Forensic Chemistry 11 (2018) 65–76

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.elsevier.com/locate/forc

An inter-laboratory evaluation of LA-ICP-MS analysis of glass and the use of a database for the interpretation of glass evidence

Tricia Hoffman[a], Ruthmara Corzo[a], Peter Weis[b], Edward Pollock[c], Andrew van Es[d], Wim Wiarda[d], Aleksandra Stryjnik[e], Hendrik Dorn[e], Alex Heydon[e], Eva Hoise[f], Sandrine Le Franc[f], Xie Huifang[g], Begonia Pena[h], Thomas Scholz[i], Jhanis Gonzalez[j], Jose Almirall[a,*]

[a] *Florida International University, Miami, FL, United States*
[b] *Bundeskriminalamt, KT 42, Wiesbaden, Germany*
[c] *Laboratory of Forensic Services, Sacramento California, United States*
[d] *Nederlands Forensisch Instituut, Laan van Ypenburg, the Netherlands*
[e] *Centre of Forensic Sciences, Toronto, Canada*
[f] *Institut National de Police Scientifique, Paris, France*
[g] *Health Sciences Authority, Singapore*
[h] *Comisaría General de Policía Científica, Madrid, Spain*
[i] *Landeskriminalamt Sachsen, Dresden, Germany*
[j] *Applied Spectra Incorporated, Fremont, CA, United States*

HIGHLIGHTS

- Ten laboratories participate in three inter-laboratory exercises in glass analysis.
- Three databases of LA-ICP-MS data were used to evaluate LR calculations.
- The ten laboratories all perform well in correctly reporting associations and non-associations.
- The LR provides an objective and quantitative *assessment* attached to a "source association".

ARTICLE INFO

Keywords:
LA-ICP-MS
Forensic glass interpretation
Glass database
Likelihood ratio
Frequency
Random match probability

ABSTRACT

Ten laboratories conducting forensic glass analysis participated in three inter-laboratory exercises to evaluate the use of a standard method (ASTM 2927-16e1) for the analysis and comparison of glass evidence using LA-ICP-MS. This study was designed to evaluate the rate of misleading evidence (ROME) when blind glass samples were distributed to the participants and asked to compare the glass samples (K vs. Q) and report their findings as they would in a case. Three different databases were used as background populations to calculate likelihood ratios (LRs) and frequency of elemental profile. The first database was composed of 420 vehicle windshield samples and the analytical data and application of this database is reported here, for the first time. The second database was provided by the BKA laboratory in Germany representing 385 casework samples including an assortment of float glass, container glass, and specialty glasses. The third background database was a combination of both databases. In the first inter-laboratory exercise, the likelihood ratio (LR) calculations result in 34/36 (94.4%) correct associations and no false inclusions for all labs. LRs in the second and third inter-laboratory exercises result in all participating laboratories correctly associating glass samples originating from the same source (57 comparisons) and all laboratories correctly discriminating glass samples from different sources (167 comparisons). The random match probability of glass samples known to originate from different glass sources was found to be ~0.1% and in agreement with previously reported values by other researchers.

* Corresponding author.
E-mail address: almirall@fiu.edu (J. Almirall).

https://doi.org/10.1016/j.forc.2018.10.001
Received 22 April 2018; Received in revised form 21 September 2018; Accepted 1 October 2018
Available online 01 October 2018

1. Introduction

Glass fragments are encountered as forensic evidence from broken windows in burglaries, from automobile hit-and-run accidents, and from other crimes. Forensic glass examiners are asked to analyze and compare the physicochemical properties of glass collected from a known source (Ks) to fragments that may have been recovered from an unknown or questioned source (Qs). The glass Ks and Qs are compared using refractive index measurements and trace elemental concentrations in order to determine whether the Q glass samples could have originated from the same K source of broken glass. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) has been referred to as the "gold standard" for the elemental analysis of glass samples measuring at least 100 μm in any direction and many researchers have reported excellent analytical figures of merit for the measurement as well as a fit-for-purpose utility for the forensic comparison [1–5].

The Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics (NITECRIME) European Network first reported an inter-laboratory evaluation of the analytical performance of LA-ICP-MS and identified optimal laser ablation and ICP-MS acquisition parameters for glass analysis [1]. Some years later the Elemental Analysis Working Group (EAWG) evaluated a number of different statistical match criteria to determine which performs best in terms of false inclusion and false exclusion rates [2]. This group varied the degree of difficulty in their tests and included samples that were produced at the same plant years, months, and weeks apart as well as samples from the same pane of glass. This was done to evaluate how well each match criteria correctly associates samples originating from the same source (same pane of glass) and discriminates among samples that originate from different panes. Based on the inter-laboratory study results, the EAWG recommended a match criterion that was a variation of the one previously reported by Weis et al at the Bundeskriminalamt (BKA) [3].The results of NITECRIME and EAWG ultimately led to the development of a standard test method of analysis, ASTM E2927-16e1 [6]. This test method recommends the use of a modified ± 4 standard deviations (SD) for the comparison between a K and Q sample. Using the K, the mean and SD for each element are calculated. A minimum SD equal to at least 3% RSD of the mean for each element is also calculated. This is sometimes referred to as the fixed relative standard deviation (FRSD). If the SD is less than the FRSD, the FRSD is used for creating a comparison interval. The K comparison interval is calculated for each element as the mean $\pm 4 \times$ SD (or $\pm 4 \times$ FRSD, whichever is greatest). The average concentration for each element of the Q sample is then calculated and compared to the K comparison interval. If the Q average lies outside the comparison interval for any element, then the K and Q are distinguished. This comparison criterion will be referred to throughout this paper as the ASTM E2927-16e1 match criterion or the simply the ASTM match criterion.

While the forensic community has reached consensus on the analytical protocol for the use of LA-ICP-MS and recommended a comparison criterion with known error rates for a limited number of scenarios, it has not yet reached consensus on how to interpret the weight of a glass comparison for reporting to the court in verbal terms. Some analysts simply state the discrimination limitations of LA-ICP-MS: *the K and Q could have originated from the same broken glass pane or another source produced with the same physical and chemical characteristics*. Other examiners report the frequency of occurrence that glass samples from different sources is expected to share the same trace elemental profile (reported to be ~0.1%) [3,4]. One approach that is gaining support is the use of a verbal scale that is divided by the presence or absence of individual or class characteristics as well as the discrimination potential of the techniques used [7]. This approach may be considered as subjective since it relies on the analyst's personal experience and assessment of the glass evidence. More objective methods include the application of statistical tools to calculate a likelihood ratio (LR) [8,9]. The calculation of a LR is an attractive alternative because it produces a number that can then be translated to a more objective verbal scale for communication to the court. In order to calculate a LR, however, a suitable database of trace elemental data from glass samples is required.

The aims of this working group, named the Glass Interpretation Working Group (GIWG), were to assess statistical models for the objective and quantitative interpretation of glass evidence using a large user community of glass examiners. This study is a result of three inter-laboratory exercises distributed to ten different laboratories (identified here as labs A-J) that examine glass evidence using LA-ICP-MS. A new database of glass was also created from the LA-ICP-MS analysis of 420 glass samples from 210 different vehicles representing 26 different vehicle manufacturers and manufacturing dates ranging from 2004 to 2017. The vehicle glass database (referred in this report as the FIU database) was used either by itself or in combination with a casework database kindly shared by the BKA in Germany for this purpose and in order to calculate LRs for the different inter-laboratory scenarios.

2. Materials and methods

2.1. Standard reference materials and glass samples

The certified standard reference materials (SRMs) NIST612 and NIST1831 (National Institute of Standards and Technology, Gaithersburg, MD, USA) were used for calibration as were the matrix-matched float glass standards FGS1 and FGS2 (available from the Bundeskriminalamt (BKA), Wiesbaden, Germany). A total of 420 vehicle glass samples from a salvage yard in Ruckersville, Virginia were collected to form the FIU vehicle glass database. The samples were analyzed at the Florida International University (FIU) laboratory using the methods recommended in ASTM E2927-16e1 prior to being distributed to the participating labs in the inter-laboratory exercises. The glass samples were collected from the windshields of vehicles representing manufacturing dates ranging from 2004 to 2017. A description of each of the glass samples is provided in the supplementary information (Table S1). All of the glass samples selected for the three inter-laboratory exercises originated from this vehicle glass collection. The inter-laboratory exercises were designed as mock cases in which participants were asked to analyze and compare Q glass samples to K glass samples. The samples selected for each inter-laboratory study are presented in Table 1. Since windshields are composed of two glass panes held together by a polyvinyl butyral (PVB) film, each K glass was sent out as two different samples (with designations as either K inner or K outer).

2.2. Description of LA-ICP-MS glass databases

Two LA-ICP-MS glass databases were used in this study: the Bundeskriminalamt (BKA) casework database and the Florida International University (FIU) vehicle database. The BKA database consisted of 370 casework samples, with 6 replicate measurements per sample. The database includes an assortment of glass types: float glass (vehicle and architectural), container glass and specialty glasses (specialty glasses were removed from consideration for this study). 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. However, ^{23}Na was omitted in this study since it is not included in the element menu suggested in ASTM E2927-16e1. It can be argued that this database is an appropriate database to consider 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 but, perhaps, even more generally.

The FIU glass database contains data from the analysis of 420 automotive glass samples with 15 replicates per sample. The samples are