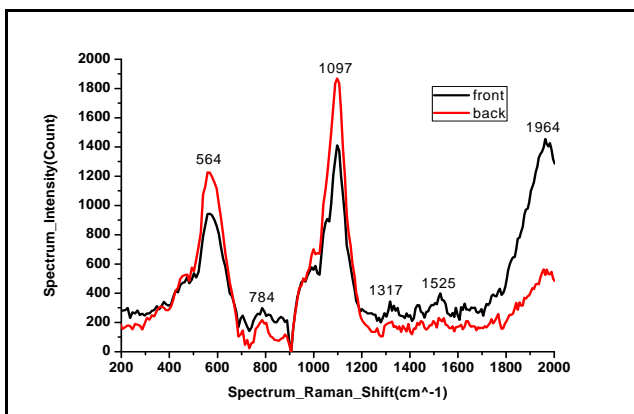
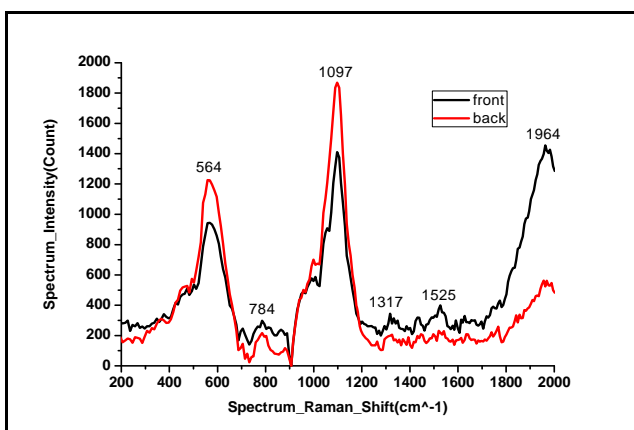


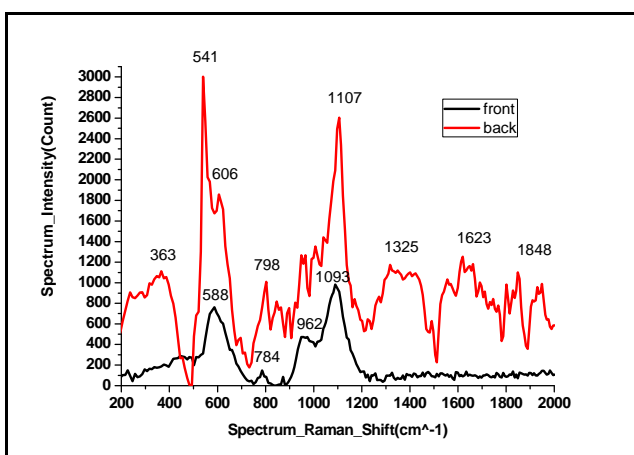
Fig. 4. The differences of FTIR spectra for one side and side-reverse of a glass sample.



Green glass



Brown glass



White glass

Fig. 5. Raman spectra of glass samples.

Colored paint layers are made from ground pigments mixed with a binding medium, commonly egg tempera or a drying oil (such as linseed oil), or a modern synthetic polymer or composite. Organic colouring materials are found entangled in a complex array of inorganic and organic paint materials. Organic lakes were particularly appreciated for their use in transparent top layers known as *glazes*. Light passes through this film and reflects from the layer beneath it, providing a unique effect of transparency.

For all the above studied pieces the Si–O stretching multiplet maximum (ν_{MAX} Si–O) of the glass bodies varies between 1050 and 1100 cm^{-1} , which corresponds to a range of mixed Na–Ca and Ca-containing Na-rich glass compositions (1070–1100 cm^{-1} range) and to mixed Na–Pb compositions (1050–1070 cm^{-1} range). The Raman spectra corresponding to Na–Ca glasses are mostly characterized by a bending massif in which three bands can usually be identified, at about 415–430, 480–505 and 545–590 cm^{-1} .

The analysis of the white pigments is also exploited as opacifying agents, offering a good example of the potential of the Raman technique to discriminate between technologies used over the centuries. Some elemental analyses reported Sn-containing ancient glazes and conclude that the artifact was opacified with tin.

3.3. Hatria glass artifacts

In Europe, numerous investigations of the 17th and 18th century glasshouses and glass waste have been achieved²¹. The study on the chemistry of late 16th century and early 17th century green container glass, similar to the materials in this study, documents the wide use of high-calcium glasses (CaO 17.9–28.5%) during this period²².

Analysis of the major and minor oxides indicated a high concentration of calcium as a result of manufacturing preferences that used wood ash as a component in the glass recipe. Due to the potash (which could contain small amounts of Fe_2O_3 , the glass could exhibit a pale green colour, or yellow-green colour, such glass being known as Waldglass (forest glass)²³. In addition to lead compounds and wood ash (potassium carbonate)(potash), two common ingredients like potassium tartrate ($\text{HOOC-CHOH-CHOH-COO}^-\text{K}^+$), Salpetre (KNO_3), sea salt (NaCl) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were used.

The presence of phosphorus oxide indicated the use of wood ash (including from bone ash). This composition is typical for the glass production in Western Europe from the tenth to seventeenth century²⁴. The presence of German glass makers from the centre of Europe in the Transylvanian manufactories could explain the types of models and techniques from the Transylvanian manufactories.

Cu, homogeneously added to white glass can produce a pale green color. The glass body contains several elements such as Pb, Si, Al, Na, Fe for yellow, Cu

²¹ Van Espen *et alii*, 1987, p. 109; Schalm, Janssens, 2003, p. 669.

²² Janssens *et alii*, 1998, p. 315.

²³ De Raedt *et alii*, 2001, p. 1012.

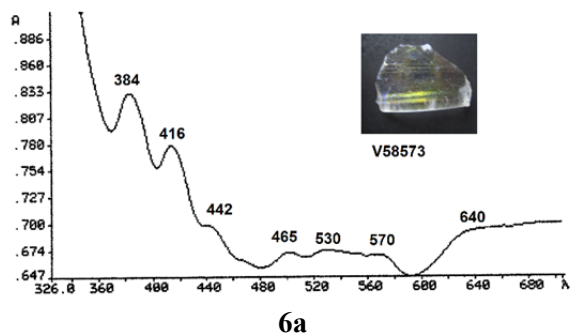
²⁴ Ion *et alii*, 2011, p. 487.

for dark green and Co for dark blue colors. It is noticed that for transparent glass the concentration of K_2O is similar with CaO , his being a first proof for the venetian receipt of glass bleaching, by glass treating with MnO . Most of the samples of blown glass objects investigated showed rather low ZrO and TiO_2 contents, less than 240 ppm and 0.25 wt.%, respectively.

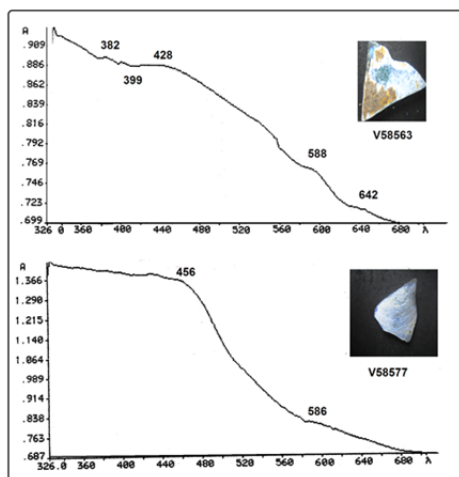
All samples of older glasses show low to very low ZrO and TiO_2 contents. TiO_2 is especially low (below 0.1 wt.%) for samples and Sr content ranges from 25 to 230 ppm. The greatest number of samples have a Zr content below 100 ppm. Samples from Histria (represented inside of UV-Vis spectra, Fig. 6)

The Sr compositions of these glasses differ, however, probably reflecting a varying ratio of limestone to shell because the sands that were utilized were from different coastal locations. A low elemental strontium, consistent with the use of limestone or limestone-rich sand in the batch. The XRF analysis of this intermediate

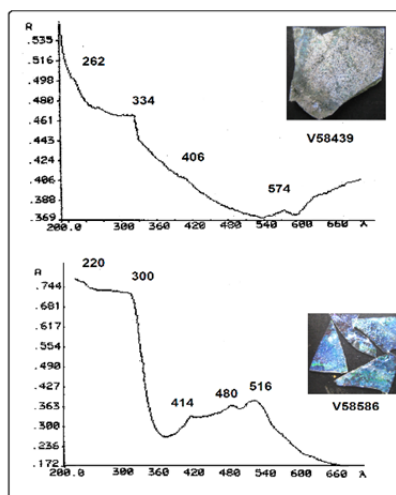
layer revealed the presence of the same chemical elements as in the clay but with different relative ratio. The white colour derived from lead or lime, black from carbonized bone or other materials. The use of organic pigments, such as red madder and murex shell purple, is also attested.



6a



6b



6c

Fig. 6. The UV-Vis DR spectra of the glass artifacts from Histria area.

4. Conclusions

This paper presented various artifacts of glass (Braşov area and Histria area), and the results obtained by diffuse reflectance absorption, Fourier transformed infrared spectroscopy, Raman spectroscopy and dispersive wavelength X-ray fluorescence spectrometer (WDXRF). All these techniques have been used in order to identify the composition, structure and impacts of environmental factors used in the restoration.

BIBLIOGRAPHY

- Bezborodov, 1975 Bezborodov, Mikhail Alekseevich, *Chemie und Technologie der antiken und mittelalterlichen Glaser*, Verlag Philipp von Zabern, Mainz, 1975, 327 pg.
- Calvi, 1968 Calvi, Maria Carina, *I vetri romani del museo di Aquileia*, Pubblicazioni dell'Associazione Nazionale per Aquileia, 7, Associazione Nazionale, Aquileia, 1968, 287 pg. + 47 pls.
- Christie *et alii*, 1979 Christie, O. H.J.; Brenna, J. A.; Straume, E., *Multivariate classification of roman glasses found in Norway*, In: *Archaeometry*, Vol. 21, Issue 2, August 1979, p. 233-241.
- Colomban, 2008 Colomban, Philippe, *Recent case studies in the raman analysis of ancient ceramics: Glaze*, In: *Journal of Cultural Heritage*, 9 (Suppl.), 2008, e55.
- Colomban *et alii*, 2003 Colomban, Philippe; March, Grégory; Mazerolles, Léo; Karmous, Tijani; Ayed, Naceur; Ennabli, Abdelmajid; Slim, Hédi, *Raman identification of materials used for jewellery and mosaics in Ifriqiya*, In: *Journal of Raman Spectroscopy*, Vol. 34, Issue 3, March 2003, p. 205-213.
- Colomban, Truong, 2004 Colomban, Philippe; Truong, Catherine, *Non-destructive raman study of the glazing technique in lustre potteries and faience (9-14th centuries): silver ions, nanoclusters microstructure and processing*, In: *Journal of Raman Spectroscopy*, Vol. 35, Issue 3, March 2004, p. 195-207.
- Colomban *et alii*, 2006 Colomban, Philippe; Tournie, Aurélie; Bellot-Gurlet, Ludovic, *Raman identification of glassy silicates used in ceramics, glass and jewellery: a tentative differentiation guide*, In: *Journal of Raman Spectroscopy*, Vol. 37, Issue 8, August 2006, p. 841-852.
- Cunningham, 2012 Cunningham, Lawrence S., *The Roman Legacy*, In: ***e-Study Guide for: Culture and Values - A Survey of the Humanities***, Cram101 Textbook Reviews, 6th Edition, Vol. I, 2012, 105 pg., ISBN 9780534582289; Chapter 4 (*on-line*).
- Degryse, Schneider, 2008 Degryse, Patrick; Schneider, Jens, *Pliny the Elder and Sr-Nd isotopes: tracing the provenance of raw materials for Roman glass production*, In: *Journal of Archaeological Science*, Vol. 35, January 2008, p. 1993-2000.
- De Raedt *et alii*, 2001 De Raedt, I.; Janssens, K.; Veeckman, J.; Vincze, Laszlo; Veke-mans, Bart; Jeffries, T. E, *Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16th and 17th century*, In: *Journal of Analytical Atomic Spectrometry*, 16 (9), 2001, p. 1012-1017.
- De Waal, 2004 de Waal, Danita, *Raman investigation of ceramics from 16th and 17th century Portuguese shipwrecks*, In: *Journal of Raman*

- Spectroscopy*, Vol. 35, Issue 8-9, August 2004, p. 646-649.
- Doncea *et alii*, 2008 Doncea, Sanda Maria; Ion, Rodica-Mariana; Niculescu, Valentin Ioan; Pavel Valeriu, *Comparative FTIR Techniques Applied To Historical Papers*, In: *Scientific Bulletin of Valahia University: Materials and Mechanics*, 8, 5(8), 2008, p. 53-60.
- Edwards, 2003 Edwards, H.G.M., *Illumination of a mediaeval mystery: The FT-Raman spectroscopic analysis of red pigment from a mediaeval corbel in the church St Clement of Rome, Fiskerton*, In: *Journal of Molecular Structure*, Vol. 661-662, 2003, p. 271-277.
- Fleming, 1999 Fleming, Stuart J., ***Roman Glass; reflections on cultural change***, Philadelphia, University of Pennsylvania Museum of Archaeology and Anthropology, 220 pg., 1999, ISBN 0924171731.
- Freestone, 2008 Freestone, Ian Charles, *Pliny on Roman glassmaking*, In: Martín-Torres, Marcos; Rehren, Thilo (eds), ***Archaeology, History and Science: Integrating approaches to Ancient Materials***, Left Coast Press, Walnut Creek, 2008, 218 pg., ISBN 978-1-59-874340-1; p. 77-100.
- Gilbert *et alii*, 2003 Gilbert, Bernard; Denoel, Savier; Weber, Gyorgy; Allart, Dominique, *Analysis of green copper pigments in illuminated manuscripts by micro-Raman spectroscopy*, In: *Analyst*, 128(10), 2003, p. 1213-1217.
- Henderson, 1985 Henderson, Julian, *The raw materials of early glass production*, In: *Oxford Journal Archives*, 4, 1985, p. 267-291.
- Ion *et alii*, 2006 Ion, Rodica-Mariana; Dinu, Monica; Coşuleţ, St.; Ion, Mihaela-Lucia; Niculescu, V.I.R.; Gorincu, Irina; Rugina, Florentina, *Spectroscopic techniques in cultural heritage conservation*, In: *Simpozionul internaţional "Priorităţile Chimiei pentru o Dezvoltare Durabilă" - PRIOCHEM, Ediţia a II-a, Bucureşti, 26-27 octombrie 2006* (Rezumatelucrărilor), 2006, 102 pg., on-line http://www.icechim.ro/priochem/2006_Volum_rezumatelucrari.pdf; p. 35.
- Ion *et alii*, 2008 Ion, Rodica-Mariana; Ion, Mihaela-Lucia; Fierăscu, Radu-Claudiu; Dumitriu, Irina; Coşuleţ, Stelian; Niculescu Valentin Ioan Remus, *Modern analytical methods for historical glass artefacts analysis*, In: [Proceedings of] *Al VI-lea Simpozion Internaţională "Mecatronica şi Inginerie Mecanică, Microtehnologii şi Materiale Noi"*, MIM.MMN - Târgovişte, 7 noiembrie 2008, 2008, p.114-118.
- Ion *et alii*, 2009 Ion, Rodica-Mariana; Boros, Doina; Coşuleţ, Stelian; Ion, Mihaela-Lucia; Dumitriu, Irina; Fierascu, Radu-Claudiu; Rado-vici, Constantin; Niculescu, Valentin Ioan Remus; Pop, Simona-Florentina; Doncea, Sanda Maria, *Analytical methods for artefact materials*, In: *The Scientific Bulletin Valahia University*,

- Ion *et alii*, 2011
 Ion, Rodica-Mariana; Dumitriu, Irina; Fierăscu, Radu-Claudiu; Ion, Mihaela-Lucia; Pop, Simona-Florentina; Radovici, Constantin; Bunghez, Raluca-Ioana; Niculescu, V.I.R., *Thermal and mineralogical investigations of historical ceramic: A case study*, In: *Journal of Thermal Analysis and Calorimetry*, 104 (2), 2011, p. 487-493.
- Jackson, 1996
 Jackson, Caroline, *From Roman to Early Medieval Glasses: Many Happy Returns or a New Birth*, In: *Annales du 13 Congrès de l'Association Internationale pour l'Histoire du Verre, Pays-Bas 1995*, Amsterdam, 1996, p. 289-302.
- Janssens *et alii*, 1998
 Janssens, Koen H.; Deraedt, Ine; Schalm, Olivier; Veeckman Johan, *Composition of 15–17th Century Archaeological Glass Vessels Excavated in Antwerp, Belgium*, In: Love, Glyn; Nicholson, W. A. Patrick; Armigliato, Aldo (eds), ***Modern Developments and Applications in Microbeam Analysis***, *Mikrochimica Acta Supplement*, vol. 15, Springer-Verlag, Wien - New York, 1998, XI + 392 pg.; p. 253-267.
- Jonynaite *et alii*, 2010
 Jonynaite, Dalia; Sentvaitiene, Jurate; Beganskiene, Aldona; Kareiva, Aivaras, *Spectroscopic analysis of blue cobalt smalt pigment*, In: *Vibrational Spectroscopy*, Vol. 52, Issue 2, 2010, p. 158-162.
- Kennedy *et alii*, 2013
 Kennedy†, C. J.; Murdoch, K. R.; Kirk, S., *Characterization of archaeological and in situ Scottish window glass*, In: *Archaeometry*, Vol. 55, Issue 3, June 2013, p. 465-478.
- Ortega-Aviles *et alii*, 2005
 Ortega-Aviles, Mayahuel; Vandenabeele, Peter; Tenorio, Dolores; Murillo, Ghiraldo; Jimenez-Reyes, Melania; Gutierrez, Novelo, *Spectroscopic investigation of a 'Virgin of Sorrows' canvas painting: A multi-method approach*, In: *Analitica Chimica Acta*, 550 (1–2), 2005, p. 164-172.
- Reiche *et alii*, 2009
 Reiche, Ina; Röhars, Stefan; Solomon, Joseph; Kanngießler, Birgit; Höhn, Yvonne; Malzer, Wolfgang; Voigt, Friederike, *Development of a non-destructive method for underglaze painted tiles – demonstrated by the analysis of Persian objects from the nineteenth century*, In: *Analytical Bioanalytical Chemistry*, 2009, 393, p. 1025-1041.
- Robinet *et alii*, 2004
 Robinet, Laurianne; Eremin, Katherine; del Arco, Belen Cobo; Gibson, Lorraine T., *A Raman spectroscopic study of pollution-induced glass deterioration*, In: *Journal of Raman Spectroscopy* 35(8–9), 2004, p. 662-670.
- Schalm, Janssens, 2003
 Schalm, Olivier; Janssens, Karen, *Quantification procedures in micro X-ray fluorescence analysis*, In: *Spectrochimica Acta, Part B: Atomic Spectroscopy*, 58 (4), 2003, p. 669-680.

- Stoia *et alii*, 2010 Stoia, Marcela; Stefanescu, Mircea; Dippong, Thomas; Stefanescu, Oana; Barvinschi, Paul, *Influence of thermal treatment on the formation of zirconia nanostructured powder by thermal decomposition of different precursors*, In: *Journal of Sol-Gel Technology*, 54, 2010, p. 49-56.
- Van Espen *et alii*, 1987 Van Espen, Pierre; Janssens, Koen; Nobels, Jenny, *XIL-PC, software for the analysis of complex X-ray spectra*, In: *Chemo-metrics and Intelligent Laboratory Systems*, 1, 1987, p. 109-114.
- Vandenabeele *et alii*, 2000 Vandenabeele, Peter; Moens, Luc; Edwards, Howell G.M.; Richard, Dams, *A Raman Spectroscopic Database of Azopigments and application to Modern Art Studies*, In: *Journal of Raman Spectroscopy*, (31), 2000, p. 509-517.
- Vandenabeele *et alii*, 2000 Vandenabeele, Peter; Wehling, Bernhard; Moens, Luc; Edwards Howell; De Reu, Martine; Van Hooydonk, Guido, *Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art*, In: *Analitica Chimica Acta*, 407, 2000, p. 261-274.
- Vandenabeele *et alii*, 2001 Vandenabeele, Peter; Verpoort, Francis; Moens, Luc, *Non-destructive analysis of paintings using Fourier transforms Raman spectroscopy with fiber optics*, In: *Journal of Raman Spectroscopy*, 32(4), 2001, p. 263-269.
- Vandenabeele *et alii*, 2005 Vandenabeele, Peter; Lambert, Karel; Matthys, Sofie; Schudel, Walter; Bergmans, Anna; Moens, Luc, *In situ analysis of mediaeval wall paintings: a challenge for mobile Raman spectroscopy*, In: *Analytical Bioanalytical Chemistry*, 383 (4), 2005, p. 707-712.
- Velde, Hochuli-Gysel 1998 Velde, Bruce; Hochuli-Gysel, Anne, *Correlations between Antimony, Manganese and Iron content in Gallo-Roman glass*, In: *Annales du 13e Congrès Internationale pour l'Histoire de Verre, Pays-Bas 1995*, Amsterdam, 1996, p. 185-192.
- Visinescu *et alii*, 2010 Visinescu, Diana; Paraschiv, Carmen; Ianculescu, Adelina; Jurca, Bogdan; Vasile, Bogdan; Carp, Oana, *The environmentally benign synthesis of nanosized $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ blue pigments*, In: *Dyes and Pigments*, Vol. 87, Issue 2, October 2010, p. 125-131.