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Validation of Novel Statistical Approaches for the Interpretation of Trace Evidence; Glass Analysis using LA-ICP-MS

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Project Abstract:

Glass is ubiquitous in our surroundings and lends itself as a common piece of evidence that can be recovered from crime scenes. Analysis and comparison of glass evidence can provide useful information to aid an investigation that leads to identifying a suspect and can also provide strong associations between the suspect and a crime event. This research aims to improve the interpretation of glass evidence using statistical analysis of collections of glass that have been analyzed by a standard method of analysis (ASTM-E2927) and other databases of glass casework that produced elemental data using the LA-ICP-MS ASTM method. Corning Inc. designed and manufactured three (3) new float glass standards (CFGS1, CFGS2 and CFGS3) and these glasses were characterized by eight (8) different laboratories for quantitative analysis using the ASTM E2927 LA-ICP-MS method. The glass was transferred to NIST for the certification of the elemental composition of these glass samples for future distribution to glass examiners for use as much-needed calibration standards in the analysis of glass. This research also continues to evaluate the collective knowledge derived from previously acquired glass datasets, surveys and databases. A newly created vehicle windshield glass database representing the LA-ICP-MS analysis of more than 900 glass samples was generated and the raw data is now freely available to the public on the FIU Library website. The new vehicle glass database was used as a background database to calculate the likelihood ratio (LR) for windshield glass comparisons and a 380-sample casework database donated by the BKA in Germany was used to calculate LRs for comparisons from additional glass sources. Several other databases from the FBI laboratory, the Health Sciences Authority in Singapore, the LKA laboratory in Germany and the NFI laboratory in The Netherlands were also used as background databases to calculate LRs. The results of this work suggests that an approach that incorporates the reporting of a LR that assigns a significance to an association provides additional information to both the forensic science community and to the general public tasked with assessing the significance of glass comparison evidence.

Project Description:

The first project aim of this effort is to manufacture three (3) new standards (CFGS1, CFGS2 and CFGS3) for use in forensic glass examination and comparison with the assistance of Corning and NIST scientists who will assist in the certification and distribution of the three glass standards to the forensic community at a minimal handling cost. The composition of each of the three glass materials is informed by 1) a successful application of the original BKA FGS1 and FGS2 and 2) data analysis of a large vehicle glass database collected during the first 2 years of the GIWG as well as data analysis of the BKA casework database. To assess the concentration range of each element in the FIU vehicle database, a box and whisker plot was produced (Figure 1a). The log_{10} of the concentration was used so that all elements could be plotted on the same scale. Figure 1a below shows the elemental distribution for the FIU vehicle glass database consisting of 420 glass samples, all collected from vehicles in a salvage yard in Ruckersville, Virginia with manufacturing dates between 2004-2017. The samples were analyzed at the Florida International University (FIU) laboratory using the methods recommended in ASTM E2927-16e1 measuring 15 replicates for each sample. This database represents a limited snapshot of the population of windshield glass for vehicles circulating in the US but can, nevertheless, be used to provide insight on the probability of a random match for glass originating from two different vehicles or to calculate a likelihood ratio based on this background dataset.

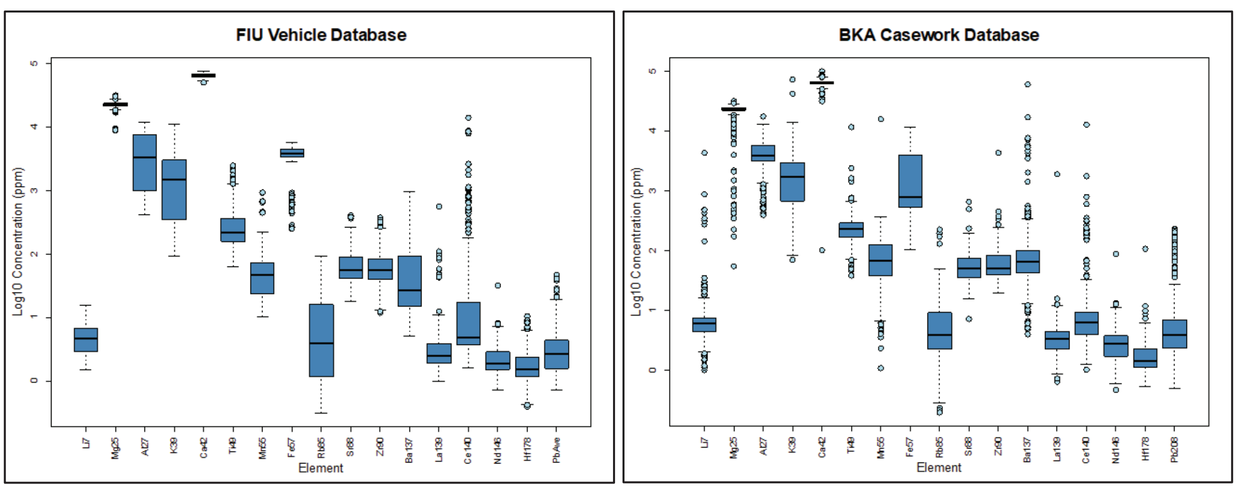

Figure 1 – a) (left) Box-and-whisker plot for the concentration range for the 420 vehicle database samples. b) (right) Box-and-whisker plot for range of the 370 BKA casework samples.

The BKA database consisted of 370 casework samples, with 6 replicate measurements per sample (Figure 1b). The database includes an assortment of glass types: float glass (vehicle and architectural), container glass, light bulbs, TV tubes and other specialty glasses. The BKA laboratory employs a close variation of the E2927-16e1 to analyze the following 18 elements: ^{7}Li, ^{23}Na, ^{25}Mg, ^{27}Al, ^{39}K, ^{42}Ca, ^{49}Ti, ^{55}Mn, ^{57}Fe, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{137}Ba, ^{139}La, ^{140}Ce, ^{146}Nd, ^{178}Hf, and ^{208}Pb. It can be argued that this database is an appropriate database to consider for general casework glass comparisons because it represents glass samples that have come to the attention of glass examiners in the course of forensic examinations and therefore is representative of glass that forensic scientists may encounter, at least in Germany and more generally. A closer examination of the distribution of the concentration ranges for the entire element menu list (recommended by ASTM E2927-16e1) reveals that while the original FGS1 and FGS2 cover a substantial range of the concentrations for the elements of interest, a third (CFGS3) is needed to account for many samples that exceed the upper concentrations in FGS2. In addition, the CFGS3 will facilitate the incorporation of a 3-point calibration curve in addition (for those researchers wanting to explore this option) to the single point calibration curve currently recommended in ASTM 2927e1. Table 1 below shows the current concentrations for the original FGS1 and FGS2 (now continued as CFGS1 and CFGS2 for this work) and also shows the suggested concentrations for the elements for a third glass reference material, CFGS3. The concentrations for the only existing float glass SRM (NIST 1831) is also listed on Table 1.

In addition to the element list on Table 1, the following elements were added to the element menu for CFGS1, CFGS2 and CFGS3: B and S (only in FGS3) and Sb, Ni, Cu, Co, Mo, Y, W, Th, U (in a range of concentrations) across all CFGS1, CFGS2 and CFGS3 glass sample.

Figure 2 and 3 shows the distribution for the Netherlands Forensics Institute (NFI) database (courtesy of the NFI).

	CFGS1	CFGS2	NIST1831	CFGS3	FIU Vehicle Minimum value	FIU Vehicle Maximum value
Al	1500	7400	**6380**	12000	419	11988
Ca	60600	59300	**58605**	75000	50242	75415
Fe	580	2600	**608**	6000	249	5750
K	920	4600	**2739**	10000	92	10956
Mg	23900	23400	**21172**	30500	8764	31643
Na	102800	100500	**98816**	100000	N/A	N/A
Sr	57	253	**85**	400	18	408
Ti	69	326	**114**	25000	63	2476
Li	6	29	**5**	1	2	16
Ba	40	199	**31.5**	1000	5	958
Mn	43	221	**13.3**	900	10	934
Rb	8.6	35	**6**	100	1	93
Zr	49	223	**37**	400	12	378

Table 1. Concentration ranges in mg/kg (ppm) for the existing FGS1, FGS2 and NIST SRM1831 glass reference materials and the proposed concentration for CFGS3 future SRM. The minimum and maximum concentration values for the 420 FIU Vehicle glass samples is also shown.

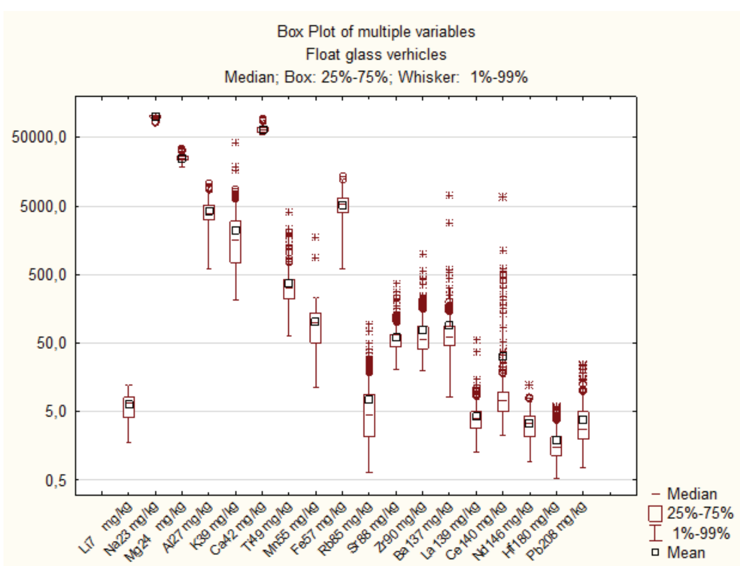

Figure 2 –Box-and-whisker plot for the concentration range for vehicle database samples at the NFI.

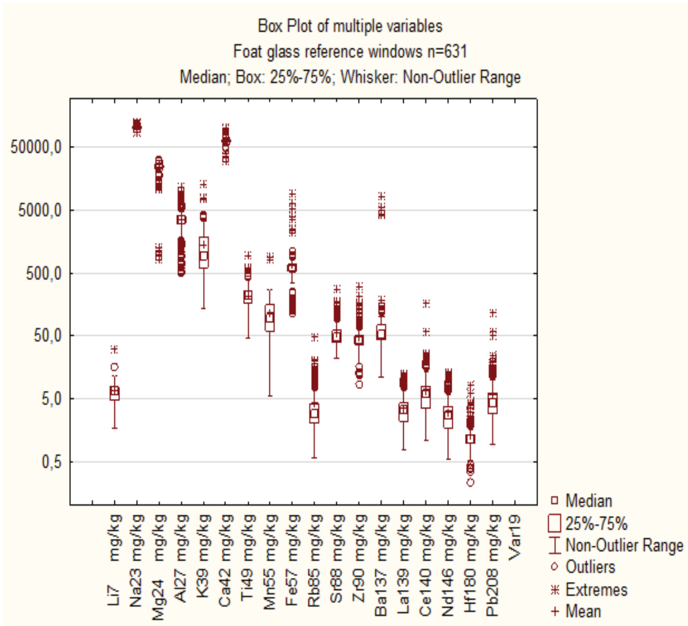

Figure 3 –Box-and-whisker plot for the concentration range for all (N=631) float glass reference windows from the NFI (courtesy of the NFI).

Results and Discussion:

The first major goal of the proposed effort was to manufacture three (3) new standards (CFGS1, CFGS2 and CFGS3) for use in forensic glass examination and comparison with the assistance of Corning scientists. These glasses were transferred to NIST scientists who will assist in the certification and distribution of the three glass standards to the forensic science community and other scientists that need glass standards, at a minimal handling cost. The second major goal was to continue to expand on the vehicle database from the current 420 samples to up to 900 vehicle glass samples of authentic (known) origin by collecting samples at a salvage yard. The third major goal is to continue the work of the Glass Interpretation Working Group (GIWG) to provide the scientific foundations for generating consensus, objective and quantitative language that can be applied to describe the significance of a glass elemental profile match for commonly encountered glass case scenarios using a series of 2 inter-laboratory exercises.

The research resulted in eight (8) publications, one manuscript submitted and one additional manuscript in preparation that is expected to be submitted to *Forensic Science International (FSI)* before the end of 2022.

The following publications describe the results of the three efforts in detail:

1. A Akmeemana, P Weis, R Corzo, D Ramos, P Zoon, T Trejos, T Ernst, E Pollock, E Bakowska, C Neumann, **JR Almirall**, Interpretation of Chemical Data from Glass Analysis for Forensic Purposes, *J. of Chemometrics,* **2020**, e3267. https://doi.org/10.1002/cem.3267
2. A Gupta, R Corzo, A Akmeemana, K Lambert, K Jimenez, JM Curran, **JR Almirall**, Dimensionality reduction of multielement glass evidence to calculate likelihood ratios, *J. of Chemometrics,* **2020**, DOI: 10.1002/cem.3298.
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6. C Martinez-Lopez, O Ovide, R Corzo, Z Andrews, JR Almirall, **T Trejos**, Homogeneity assessment of the elemental composition of windshield glass by LA-ICP-MS, LIBS and μ-XRF analysis, 27, **2022,** *For. Chem.,* 100384. https://doi.org/10.1016/j.forc.2021.100384
7. K Lambert, S Montero, A Akmeemana, R Corzo, G Gordon, E Haase, P Jiang, O Ovide, K Prasch, K Redman, T Scholz, T Trejos, J Webb, P Weis, W Wiarda, S Wilczek, H Xie, P Zoon and **JR Almirall,** An Interlaboratory Study to Evaluate the Forensic Analysis and Interpretation of Glass Evidence, 27, **2022,** *For. Chem.,* 100378., https://doi.org/10.1016/j.forc.2021.100378
8. A Akmeemana, R Corzo, and **JR Almirall,** Calculation and Comparison of Likelihood Ratios in Forensic Glass Comparisons Using an R Code and Shiny App Applied to Existing Background Elemental Databases**,** 27, **2022,** *For. Chem.,* 100390., https://doi.org/10.1016/j.forc.2021.100390
9. **P Ramirez-Hereza**, D. Ramos, J. Maroñas, S. A. Balanya and J.R. Almirall, Gaussianization of LA-ICP-MS Features to Improve Calibration in Forensic Glass Comparison, **2022**, *Forensic Science International*, submitted.
10. K Lambert, A Akmeemana, R Corzo, G Gordon, C Gruber, S Gwak, E Haase, P Jiang, S Montero, O Ovide, K Prasch, P Ramirez-Hereza, D Ramos, K Redman, M Sakayanagi, T Scholz, T Trejos, J Webb, P Weis, W Wiarda, S Wilczek, H Xie, P Zoon and **JR Almirall,** Global Interlaboratory Study to Evaluate Background Databases for the Calculation of Likelihood Ratios in the Interpretation of Glass Evidence utilizing LA-ICP-MS , *Forensic Science International*, in preparation.

In addition to the publications, a new Shiny App was created to facilitate the calculation of likelihood ratios by forensic science practitioners and by researchers. The shiny app is available freely on the FIU Dataverse website through the library here:

https://dataverse.fiu.edu/dataset.xhtml?persistentId=doi:10.34703/gzx1-9v95/OB8BS9

The link to the software also includes the raw data generated containing LA-ICP-MS elemental analysis of > 900 vehicle glass samples of known origin. The abstracts of selected publications are quoted below.

A study that described the utility of likelihood ratio (LR) calculations using novel datasets of glass samples of known manufacturing history was published [**1**]. The LRs calculated from comparing glass manufactured at three different plants over relatively short periods (over 2-6 weeks) range from very low values (LR~10^{-3}) when the glass are manufactured at different plants or manufactured weeks-months apart in the same plant to very high values (LR~10^{3}) when the glass samples are manufactured on the same day. Although the glass samples being compared may not originate from the same broken window source, they do exhibit chemical similarity within these lower and upper bounds and the LRs presented, for the first time, closely correlate chemical relatedness to manufacturing history, specifically the time interval between production. The work reported support for the use of the match criteria recommended within ASTM E2927-16e1 and provides a data-driven path forward to expand on the interpretation of glass using LRs. Dimensionality reduction of multivariate elemental concentrations of glass was reported for computing likelihood ratios (*LR*s) [**2**]. The *LR*s calculated using principal component analysis (PCA) and a post-hoc calibration step previously suggested by van Es et al. in 2017 resulted in very low (< 1%) false inclusions when comparing glass samples known to originate from different sources and very low (< 1%) false exclusions when comparing glass samples known to originate from the same source. The *LR*s calculated using the novel PCA approach are compared to previously reported *LR*s calculated using a more computationally intensive Multivariate Kernel (MVK) model followed by a calibration step using a Pool Adjacent Violators (PAV) algorithm. In both cases, the calibrated likelihood ratios limited the magnitude of the misleading evidence, providing only weak to moderate support for the incorrect hypotheses. Most of the different pairs that were found to be falsely included were explained by chemical relatedness (same manufacturer of the glass sources in very close time interval between manufacture). The computation of *LR*s using dimensionality reduction of elemental concentrations using PCA may transfer to other multivariate data-generating evidence types. Consensus concentration values for seventeen (17) major and trace elements typically present in soda-lime glass manufactured using the “float” process and used in the quantitative analysis and forensic comparison of glass samples were determined using laser ablation (LA) micro sampling coupled to inductively coupled plasma mass spectrometry (ICP-MS) [**3**]. This is the first reporting of the chemical characterization of a new set of float glass intended for use as matrix-matched calibration standards in quantitative analysis by LA-ICP-MS using a standard test method (ASTM E2927-16e1). Three Corning Float Glass Standards (CFGS) were manufactured at low, medium, and high concentrations of 32 elements typically encountered in float glass samples as found in forensic casework. This work describes an international collaboration amongst seven (7) laboratories to evaluate the homogeneity of the three glass materials and reports the consensus concentrations values of 17 elements at three concentration levels. Eight (8) sets of independent results from LA-ICP-MS analysis using the standard test method of analysis and one set of micro-X-ray Fluorescence Spectrometry (μXRF) data (using method ASTM E2926-17) resulted in typically < 3 % relative standard deviation (RSD) within each lab and < 5 % RSDs among all labs participating in the study for the concentration ranges using sampling spots between 50 μm - 100 μm in diameter. These results suggest that the new calibration standards are homogeneous for most elements at the small sampling volumes (~ 90 μm deep by ~ 80 μm in diameter) reported and show excellent agreement among the different participating labs. Consensus concentration values are determined using a previously reported calibration standard (FGS 2) and checked with a NIST 1831 SRM®. In addition to the forensic glass analysis community, the CFGS glasses described here may be of interest to a broader group of analytical scientists in need of additional glass calibration standards for use in micro analysis techniques. A collaboration with National Institute of Standards and Technology (NIST) scientists to certify these glasses as SRMs for future distribution by NIST is ongoing. Seventeen (17) laboratories participated in three interlaboratory exercises to assess the performance of refractive index, micro X-ray Fluorescence Spectroscopy (μXRF), and Laser Induced Breakdown Spectroscopy (LIBS) data for the forensic comparison of glass samples [**5**]. Glass fragments from automotive windshields were distributed to the participating labs as blind samples and participants were asked to compare the glass samples (known vs. questioned) and report their findings as they would in casework. For samples that originated from the same source, the overall correct *association* rate was greater than 92 % for each of the three techniques (refractive index, μXRF, and LIBS). For samples that originated from different vehicles, an overall correct *exclusion* rate of 82 %, 96 %, and 87 % was observed for refractive index, μXRF, and LIBS, respectively. Special attention was given to the reporting language used by practitioners as well as the use of verbal scales and/or databases to assign a significance to the evidence. Wide variations in the reported conclusions exist between different laboratories, demonstrating a need for the standardization of the reporting language used by practitioners. Moreover, few labs used a verbal scale and/or a database to provide a weight to the evidence. It is recommended that forensic practitioners strive to incorporate the use of a verbal scale and/or a background database, if available, to provide a measure of significance to glass forensic evidence (i.e., the strength of an association or exclusion). The results of an interlaboratory study by ten different laboratories using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and standard test method (ASTM E2927-16e1) for the analysis and comparison of glass evidence was reported [**7**]. The aims of this work were to evaluate the performance of the new CFGS2 calibration standard for the quantitative analysis of simulated casework samples, evaluate the comparison criterion as recommended by the ASTM E2927 method (association or non-association) and the use of a likelihood ratio (LR) as a quantitative determination of the strength of evidence found. Each laboratory calculated a LR to report the significance of glass source comparisons for a set of glass samples of known origin. Two different types of background databases were used for the calculation of the LR to evaluate the effect of the size and composition of the databases on the calculation of the LR. As expected, glass that originated from the same windowpane was found to be indistinguishable using the ASTM E2927 match criteria and result in a high LR value (strong support for an association) and glass that originated from different vehicles are distinguished (strong support for an exclusion). Glass samples that originated from different vehicles but that were the same make, model and year (or comparisons between the inner and outer pane of the same windshield) were chemically similar and reflected in a low LR. Good agreement among the laboratories was reported with < 5 % relative standard deviations (RSDs) among participants with few exceptions.

Another publication [**8**] introduces an R Shiny graphical user interface (GUI) to calculate calibrated likelihood ratios using three different background databases of glass composition: a new survey vehicle glass database generated at Florida International University (FIU), a combination casework and vehicle survey database from the Federal Bureau of Investigation (FBI) Laboratory, and a previously reported casework database from the Bundeskriminalamt (BKA) Laboratory. The likelihood ratios are calculated using a previously reported two-level multivariate kernel (MVK) model and calibrated using the Pool Adjacent Violators (PAV) algorithm. The log-likelihood ratios (LLR) calculated using these three background databases are compared using a typical glass evidence case scenario, along with the ASTM E2927-16e1 recommended comparison criterion for the same glass cases. The LLR values increase as the size of the background database increases, as expected. The R Shiny app and the new FIU vehicle background database are provided to researchers in the supplementary materials of the manuscript and published in a freely available link on the FIU Library [**11**].

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2. A Gupta, R Corzo, A Akmeemana, K Lambert, K Jimenez, JM Curran, **JR Almirall**, Dimensionality reduction of multielement glass evidence to calculate likelihood ratios, *J. of Chemometrics,* **2020**, DOI: 10.1002/cem.3298.
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