B73 An Assessment of Elemental Homogeneity in Glass Using Micro-X-Ray Fluorescence Spectroscopy (µ-XRF) and Laser-Induced Breakdown Spectroscopy (LIBS)

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Learning Overview: After attending this presentation, attendees will have a better understanding of elemental homogeneity within a glass source and insight on the capabilities of XRF and LIBS for the forensic analysis of glass.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by comparing modern instrumentation (Silicon Drift Detectors [SDD] -XRF and LIBS) to traditional instrumentation currently utilized in forensic laboratories.

Glass is an important type of forensic trace evidence that can be encountered at various crime scenes, such as hit-and-runs, homicides, and burglaries. The elemental analysis of glass is useful for the discrimination of glass samples originating from different sources and for the association of glass samples originating from the same source. µ-XRF is the most commonly used technique for the elemental analysis of glass in forensic casework. The elemental compositions of the known and questioned samples are compared using a match criterion (range overlap or ±3σ) outlined in the standard method American Society for Testing and Materials (ASTM) E2926. However, the match criteria recommended in ASTM E2926 were selected based on error rates obtained for the analysis of glass samples using older instrumentation equipped with Si(Li) detectors. Modern XRF instruments equipped with SDDs are expected to provide better precision, which may increase the risk of false exclusions. Therefore, this study aims to assess the micro-homogeneity of glass using newer instrumentation to establish an appropriate pairwise comparison criterion that minimizes false exclusion rates.

An alternative to µ-XRF is Laser-Induced Breakdown Spectroscopy (LIBS), a relatively new analytical technique. Its rapid analysis times and relative affordability make it an attractive option for the elemental analysis of glass. To date, no studies on micro-homogeneity of glass using LIBS have been published, and no standard method for the analysis of glass using LIBS is available. Thus, a secondary aim of this study is to assess sources of variability when using LIBS for glass analysis and establish an appropriate comparison criterion.

The reference glass material National Institute of Standards and Technology (NIST) 1831 was used to compare the analytical performance of µ-XRF and LIBS in terms of limits of detection, limits of quantitation, inter-day variability, and intra-day variability. The performance of the µ-XRF-SDD system used in this study was also compared to µ-XRF-SiLi detectors' data reported in the ASTM method. A vehicle windshield was used to assess the variability of the elemental composition within a single pane. Each of the inner and outer glass panes was divided into 100 sections. Then, a random number generator was used to select 50 sections within each pane randomly. The glass pane was then broken, and 50 glass fragments were collected from both the inner and outer pane of a single windshield and analyzed using µ-XRF and LIBS. Each fragment was measured in replicates from different locations (*LIBS n*=4, *µ-XRF n*=5).

The µ-XRF method detected nine elements above the quantitation limit for both windshields (Sodium [Na], Magnesium [Mg], Silicon [Si], Calcium [Ca], Titanium [Ti], Manganese [Mn], Iron [Fe], Strontium [Sr], and Zirconium [Zr]), which were further used for comparison between fragments. The false exclusion rates using the ASTM E2926 match criteria was >45% for the inner pane and >50% for the outer pane. Using a modified match criterion (±3σ, with a minimum σ equal to 3% of the mean), the false exclusion rates were reduced to 11% and 7% for the inner and outer pane, respectively. The LIBS method detected eight elements in the windshields' glass fragments (Aluminum [Al], Barium [Ba], Ca, Potassium [K], Mg, Na, Si, and Sr) with precision ranging between 1%–15%, depending on the element, emission line, and concentration. The LIBS intra-day variability and inter-day variability was inferior to µ-XRF but were reduced by estimating Signal to Noise Ratios ([SNR], signal to background near the peak) for each analyte of interest and then using ratios of SNRs to other elements or emission lines. The overall distribution of elemental composition within each glass pane was observed via heatmaps, box-plots, and Analysis of Variance (ANOVA). For pairwise comparisons, different criteria, including range overlap, ±3σ, ±4σ was evaluated using three randomly selected fragments as the known sample and compared to one fragment as the questioned item. False exclusion rates were improved from 60% to 8% depending on the comparison criterion applied, the number of replicate measurements, the number of fragments used for comparison, and the data pre-processing methods.

Glass, Forensic Science, Elemental