Materials Subcommittee response to LRC comments on ASTM 2330 and ASTM E2926 methods

The following section aims to address and clarify some general misconceptions reported by the LRC members in both documents (E2330 and E2926). Some general observations are provided below, while more specific answers are provided later in the document next to their respective LRC questions/comments.

1. The OSAC Materials Subcommittee would like to clarify that several of the LRC comments are beyond the scope of an ASTM **standard test method**:

A. An ASTM standard is a document that has been developed and established within the consensus principles of the society and that meets the approval requirements of ASTM procedures and regulations.

B. There are various types of ASTM standards depending on the technical content and intended use (test methods, guide, practice, etc).

C. These two ASTM methods discussed here are "standard test methods." The primary **scope of a standard test method** is to "describe a definitive procedure that produces a test result", such as identification and measurement of the elemental profiles of glass.

D. The **intended audience** of these ASTM documents is the forensic practitioners who conduct the glass analyses.

E. As per the ASTM internal guide, documents require language consistency: use the word ***shall*** when stating mandatory requirements, use the word ***should*** as advisory, use the word ***may*** to indicate optional directives, avoid use of *must* whenever possible. The whole process of changing shall/should/must requires new balloting. Both of the revised methods were developed keeping this in mind with thorough consideration of the practical implications on when/why to use one term over the other.

F. The ASTM international guide requires the use of SI units.

G. With respect to comments regarding the references for a particular statement or recommendation, the ASTM international guide has requirements for the references to be included in the standard. They read, "Include only references to publications supporting or providing needed supplementary information. Historical and acknowledgment references are not desirable." Per this requirement, background data about the value of elemental analysis of glass is beyond the scope of the standard.

H. The statement about safety concerns is a required caveat by ASTM.

I. The statement "This guide cannot replace knowledge, skill, ability acquired…" is not required by ASTM but is highly recommended by the E30 ASTM committee.

The intent of this wording appears to have been misinterpreted by the members of the Legal Resource Committee. This is standard ASTM E30 wording that was intentionally placed into all ASTM forensic standards. The purpose of the wording is to prevent people who do not have any training from picking up the standard and performing the work without the proper background (training and demonstration of competence and proficiency). Hence the wording that is used in this standard cannot replace training and experience. People who use this standard should also have the knowledge, training, and experience necessary to perform the work. (Statement provided by Fire Debris Subcommittee)

Issues of interpretation, documentation, and training raised by the LRC are **beyond the scope** of these documents. Although we recognize that some of these concerns are valid for the overall practice of trace evidence, they can't be addressed in an ASTM test method and therefore should not apply to the decision/recommendation of whether or not the test method should be included in the OSAC registry. See *Form and Style for ASTM Methods* (http://www.astm.org/COMMIT/Blue_Book.pdf).

2. The OSAC Materials Subcommittee would like to provide some **background on how the test criteria** (a.k.a match criteria) were included in the ASTM standard test methods:

A. These methods are **documents developed through a structured and rigorous consensus process that establish criteria for the analysis or methodology used during a particular examination. In the particular case of these two methods, they are designed to specify how the elemental analysis of glass is conducted for forensic comparisons (by ICP-MS or µXRF, respectively).**

B. These ASTM standards were drafted by a NIJ-funded scientific group (the Elemental Analysis Working Group, a group of 34 scientists with particular expertise in elemental analysis of glass materials (forensic glass practitioners, researchers, and statisticians). The method was then exposed to revision by ASTM subcommittee and later exposed to the main committee and balloting/review process.

C. The test criteria reported on these methods were based on inter-laboratory studies designed to minimize both type I and type II errors in the comparison of elemental data. Several test criteria were tested on these studies based on statistical methods previously reported in validation/population/survey studies. Some methods that the forensic community was using in their protocols were also included in the study - no consensus on match criteria existed within the community at the time the inter-laboratory tests were started.

D. The inter-laboratory tests not only provided an effective way of cross-validating methods used for the elemental analysis of glass but also demonstrated which match criteria were more appropriate for elemental analysis of glass. The studies showed that the selection of test criteria was dependent on the capabilities, limitations and precision of the method of analysis. After thorough evaluation of the data derived from "worst case scenarios" the group arrived at a consensus on the best test criteria for glass examinations (by ICPMS, LAICPMS or μXRF). Decisions were made on the basis of lowest type I and type II error rates.

For example, ICP-MS and LA-ICPMS provide quantitative data with the precision of the measurements typically lower than 3%RSD, while μXRF produced semi-quantitative data with typical precision ranging from 2-25%RSD, depending on the element and its concentration.

Variability between the measurements is a combined effect of natural heterogeneity of the sample and the precision of the method. For methods with low variability of the measurements, (such as ICPMS) a narrow test criterion such as 2s or 3s produced high false exclusions. On the other hand, for a method with larger variability such as μXRF, a wide criterion of 4s would introduce an unacceptably high number of false inclusions. For a detailed description of the results the following scientific publications are provided:

a. T. Trejos, R. Koons, S. Becker, T. Berman, J. Buscaglia, M. Dueckin, T. Eckert-Lumsdon, T. Ernst, C. Hanlon, A. Heydon, K. Mooney, R. Nelson, K Olsson, C. Palenik, E. Pollock, D. Rudell, S. Ryland, A. Tarifa, M. Valadez, P. Weis and J. Almirall. Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ-XRF, ICP-MS and LA-ICP-MS, *Journal of Anal. Bional. Chem*, 2013, 405: 5393-5409
b. T. Trejos, R. Koons, P. Weis, S.Becker, T. Berman, C. Dalpe, M. Duecking, J. Buscaglia, T. Eckert-Lumsdon, T. Ernst, C. Hanlon, A. Heydon, K. Mooney, R. Nelson, K. Olsson, E. Schenk , C. Palenik, E. Chip Pollock, D.Rudell, S. Ryland, A. Tarifa, M.Valadez, A. van Es , V. Zdanowicz, and J.R. Almirall· Forensic analysis of glass by μ-XRF, ICP-MS, LA-ICP-MS and LA-ICP-OES: Evaluation of the performance of different criteria for comparing elemental composition, *Journal of Analytical Atomic Spectrometry,* 2013, 38, 1270-1282
c. Ernst, T.; Berman, T.; Buscaglia, J.; Eckert-Lumsdon, T.; Hanlon, C.; Olsson, K.; Palenik, C.; Ryland, S.; Trejos, T.; Valadez, M.; Almirall, J. R. Signal-to-noise ratios in forensic glass analysis by micro X-ray fluorescence spectrometry. *X-Ray Spectrom.* 2012*, 43*, 13-21.
d. Weis, P.; Dücking, M.; Watzke, P.; Menges, S.; Becker, S. Establishing a match criterion in forensic comparison analysis of float glass using laser ablation inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* 2011*,*

26, 1273-1284.

e. Berends-Montero, S.; Wiarda, W.; de Joode, P.; van der Peijl, G. Forensic analysis of float glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): validation of a method. *J. Anal. At. Spectrom.* 2006*, 21*, 1185-1193.
f. Hendrik Dorn, David E. Ruddell, Alex Heydon & Brenda D. Burton (2015)Discrimination of float glass by LA-ICP-MS: assessment of exclusion criteria using casework samples,Canadian Society of Forensic Science Journal, 48:2, 85-96.

E. The match/test criteria used for glass examinations cannot be directly applied to other materials because the selection of match criteria is not only dependent on the analytical method performance as described above but also on the natural heterogeneity of the sample. With this said, it is inappropriate to compare the case/scope/purpose of elemental analysis of bullet lead to glass. There are significant differences between the materials in terms of manufacturing, packaging, distribution, heterogeneity and chemical composition.

The use of elemental analysis for glass comparisons has a very strong foundation with dozens of scientific articles describing the heterogeneity and distribution of elements on glass panes, variability, origin, and reasoning on which elements are more discriminating/informing and how they were selected for chemical profiling/comparison of glass. A few of these publications are listed below:

a. Almirall, J. R.; Trejos, T. Advances in forensic analysis of glass fragments with a focus on refractive index and elemental analysis. *Forensic Sci. Rev. 18* **2006***, 2*, 74-96.
b. Almirall, J. R.; Trejos, T. Forensic Applications of Mass Spectrometry. In *Encyclopedia of Mass Spectrometry, 1st ed.*; Beauchemin, D.; Matthews, D., Eds.; Elsevier, **2010**; Vol. 5, pp 705-717.
c. Andrasko, J.; Maehly, A. C. The discrimination between samples of window glass by combining physical and chemical techniques. *J. Forensic Sci.* **1978***, 23*, 250-262.
d. Becker, S.; Gunaratnam, L.; Hicks, T.; Stoecklein, W.; Warman, G. The differentiation of float glass using refractive index and elemental analysis: Comparisons of techniques. *Probl. Forensic Sci.* **2001***, 47*, 80-92.
e. Berends-Montero, S.; Wiarda, W.; de Joode, P.; van der Peijl, G. Forensic analysis of float glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): validation of a method. *J. Anal. At. Spectrom.* **2006***, 21*, 1185-1193.
f. Buscaglia, J. Elemental analysis of small glass fragments in forensic science. *Anal. Chim. Acta* **1994***, 288*, 17-24.
g. Duckworth, D. C.; Baynes, C. K.; Morton, S. J.; Almirall, J. R. Analysis of variance in forensic glass analysis by ICP-MS: Variance within the method. *J. Anal. At. Spectrom.* **2000***, 15*, 821-828.

h. Duckworth, D. C.; Morton, S. J.; Baynes, C. K.; Koons, R. D.; Montero, S.; Almirall, J. R. Forensic glass analysis by ICP-MS: A multi-element assessment of discriminating power via analysis of variance and pairwise comparisons. *J. Anal. At. Spectrom.* **2002***, 17*, 662-668.
i. Hicks, T.; Monard Sermier, F.; Goldmann, T.; Brunelle, A.; Champod, C.; Margot, P. The classification and discrimination of glass fragments using non destructive energy dispersive X-ray µ fluorescence. *Forensic Sci. Int.* **2003***, 137*, 107-118.
j. Koons, R. D.; Fiedler, C.; Rawalt, R. C. Classification and discrimination of sheet and container glasses by inductively coupled plasma-atomic emission spectometry and pattern recognition. *J. Forensic Sci.* **1988***, 33*, 49-67.
k. Koons, R. D.; Peters, C. A.; Rebbert, P. S. Comparison of refractive index, energy dispersive X-ray fluorescence and inductively coupled plasma atomic emission spectrometry for forensic characterization of sheet glass fragments. *J. Anal. At. Spectrom.* **1991***, 6*, 451-456.
l. Latkoczy, C.; Becker, S.; Dücking, M.; Günther, D.; Hoogewerff, J. A.; Almirall, J. R.; Buscaglia, J.; Dobney, A.; Koons, R. D.; Montero, S.; van der Peijl, G. J.; Stoecklein, W. R.; Trejos, T.; Watling, J. R.; Zdanowicz, V. S. Development and evaluation of a standard method for the quantitative determination of eements in float glass samples by LA-ICP-MS. *J. Forensic Sci.* **2005***, 50*, 1327-1341.
m. Montero, S. Trace elemental analysis of glass by inductively coupled plasma-mass spectrometry (ICP-MS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), Florida International University, Miami, Florida, 2002.
n. Naes, B. E.; Umpierrez, S.; Ryland, S.; Barnett, C.; Almirall, J. R. A comparison of laser ablation inductively coupled plasma mass spectrometry, micro X-ray fluorescence spectroscopy, and laser induced breakdown spectroscopy for the discrimination of automotive glass. *Spectrochim. Acta, Part B* **2008***, 63*, 1145-1150.
o. Parouchais, T.; Warner, I. M.; Palmer, L. T.; Kobus, H. The analysis of small glass fragments using inductively coupled plasma mass spectrometry. *J. Forensic Sci.* **1996***, 41*, 351-360.
p. Roedel, T. C.; Bronk, H.; Haschke, M. Investigation of the influence of particle size on the quantitative analysis of glasses by energy-dispersive micro x-ray fluorescence spectrometry. *X-Ray Spectrom.* **2002***, 31*, 16-26.
q. Ryland, S. G. Discrimination of flat (sheet) glass specimens having similar refractive indices using micro X-ray fluorescence spectrometry. *Journal of the American Society of Trace Evidence Examiners* **2011***, 2*, 2-12.
r. Suzuki, Y.; Sugita, R.; Suzuki, S.; Marumo, Y. Forensic discrimination of bottle glass by refractive index measurement and analysis of trace elements with ICP-MS. *Anal. Sci.* **2000***, 16*, 1195-1198.
s. Trejos, T.; Almirall, J. R. Sampling strategies for the analysis of glass fragments by LA-ICP-MS Part I. Micro-homogeneity study of glass and its application to the interpretation of forensic evidence. *Talanta* **2005a***, 67*, 388-395.
t. Trejos, T.; Almirall, J. R. Sampling strategies for the analysis of glass fragments by LA-ICP-MS Part II: Sample size and sample shape considerations. *Talanta* **2005b***, 67*, 396-401.

u. Trejos, T.; Montero, S.; Almirall, J. R. Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-MS. *Anal. Bioanal. Chem.* **2003**, *376*, 1255-1264.
v. Trejos, T.; Koons, R.; Becker, S.; Berman, T.; Buscaglia, J.; Duecking, M.; Eckert-Lumsdon, T.; Ernst, T.; Hanlon, C.; Heydon, A.; Mooney, K.; Nelson, R.; Olsson, K.; Palenik, C.; Pollock, E. C.; Rudell, D.; Ryland, S.; Tarifa, A.; Valadez, M.; Weis, P.; Almirall, J. R. Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ-XRF, ICP-MS, and LA-ICP-MS. *Anal. Bioanal. Chem.* **2013a**, *405*, 5393-5409.
w. Trejos, T.; Koons, R.; Weis, P.; Becker, S.; Berman, T.; Dalpe, C.; Duecking, M.; Buscaglia, J.; Eckert-Lumsdon, T.; Ernst, T.; Hanlon, C.; Heydon, A.; Mooney, K.; Nelson, R.; Olsson, K.; Schenk, E.; Palenik, C.; Pollock, E. C.; Rudell, D.; Ryland, S.; Tarifa, A.; Valadez, M.; van Es, A.; Zdanowicz, V.; Almirall, J. R. Forensic analysis of glass by μ-XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: evaluation of the performance of different criteria for comparing elemental composition. *J. Anal. At. Spectrom.* **2013b**, *28*, 1270-1282.
x. Weis, P.; Dücking, M.; Watzke, P.; Menges, S.; Becker, S. Establishing a match criterion in forensic comparison analysis of float glass using laser ablation inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **2011**, *26*, 1273-1284.
y. P.M.L. Sandercock (2000) Sample Size Considerations for Control Glass in Casework, Canadian Society of Forensic Science Journal, 33:4, 173-185
z. Hendrik Dorn, David E. Ruddell, Alex Heydon & Brenda D. Burton (2015)Discrimination of float glass by LA-ICP-MS: assessment of exclusion criteria using casework samples, Canadian Society of Forensic Science Journal, 48:2, 85-96.

We would like to stress that the overall scientific foundation of glass examinations includes aspects of transfer, persistence, and methodology validity. The principles and utility of forensic glass examinations is supported by at least 130 publications over the last 3 decades. The list provided above represents only a snapshot of the scientific support on the particular topics of sampling, homogeneity, and discrimination/variations in glass populations.

F. We are aware of Bayesian/likelihood approaches for the interpretation of glass evidence. We are not against these strategies. However, the test methods discussed here are limited to the comparison of "elemental data" to determine whether the elemental compositions of two glass samples (aka K/Q) are distinguishable or not.

What the scientists conclude based on the evaluation of the data is outside the scope of these test methods. After applying these test methods, the practitioner will need to follow an interpretation guide/standard to write a conclusion (whether they decide to use Bayesian or traditional approaches).

The test criterion is a necessary step prior to any further data interpretation. These test methods aim to standardize the way in which practitioners should conduct data analysis to determine if the elemental composition is different or not. Nonetheless, conducting elemental analysis via either of these test methods is only one of many steps/examinations that the glass examiner must follow and later put together to evaluate the evidence and write a conclusion based on the overall glass examination (physical, optical and chemical).

It is critical to keep in mind the scope of the test method when evaluating these documents.

3. Implications of the use of different types of data in forensic science: The elemental composition of materials can be obtained by spectrochemical methods (i.e. µXRF, ICP) in three main forms:

a) qualitative
b) quantitative
c) semi-quantitative

All 3 forms of data comprise true/valid scientific information/data that can be used to determine the source of a material or make inferences about commonality, similarity or difference of chemical composition.

The decision of whether we use one form of data or another is dictated by the nature of the material, the limitations/capabilities of the technique, and the purpose of the analysis.

A. **Qualitative data:** this is, for example, a graphical representation of a spectrum that shows the identification of elements present/detected in a specimen, such as iron, calcium, etc. You can use qualitative data to determine which elements are present or absent in a sample and/or to compare if the same elements are present or absent in a comparison sample. You can overlay two spectra to compare their qualitative profile.

B. **Quantitative data:** quantitative data involves the identification of the element followed by the calculation of the absolute concentration (amount). In solid materials such as glass this is typically reported in ug/g. Calibrations are made by using certified standards of known concentration. For instance, ICPMS is a method able to generate quantitative data with excellent precision and accuracy. You can not only determine that iron and calcium are present, you can also report the actual concentration and uncertainty for each element. This data can be used to detect significant differences in the composition of the elements in comparison samples.

C. **Semi-quantitative data:** in some instances, the conditions for reliable quantitative data are not met. For example, in the case of µXRF quantitative data requires calibration with solid standards of glass at concentrations detectable by this method and the glass fragment must have minimum thickness/shape requirements to attenuate differences in the way that the X-rays are released from the glass into the detector.

Because of the typical sample/shape of glass fragments, these limitations prevent quantitative measurements by μXRF. Instead, ratios of elements are used to compensate for those variations. The ratios of elements are selected/recommended based on similar anticipated behavior to optimize that normalization of the data. For example, these ratios of the peak areas of calcium to iron generate "numerical" data. That ratio data is not "quantitative" but due to its numerical nature it is considered "semi-quantitative" because you are comparing the relative amounts of these elements in the samples.

Semi-quantitative data allows the calculation of uncertainties and is widely accepted in the scientific community. Semi-quantitative data is the foundation of other forensic materials, such as DNA analysis.