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IBA of iridescent Art Nouveau glass – comparative studies

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Abstract

Simultaneous PIXE, PIGE, and RBS in air were employed to characterise the surface structure of iridescent Art Nouveau glass artefacts produced around 1900 by Tiffany, USA and Loetz, Austria. Using PIXE and PIGE, the chemical composition of the bulk glass and the overlays was determined in a non-destructive manner. Furthermore, the combination of PIXE and RBS enabled the layer structure of the analysed glasses (bulk, overlays, and iridescent layers) and the thicknesses of the thin layers in the near-surface domain to be determined. The measurement and evaluation procedure is demonstrated on blue iridescent glass fragments of Tiffany and Loetz by way of example. The initial results showing similarities but also differences in the layered glass structure of Tiffany and Loetz objects are presented.

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1. Introduction

Among many manufacturers that have produced iridescent Art Nouveau artefacts around 1900, Tiffany (USA) and Loetz (Austria) are the most famous. The development of their glass technology resulted in the highest quality glass objects and brilliant iridescent effects which can be found on the surfaces of such artefacts (vases, lamps, bowls etc., showing irregular forms and shapes). As already reported [1] the surface iridescence found on the artefacts of the Art Nouveau period was achieved artificially (in contrast to similar optical effects found on naturally weathered glasses). For that purpose, the hot glass surface was sprayed with an alcoholic solution of stannous chloride or with mixtures of various metallic salts and then reheated in an oven in a reducing

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atmosphere [2]. During this process the hot chlorine fumes etch the glass and consequently a very thin layer of SnO_2 is formed on its surface.

Scientific investigations have been carried out with energy dispersive X-ray microanalysis in a scanning electron microscope (SEM/EDX) [3] on a few selected glass cross-sections (glass samples embedded in resin and sectioned perpendicular to their iridescent surfaces). Even at magnifications as high as 20 000× the thin Sn-containing layer on the surface could not be characterised due to its low thickness. In this study therefore, ion beam analysis (IBA) with an external proton beam was applied using particle-induced X-ray emission (PIXE), particle-induced γ-ray emission (PIGE), and Rutherford backscattering spectrometry (RBS). The great advantage of the external proton beam is the possibility to perform non-destructive measurements on glass art objects in air. Further, the simultaneous combination of the three analytical techniques allows a complete characterisation of the glass layers (their chemical composition and their thicknesses), as well as the thin Sn-containing outermost layer.

Test results of the analytical procedure when applied to original glass fragments of Tiffany and Loetz are reported. The intention was to demonstrate the performance of IBA in ascertaining both the chemical composition and the structure of a glass artefact in order to classify different glass technologies.

2. Experimental

The analytical investigations were carried out with the external ion beam of the 5 MV Tandem accelerator in Rossendorf, Germany. Protons of 3.85 MeV energy were used for the measurements. Non-destructive analysis of blue iridescent glass fragments was ensured using a beam current of only 0.5 nA with a 1.8 mm^2 spot size and an acquisition time of 500 s per spot. A detailed description of the measuring conditions and the Rossendorf set-up was already given in [4,5]. The feature of interest is the combination of the three ion beam techniques PIXE, PIGE and RBS simultaneously in a single measurement.

The measurements were performed on original glass fragments of Tiffany and Loetz. The basic colour of the fragments analysed is blue and they are characterised by only slight curvatures of the surfaces. Such a shape offers the possibility to analyse and compare both the iridescent (front) and the non-iridescent (rear) side of the glass. For those glasses also showing minor iridescence on the rear side, additional analysis was carried out on the fracture surface.

The surfaces of Tiffany glasses evaluated so far show iridescence without any additional patterns, whereas the surfaces of Loetz glasses in some cases show the so-called Papillon (butterfly) patterns. This special optical effect was already investigated and described elsewhere [1]. In this work only the results for un-patterned surfaces are presented and compared.

The combined evaluation of PIGE and PIXE spectra allows a complete characterisation of the glass composition. As shown in Fig. 1, PIGE detects the light elements with $Z < 15$, e.g. boron, sodium, aluminium, and silicon. Concentrations of these glass constituents can be calculated using reference materials. Concentrations of chemical elements heavier than aluminium are given by PIXE using the GUPIX software package [6].

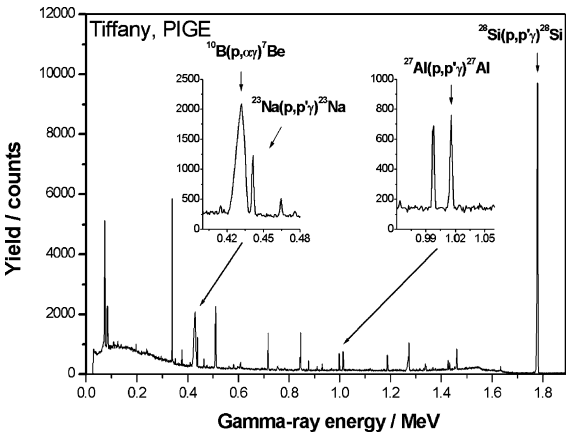

Fig. 1. PIGE spectrum of Tiffany glass T10 taken from the rear side (bulk material). The insets show parts of the spectrum enlarged. The elements B, Na, and Al can be clearly identified as glass components.