



An experimental approach to manufacturing technology of historical glass (XIII-XV centuries). Comparison with current glassmaking technology.

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One of the major and less explored issues in the characterization of historical glasses is the determination of their viscosity as a function of temperature in order to constrain technological aspects of glass production. Until now, assumptions on temperatures have been based on mathematical models based on chemical compositions. Hence, the topic of this work is to explore the technology of stained glass production related to the workability and melting process of the glass by experimental laboratory measurements.

This work presents the analysis of viscosity of glasses from different historical sites and chemical compositions: four from Santes Creus (Tarragona, XIII century), two of classical medieval stained glass window from Santa Maria de Pedralbes (Barcelona, mid XIV century), and three of evolved late-medieval type from Santa Maria del Mar (Barcelona first half of XV century), and one sample of soda-lime industrial glass by means of Hot-Stage Microscopy and glass transformation temperature T_g by dilatometry. These data are then compared to the predictions on theoretical viscosity obtained from mathematical models based on chemical composition.

These samples are classified according to their major modifier in: Na-rich (12-17% of Na_2O , between 65-77% of SiO_2 and less than 3 % of K_2O); Ca-rich (29% of CaO , 54% of SiO_2 , 4% of K_2O , and 4% of Na_2O); K-Ca-rich (17 to 21% of K_2O , more than 14% of CaO , 49-55% of SiO_2 and less than 2% of Na_2O); Na-Ca-rich (12-14% of Na_2O , 9-15% of CaO , 57-71% of SiO_2 and < 6% of K_2O).

Glass transition temperature (T_g) is correlated to chemical composition: 464-492 °C for Na-rich, 645 °C for Ca-rich, 582-586 °C for K-Ca-rich and 497-542 °C for Na-Ca-rich glasses.

Experimental viscosity-temperature curves are traced using T_g and fixed viscosity points measured by Hot-Stage microscopy (according to German standard 51730) in order to provide more accurate insight into the phases of glass production process (melting, working, conditioning and annealing ranges). These results are also compared to mathematical models of glass viscosity based on chemical composition.

The annealing range (viscosity between $10^{13.5}$ and 10^{12} Pa·s) is reached at temperatures between 484-633°C (strain point) and 509-664°C (upper limit). The working point (viscosity of 10^3 Pa·s) has temperature values in the range between 958 and 1097°C.