ANALYSIS OF AUTOMOTIVE GLASS OF VARIOUS BRANDS USING EDXRF SPECTROMETRY*

NIKOLLA CIVICI1, ESMERALDA VATAJ2

1 University of Tirana, Centre of Applied Nuclear Physics, Faculty of Natural Sciences, P.O.Box 85, Tirana, Albania, E-mail: nikocivici@yahoo.com.
2 University of Tirana, Faculty of Natural Sciences, Department of Physics, Tirana, Albania, E-mail: evataj@yahoo.com.

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Abstract. An analytical procedure based on EDXRF spectrometry was used for the elemental analysis of automotive glass samples. Using different excitation modes we could measure about 15 low- and medium-Z elements in each sample. The obtained results allowed us to conclude that the investigated car glasses were produced by the method of float glass from rather pure raw materials, and belong to the type silica-soda-lime glass. The relationship between the concentration of some elements (Fe, Zr) and different features of glasses (color and transparency) are discussed.

Key words: automotive glass, spectrum, quantitative analysis, energy dispersive X-ray fluorescence.

1. INTRODUCTION

Glass is an amorphous solid material, optically transparent and brittle. The most common material used for the production of glass is silica (SiO₂). Various additives such as sodium carbonate (soda), lime and various oxides are used to produce more durable glass known as soda-lime glass, the most dominant industry glass produced.

During the early 20th century, horseless carriages started using glass to protect drivers from harsh winds. In 1903, French chemist Edouard Benedictus stumbled upon the secret to shatter-resistant glass when he dropped a glass flask filled with a dried collodion film. He found that the glass coated with the film cracked, but kept its original shape. However, this laminated glass wouldn't be implemented in automobiles until the 1920s [2, 3]. In addition to laminated glass, automakers began to use tempered glass in the late 1930s. This type of glass is used in the vehicle's side and back windows [4].

The glass can now be further processed in one of two ways:
– as single-pane toughened safety glass (TSG) or
– as laminated safety glass (LSG) which is primarily used for automotive windshield.

Today's laminated glass consists of a thin layer of polyvinyl butyral (PVB) inserted between two layers of solid glass [2].

Manufacturing companies of car winder use the commercialized float glass method, where sheets of glass are produced or “floated” on molten metals such as tin and lead.

Typical approximate composition of automotive windshield: 72% SiO2 as vitrifier14% Na2O as flux, 10% CaO as stabilizer and 4% MgO as stabilizer [5, 6].

The study in terms of chemical composition of glass objects, which provides information for the raw materials used for its production, is important not only in the areas of production and its usage but also in other areas such as criminology, cultural heritage, etc., in which knowledge of the chemical composition of glass may provide useful information for the solving problems.

Energy dispersive X-ray fluorescence (EDXRF) spectrometry was used in our study for the elemental analysis of glass samples. This non-destructive technique is capable of quantifying chemical elements from Na to U, within the concentration range from parts per million to percentages. EDXRF is also a multielemental technique which allows the relatively fast analysis of samples.

In this work, we will try to describe the analytical procedure for the non-destructive analysis of glass samples using EDXRF and to present some data obtained from the analysis of small group of car glass samples. This is our first attempt to create a data base for the elemental composition of automotive glass samples of various brands.

2. MATERIAL AND METHODS

28 pieces from different car glass producers and belonging to different car brands were collected in a car glass servicing company. Samples were taken from the front windshield of the car, which is made of two glass sheets kept together by a thin layer of plastic glue.

The samples were cut according to the size of the irradiation window of the EDXRF system, cleaned, dried and measured by both sides. Generally, when viewed from the cross section, one of the glass sheets has a darker greenish tint (side 2).
2.1. ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) SYSTEM

The samples were measured in secondary target excitation EDXRF system, using Cu and Mo secondary targets for excitation of low- and medium-Z elements, respectively.

The system consists of a Philips 1729 X-ray generator equipped with a Mo anode x-ray tube, a 30 mm² Princeton Gamma Tech (PGT) Si(Li) detector, a Canberra Model 2024 Fast Spectroscopy Amplifier, a Canberra Model 8706 Fast ADC and a PC-based Canberra S-100 multichannel analyzer.

The low Z elements were excited in vacuum using the K radiation of Cu secondary target while the other elements were excited in air by Mo secondary target. The x-ray generator was operated at 20 kV for Cu target and at 35 kV for Mo target. The samples were measured for 1000–2000 s. The intensities of the analytical lines were calculated by fitting the spectra with the program Axil [1]. The program Corex [8], which uses fundamental parameters and backscattered peaks from the measurements, was used for the calculation of the concentrations.

In these conditions we could detect more than 15 elements in each of the glass samples.

Calculated values of detection limits that vary from about 1% for Na to a few mg/kg for Sr and Zr, meet the requirements for almost all elements. The precision and accuracy of the results were tested with reference standard materials [9]. More detailed information on the procedure and analytical parameters can be found in [7].

Additional measurements were carried out on micro-XRF system (ARTAX, Bruker). The spectrometer was equipped with 3W air cooled Rhodium X-ray tube, a polycapillary lens that focuses the radiation spot at 60 µm and a SDD (silicon drift detector) with resolution of 145 eV for Mn Kα.

3. RESULTS AND DISCUSSION

Elemental concentrations obtained from the analysis of automotive glass samples are presented in Tables 4 and 5.
3.1. MAJOR ELEMENTS

Main components of the analyzed glass samples are SiO$_2$ (74–86.8%), Na$_2$O (4–11.8%) and CaO (6–8.5%), which characterizes all of them as silica-soda-lime glasses. The variation of SiO$_2$, Na$_2$O and CaO concentrations should be related with the different technologies and raw materials used for their production. In Fig. 2 is presented the tertiary plot built with the analytical data of these three components.

The concentrations of the other major elements are presented in Table 1.

It is observed that generally their concentration is quite low indicating that the production is carried out from clean raw materials which mean that impurities have been within the technological requirements.

![Tertiary plot of three main components.](image)

The measurements indicate that there is no difference in the composition, as regards most of the major elements, between the two different glass sheets (sides) of one sample. In Table 2 are presented the average concentrations of major elements measured on both sides of the whole group of samples.

### Table 1

Variation of the content of some elements

<table>
<thead>
<tr>
<th>Al$_2$O$_3$ (%)</th>
<th>MgO (%)</th>
<th>K$_2$O (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>TiO$_2$ (%)</th>
<th>MnO (%)</th>
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<tbody>
<tr>
<td>0.00–2.77</td>
<td>0.00–4.71</td>
<td>0.00–0.80</td>
<td>0.064–0.890</td>
<td>0.011–0.115</td>
<td>0.001–0.022</td>
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</table>

The measurements indicate that there is no difference in the composition, as regards most of the major elements, between the two different glass sheets (sides) of one sample. In Table 2 are presented the average concentrations of major elements measured on both sides of the whole group of samples.
Table 2

Average concentration of major elements on both sides, whole group of samples

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<thead>
<tr>
<th></th>
<th>Na₂O (%)</th>
<th>MgO (%)</th>
<th>Al₂O₃ (%)</th>
<th>SiO₂ (%)</th>
<th>K₂O (%)</th>
<th>CaO (%)</th>
<th>TiO₂ (%)</th>
<th>MnO (%)</th>
<th>Fe₂O₃ (%)</th>
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<td>7.72</td>
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</table>

The only element whose concentration shows significant difference on the different sides of one sample is iron and this should be related with the observed differences in tint of the different glass sheets. Looking more closely at the obtained data for iron we observe that it is distributed in three almost distinct different levels (Fig. 3). A big group, mostly side 1 of the samples, have an almost constant concentration around 0.1%. The other big group, mostly side 2 with darker greenish tint, have iron concentration in the range 0.5–0.6% and a few “side 2” samples have higher concentrations in the range 0.7–0.8%. The colour differences are reflected in the differences of Fe concentrations (Fig. 3).

![Fig. 3](image)

Fig. 3 – The variation of the concentration of Fe₂O₃ from the concentration of CaO on different sides of the car Windows.

3.2. THE PRESENCE OF TIN

Tin was detected frequently on the surface of glass samples. Measurements on both sides of glasses (Fig. 4) and a scan over the cross section of glass performed with the micro XRF system (Fig. 5) showed that Sn is a surface contamination due to the manufacturing process. As we have mentioned above, flat glass used in car glasses are produced using the float glass process, where molten glass is cooled floating on molten metals such as tin [5, 6].
3.3. MINOR ELEMENTS

Minor elements coming from the raw materials or being added to affect certain characteristics of glass could be easily analyzed by EDXRF. In Table 3 are presented the average concentrations of minor elements measured on both sides of the whole group of samples.

In Fig. 6 is presented the variation of Zr to Sr in all the analyzed samples. Most of the samples fall in two main patterns with different Sr concentration but in one sample (Saint-Gobain Sekurit E1, side 2) we observe a significant change in the concentration of Sr and Zr. Usually the addition of Zr in the glass is used to make it opaque [10].
4. CONCLUSIONS

The EDXRF was found to be a powerful tool for the analysis of automotive glass samples, without any special sample preparation or surface treatment.

The results obtained by EDXRF analysis for automotive glass samples allowed us to conclude that the investigated car glasses belong to the types produced with silica-soda-lime and from rather pure raw materials. There was observed no compositional difference between the two sheets that make up the car glass windshield except the iron concentration that is related with the different color tint. The observed presence of tin on the surface confirms that the automotive glasses are produced by the method of float glass. The relationship between the concentration of some elements (Fe, Zr) and different features (color and transparency) are discussed.

Table 4

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<tr>
<th>Brands</th>
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<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
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