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

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Rezumat. Examinarea spectroscopică a operelor de artă este de mare importanţă pentru conservatori, istorici de artă şi colecţionari din muzee. Aceste investigaţii oferă informatii utile despre contextul istoric şi despre interacţiunile dintre diferite culturi şi rutele comerciale ce au contribuit la acestea. În ştiinţa 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 pigmenţi anorganici / organici, şi contribuie la identificarea cu uşurinţă a noilor pigmenţi sintetici obţinuţi din minerale extrase din sol, precum şi a liantului şi a lacurilor utilizate. Această metodă a fost deja utilizată pentru a investiga diverse artefacte din sticlă (zona Braşov şi zona Histria), iar rezultatele vor fi prezentate în această lucrare completate cu alte tehnici analitice necesare pentru a elucida structura şi componenţa artefactelor investigate: reflectanţa cu absorbţie difuză, spectroscopie în infraroşu cu transformată Fourier şi spectrometrie de fluorescenţă cu raze X cu dispersie după lungime de undă (WDXRF). Spectroscopia Raman este de asemenea utilizată pentru a identifica compoziţia, structura şi impactul factorilor de mediu asupra procedurilor de restaurare.

Cuvinte cheie: Raman, sticlă, artefacte, reflectanţa cu absorbţie difuză, WDXRF.

1. Introduction

In conservation science, the non-destructive techniques are extremely important. In this context, Raman spectroscopy is one of these echniques, which allows material identification from different artifacts, including panel paintings[1], glass[2], wall paintings[3], and manuscripts[4]. This technique is useful for understanding

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[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 inorganic[5] and organic pigments[6], as well as binding media and varnishes[7]. 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

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[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 mm^2 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 (Brașov 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, seashells[8] 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 Empire[9].

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 Elder[10].

In the Antique to the post-Roman period, glass was made with Natron as fluxing agent, a mixture of $NaHCO_3$, Na_2CO_3 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 (Na_2O>6% w/w);
- calco-potassic glass (K_2O+CaO > 22% w/w);
- lead glass (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 literature[12], 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 AD[13]. 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 less[14].

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. Brașov 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 Cr^{3+} ions[15]. 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 significant[16]. Brown glass absorption curves exhibit a maxima spreading from about 350 nm to about 450 nm with long tales in the visible region of the absorption spectra, while the maxima for the dark brown curves is clearly located in the UV.

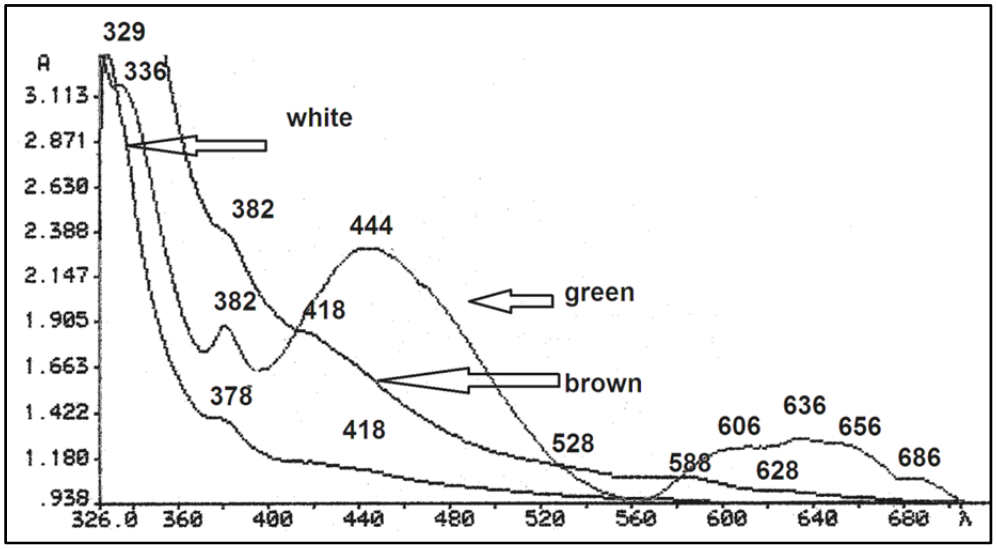


Fig. 2. The UV-Vis DR spectra of glass samples.

Sample color	Brown	Green	White
Na_2O	3	5.2	5.4
MgO	0.8	1.6	1.6
Al_2O_3	3.8	6	3.5
SiO_2	69.4	72.3	59.1
P_2O_5	9.12	0.56	0.93
SO_3	1	0.71	0.2
Cl	1.73	1.95	2.7
K_2O	2.15	0.47	10.5
CaO	7.37	10.4	12.8
MnO	1	0.028	0.563
Fe_2O_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 glasses[17].

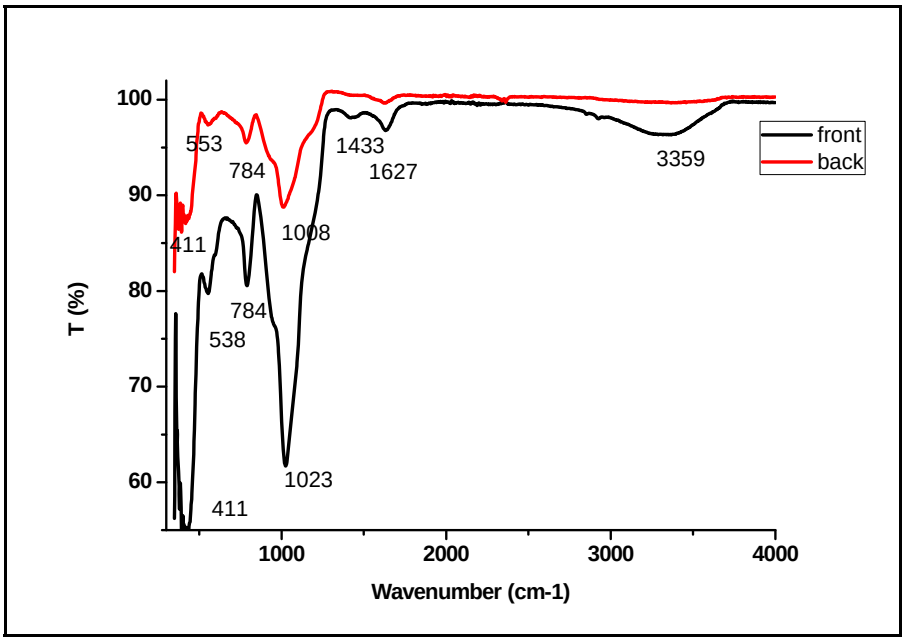
Cu, homogeneously added to white glass, can produce a pale green color. The glass body contains several elements such as Pb, Si, Al, Na, Fe for yellow, Cu for dark green and Co for dark blue colors. The presence of the elements K, Ca and S indicates the formation of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot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

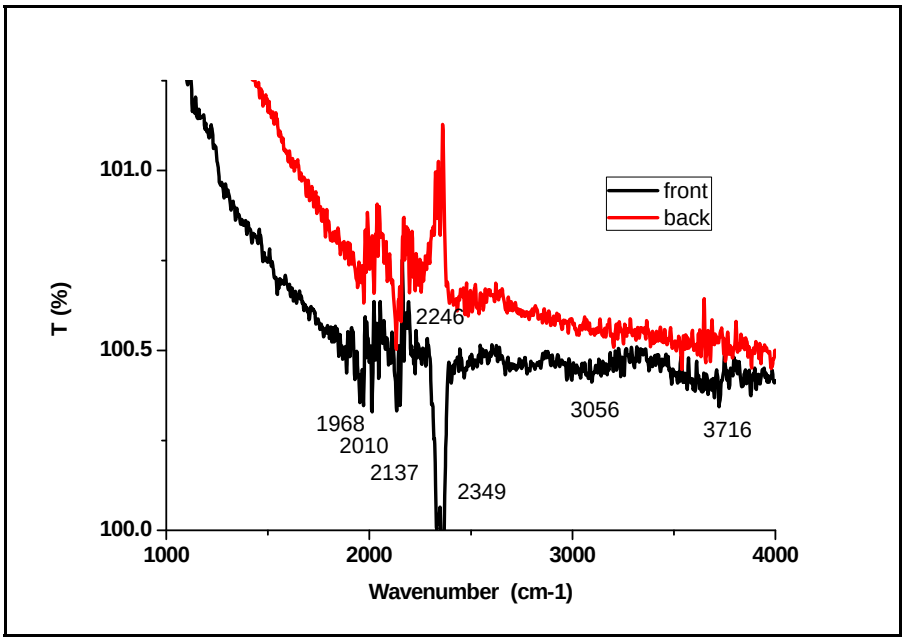
All FTIR spectra are dominated by the aluminosilicate network absorption bands at 1057, 797–781 and 465 cm^{-1}, which are characteristic of silica rich matrix: Si–O–Si antisymmetric stretching band, Si–O symmetric stretching and Si–O rocking motion, respectively[18]. Also, the 1650cm^{-1} (H–O–H) and 3400–3500cm^{-1} (–OH) are present in all pastes (Fig. 3). The characteristic absorptions of calcium carbonate ($CaCO_3$) is observed[19] 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 ~500 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 documented[20].

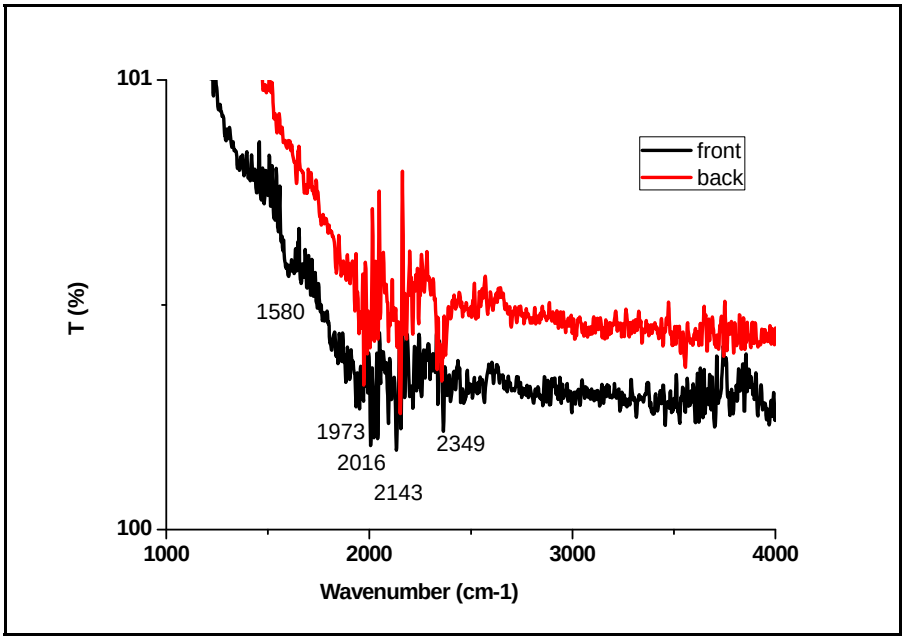


Brown

[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.

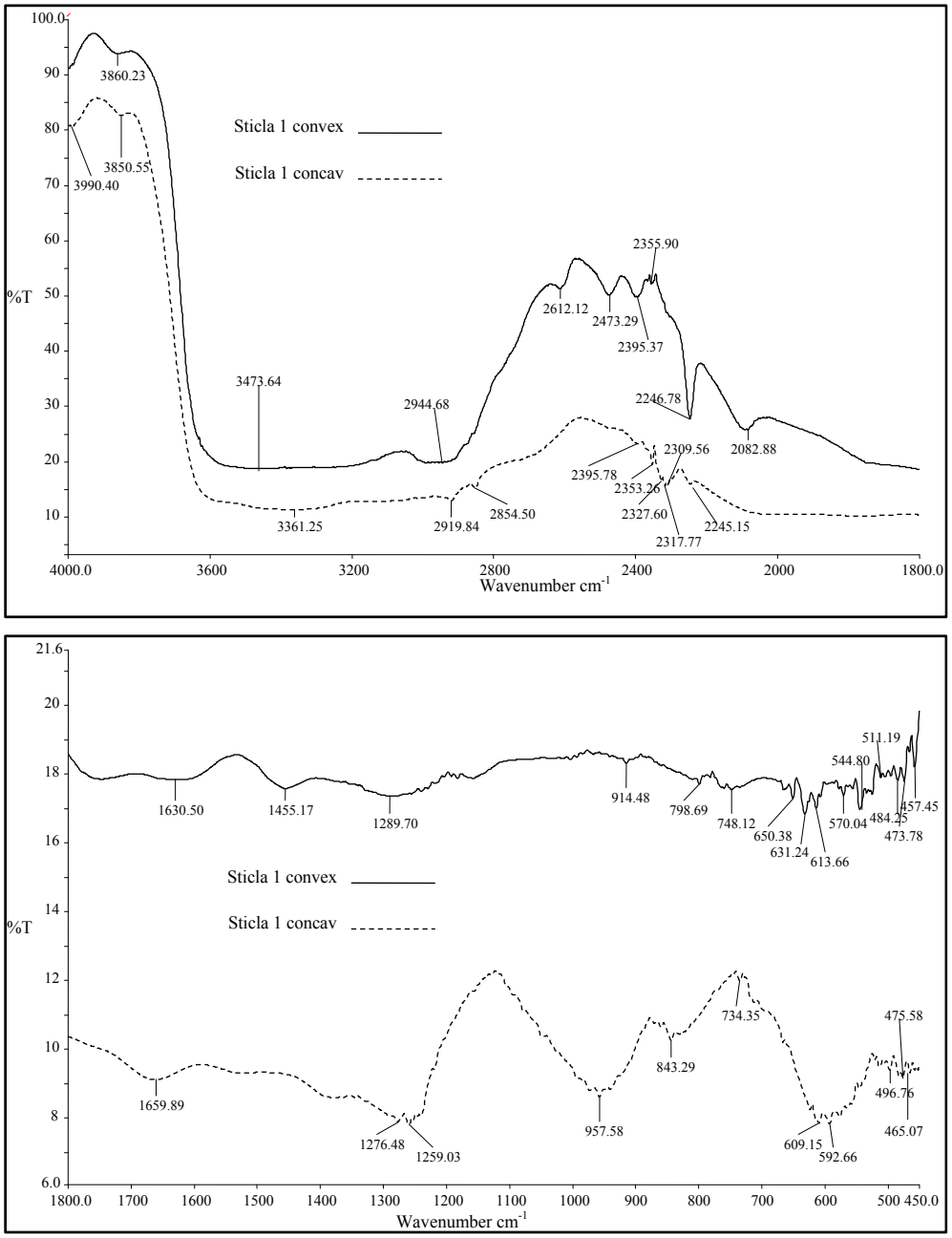
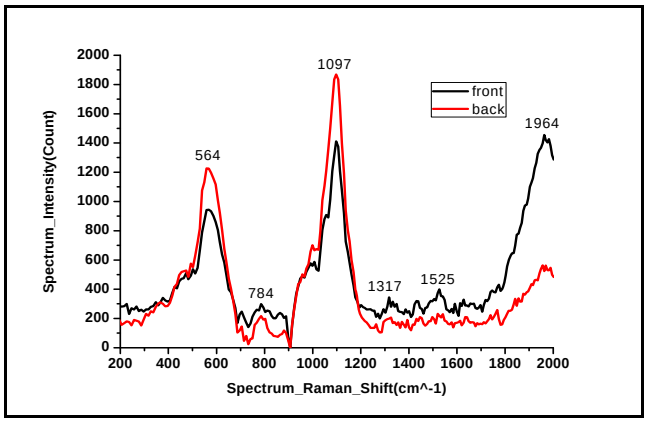
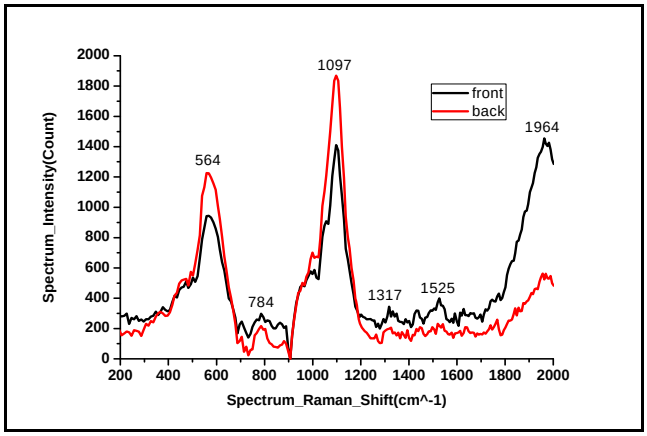


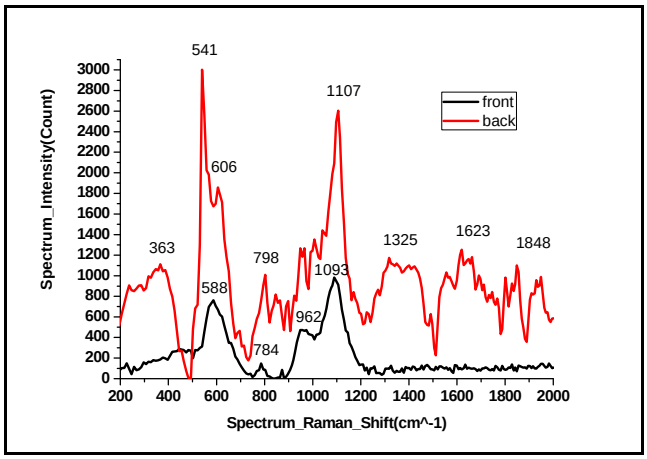
Fig. 4. The differences of FTIR spectra for one side and side-reverse of a glass sample.



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. Histria glass artifacts

In Europe, numerous investigations of the 17th and 18th century glasshouses and glass waste have been achieved[21]. 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[22].

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 contains 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 (potasium carbonate)(potash), two common ingredients like potassium tartrate ($HOOC\text{-}CHOH\text{-}CHOH\text{-}COO^-K^+$), Salpetre ($KNO_3$), sea salt (NaCl) and borax ($Na_2B_4O_7.10H_2O$) 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 sevententh century[24]. The presence of German glass makers from the centre of Europe in the Transylvanian manufacturies could explains the types of models and techniques from the Transylvanian manufacturies.

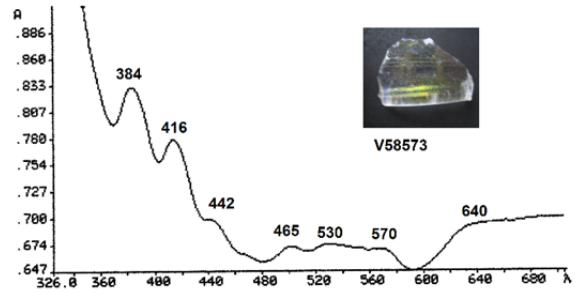
Cu, homogeneously added to white glass can produce a pale green color. The glass body contains several elements such as Pb, Si, Al, Na, Fe for yellow, Cu

[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.



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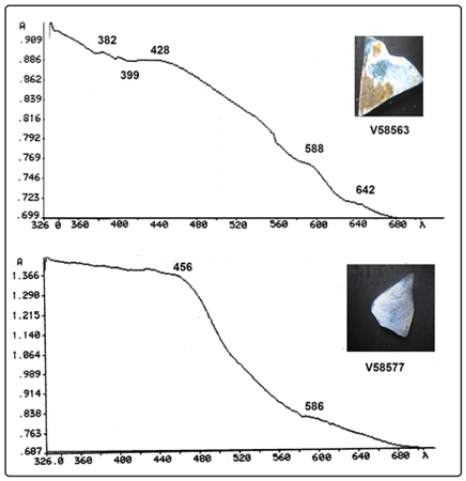
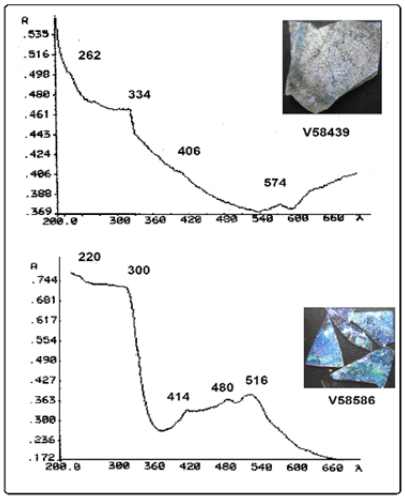


6b



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 compozition, structure and impacts of environmental factors used in the restoration.

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