IFRI International Forensic Research Institute
Florida International University

Introduction to the Examination and Comparison of Glass Evidence

Web-based course

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This work is designed as an introductory course to the forensic examination of glass evidence. The purpose of this on-line version is to disseminate the training material to forensic examiners at an entry-level.

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Introduction to the Examination and Comparison of Glass Evidence

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Learning Objective

This course will provide a thorough introduction to forensic examination of glass including: a) glass composition, terminology and manufacturing processes b) forensic examination of glass by physical measurements, refractive index, annealing and elemental analysis, c) fundamentals on elemental analysis techniques, d) statistical analysis and evaluation of match criteria, e) interpretation of glass data and f) introduction to the legal framework and its limitations.

After the completion of the modules the student should be familiarized with:

a) Basic terminology of glass and glass manufacture
b) Main similarities and differences in the raw materials and major formulations of glass commodities
c) Major manufacturing processes for glass
d) Significance, advantages and limitations of the methods used for forensic glass examinations (Physical Fit, Physical Measurements, Thickness, Density, Refractive Index, Dispersion, Annealing, Fluorescence, Manufacturers Markings, elemental analysis)
e) Fundamentals of different methods available for elemental analysis of glass (SEM-EDS, XRF, ICP methods, LAICPMS and LIBS)
f) Basics of statistical analysis available for data analysis, quality control and interpretation of glass evidence
g) Sampling considerations for glass examinations

Please click on the link below to access each module

Module 1. Introduction to glass examinations and legal framework

Module 2. History of the Glass Industry, Terminology and Definitions

Module 3. Forensic glass examinations

Module 4. Elemental analysis of glass examinations

Module 5. Sampling strategies for glass examinations

Module 6. Introduction to Statistics for Evaluation of Glass Comparisons

Module 1. Introduction to glass examinations and legal framework

Trace **evidence** could become a fundamental piece to complete a puzzle that may lead to the solution of a case. Glass fragments are a common type of trace evidence found in case scenarios such as car accidents, break and entries and assaults.

Due to its **fragile nature** and abundance, glass is one of the mayor types of trace evidence encountered in crime scenes such as **burglaries, car accidents, hit and runs, assaults, drive-by shootings and bombings**.

Glass examiners could determine if a glass fragment is associated to another object in order to establish whether or not a particular person *could be* **or** *could not be* associated with:

a) a given place at a given moment,
b) another person or
c) an activity.

Glass comparisons have the capability to provide investigators with **answers on how things happened** during the crime.

Example:

> *"A young woman was found dead at the side road. Two witnesses reported a blue Cadillac vehicle leaving the scene. Upon arrival to the scene, the investigators collected glass fragments from the victim's body and labeled them as the known sample **K1**.*
>
> *Few hours later the suspect car was found abandoned with serious damage to the headlamp. Glass from the **headlamp** was collected as the **"questioned" glass** sample and labeled as **Q1**.*
>
> *A search warrant was issued, the suspect claim that the vehicle was robbed the night before and therefore he wasn't driving the car during the accident. **Suspect's house was search** and **several glass fragments** were found on **his clothing**. Glass fragments from his **shirt** were recovered and labeled as "questioned" samples, **Q2**.*
>
> *Samples were submitted to the forensic laboratory. Glass examiner reported that the results give strong support to the thesis that samples Q1 and Q2 (questioned) originate from the same source as the control sample K1"*
>
> *In the previous example, if it is shown that there is a strong association or "match" between the known glass recovered from the victim and the fragments recovered from the suspect's car and clothing, such association could link the source of origin –the broken headlamp- to the victim and suspect at a given event at a given place and at a given time. The significance of this finding relies on several factors that may be taken into account.*
>
> ***The significance of such findings will be explored in more detail in the following modules.***

Trace evidence such as glass usually exhibit **class characteristics** and therefore the value of evidence will depend on the discrimination power of the techniques used for its comparison. The value of evidence can also be enhanced by cross transfer of evidence between victim and suspect, multiple transfer of evidence and rarity of the characteristics of the evidence.

Glass can also provide **individual characteristics** in cases where there is a significant fitting of two glass fragments. Nonetheless, such as match is rarely found in typical cases. Glass examiners should always consider this possibility during the physical and microscopic examination of the specimens.

Typical glass examinations involve the physical and optical measurements, such as thickness, density, dispersion, fluorescence, refractive index and annealing. Improvements in the quality assurance of the manufacture of glass have encouraged the forensic community to look for complementary techniques with greater sensitivity, greater discrimination power such as elemental analysis methods (XRF, ICP methods, LAICPMS, LIBS).

There are some scientific groups around the world, such as SWGMAT, NITECRIME, ENFSI that have focused their interest in evaluating, reviewing and standardizing new techniques and methodologies for forensic examination of glass.

Glass examiners should be aware that in order to evaluate the **value of glass as evidence**, it is necessary to **understand the nature and chemistry** of this material, **the transfer and persistence** of small fragments and **the advantages and limitations of the analytical techniques** used for its examination.

The following modules will provide a basic understanding of the nature of glass, manufacturing process, techniques available for analysis and significance of the evidence.

Suggested readings

1. ET Miller, "Forensic glass comparisons," In Forensic Science Handbook, ed. R Saferstein, Prentice-Hal, Englewood Cliffs, NJ, 1982, pp.139-183.
2. RD Koons and J Buscaglia, "The forensic significance of glass composition and refractive index measurements," J. Forensic Sciences, 1999, 44:496-503.
3. IW Evett and JA Lambert, "The interpretation of refractive index measurements III.," Forensic Science International, 1982, 20: 237-245.
4. KAJ Walsh, CM Triggs, and JS Buckleton, "A practical example of glass interpretation," Science and Justice, 1996, 36: 213-218.
5. RD Koons, CA Peters, and PS Rebbert, "Comparison of refractive index, energy dispersive x-ray fluorescence and inductively coupled plasma atomic emission spectrometry for forensic characterization of sheet glass fragments," J. Analytical Atomic Spectrometry, 1991, 6:451-456.
6. RD Koons, C Fiedler, and RC Rawalt, "Classification and discrimination of sheet and container glasses by inductively coupled plasma-atomic emission spectrometry and pattern recognition" J. Forensic Sciences, 1988, 33:49-67.
7. JM Curran, CM Triggs, JR Almirall, JS Buckleton, and KJ Walsh, "The interpretation of elemental composition measurements from forensic glass evidence: I," Science and Justice, 1997, 37:241-244.

Click on **Module 1 additional material** to learn more about glass as trace evidence

Module 2. History of the Glass Industry, Terminology and Definitions

This module will discuss the history of glass industry as well as terminology and definitions that glass examiners should be aware of as part of their training. The module will also discuss the main components and uses of glass. Student should be familiar with the major differences in composition of the different types of glass.

2.1. Physical and Chemical Properties of glass

Glass is defined as an "inorganic production of fusion that has been cooled to a rigid condition without crystallization" (ASTM, 2000). This material is composed of a mixture of inorganic materials that are responsible of its different physical properties.

> Glass is a **mixture of inorganic components** present at different concentration levels (major, minor and trace levels ranging from %w/w to ppb levels)
>
> Some of these components are added **intentionally** to assure the glass structure; to decrease the cost of manufacture or to provide desired properties such as color, heat resistance and safety. Some other components are present **un-intentionally** at trace levels in the final product as contaminants from the raw materials or the manufacturing process.

Glass can be classified in different groups according to their **intended use** as:

a) flat glass (for architecture and automobiles)
b) containers (bottles, glasses and jars)
c) glass fibers (for insulation) and
d) specialty glass.

They can also be classified by their **main raw materials** as

a) soda lime (containers and windows)
b) leaded glass (houseware and decorations)
c) borosilicate glass (industry, lamps and cookware) and
d) special (optical, electronics)

The main raw materials utilized for the manufacture of soda lime glasses are sand (SiO_2), soda ash (Na_2CO_3) and limestone (CaO). Borosilicate glass contains Boron as a supply of heat resistance, and "leaded" glasses, as its name implies uses lead as an additional raw material (Almirall, 1999).

Sand, the major source of silica, requires certain characteristics in order to be employed in the manufacturing of glass. Small impurities present in the sand could produce undesired properties in the final product such as color, alter furnace temperatures or produce non-glassy impurities (Koons, 2002).

The components of glass are classified according to their function as: formers, fluxes, modifiers, stabilizers, colourants, decolourants, acceleranting, refining and opalisers agents. (Almirall, 1999; Koons, 2002, Almirall 2006).

a) **Former** agents are products that generally form the framework of the glass structure and when cooled quickly after melting they solidify without crystallizing
b) **Fluxes** are components that are added to the formers to lower the melting temperature and to reduce cost of production.
c) **Stabilizers** are added to offer chemical resistance to the glass, while decoulorants are used to clarify the glass.

d) **Refining** agents are also an important component of glass that help to remove bubbles from the molten glass during its production.

The use of reutilized glass (recycled glass) or **cullet** is commonly employed in the manufacture of glass to decrease the melting temperature and reduce the cost of the manufacturing process. Most of the cullet used in sheet glass is recycled within the plant while some container plants use recycled consumer glass, which adds some heterogeneity between batches originated from the same plant. That is favorable from a forensic point of view because the elemental profiling will differ widely amongst different sources but also adds more heterogeneity to the sample that need to be taken into account to make decisions about sampling strategies.

In addition, for float glass production, as the furnace inner brick-walls get older, there is a larger probability of some elements, such as Zr and Al, to leach into the molten glass (Koons, 2002).

These contaminants or unintended inorganic components are the ones that allow the forensic chemists to apply elemental analysis to discriminate between glass fragments that came from different sources and to associate glass fragments that originate from the same source.

The value of glass as trace evidence relies on the premise that regardless of advances and standardization in the manufacture of glass, **minor variations in the physical properties and chemical composition** of the glass remain between and within batches due to the innate trace contaminations of raw materials.
These **differences are detectable** by a variety of analytical methods available to forensic examiners.

2.2. Manufacturing

Glass was first formulated in 1500 B.C. by the Egyptians mainly in the manufacture of vessels and jewelry. Later, press molded glass was formulated in Alexandria (400 B.C.) and the Syrians introduced (200 B.C.) the first examples of flat glass for use in windows.

A major improvement on the manufacturing of glass was achieved with the introduction of oven technology by the Romans. The Germans in the 19th century manufactured optical glass and heat-resistant glass for use in thermometers and cooking glassware (Koons, 2002).

Since then, the manufacture of glass has been in continuous improvements in order to look for better quality, automated processes and cheaper products.

Nowadays, glass is one of the products most utilized in society for many reasons. Glass production ranges from simple glass containers to advanced micro-components. The manufacturing of glass usually follows five steps:

a) Preparation of raw materials (storage, weighing and mixing),
b) Melting
c) Forming
d) Annealing and cooling
e) Warehouse or secondary processing.

The first step consists on the **preparation of raw materials** including transport, storage of materials, weighing the materials for the formulation and finally pre-mixing them.

The **melting process** occurs at very high temperatures (>1500°C). Special furnaces are required to maintain an efficient melting process. A continuous flow of the melted glass is fed into automatic forming machines (Copley, 1999). The melting step also includes refining and homogenization of materials. During the **refining process**, the homogenization of glass takes

place along with the elimination of bubbles from the molten glass, which is necessary to offer uniform appearance and homogeneous refractive index in the final product.

The **forming** procedure is then followed by gradual changes in viscosity. After the forming step, the **annealing** of the glass takes place and the glass is cooled at a specific rate to solidify without crystallization.

Some glass products require a **secondary processing** such as tempering, coating and coloring or decolorizing. Tempered glass is ordinary glass that has followed a process to provide additional strength and more safety breakage pattern; it is widely employed in the manufacturing of automobile windows (Copley, 1999).

The **coating method** is used for decoration, protection or strengthening of the glass. This is a usual method in the manufacture of containers to improve the handling of the material. Coating layers may contain inorganic components such as titanium or tin or organic waxes or fatty acids. Coating layers are commonly found in containers and in less extent in some flat glass.

Clear glass may require also and additional **de-coloring process**, which is achieved by spiking the product with additional amounts of elements such as selenium and cobalt to counterbalance the green or yellow color caused by iron.

On the other hand, some products are **colored** intentionally for decorative purposes. Common inorganic colorants are iron (green, brown or blue), manganese (purple), cobalt (blue, green, pink), titanium (purple, brown), cerium (yellow) and gold (red) (Copley, 1999).

There are many different glass compositions, but in general terms glass industry deals with the manufacture of products such as: flat glass (architectural and automobile), containers (bottles, jars), domestic glass (tableware), technical glass (laboratory glassware) and glass fibre (insulators).

Glass examiners should be aware of the main differences in the manufacturing processes of glass according to their end-use. It is strongly recommended that glass examiners visit a glass manufacturing plant to better understand the manufacturing process.

The Glass Association of North America (GANA) has several videos describing the manufacturing process of glass at their website http://www.glasswebsite.com/video/default.asp

Click on Module 2 additional material to learn more about glass history and manufacture

Click on **Module 2 additional material** to learn more about glass history and manufacture

Module 3. Forensic glass examinations

This module will discuss the screening methods used in glass examinations including physical measurements, thickness, density, refractive index, dispersion, annealing, fluorescence, manufacturer's markings and their significance. The usefulness of physical fit in glass analysis will be also discussed.

3.1. Standard Laboratory Practices

Glass examiners often measure the physical and optical properties of glass such as color, thickness, density, refractive index (RI) and also, if necessary, they conduct elemental analysis to enhance the value of an association. Figure below shows the typical scheme for the forensic analysis of glass fragments.

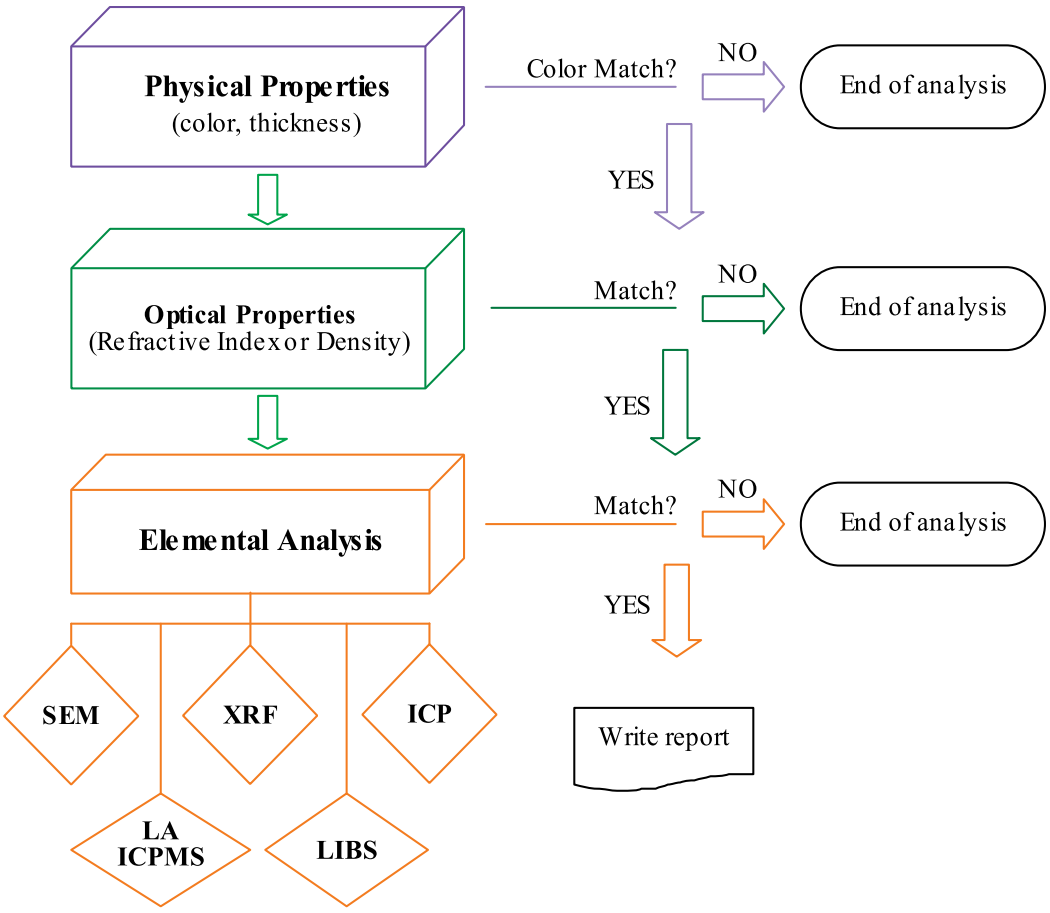

***Figure 1**. Typical scheme for the forensic analysis of glass.*

3.2. Fractures and their significance

There is published work on the nature of glass fractures and their use on forensics (McJunkins et al, 1973, Thronton et al, 1986, Mencik, 1992, Kepple 1994, Koons, 2002). However, the interpretation of the fractures still relies on the experience of the examiner.

The study of glass fractures may help to determine the direction of the force that produces the fracture. Glass is broken by tension rather than compression, the surface that breaks first is the opposite side of the impact zone. Figure 2 shows the process involved in the breaking of flat glass.

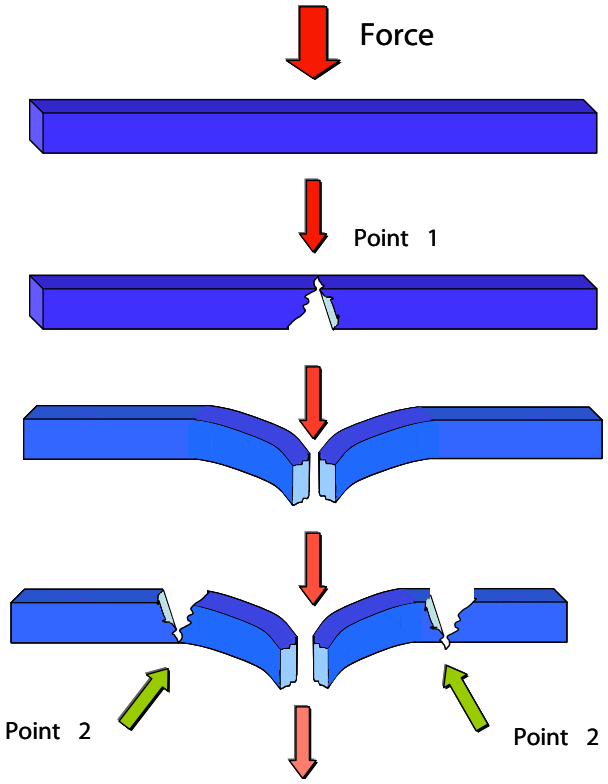

Figure 2. *Diagram of the breakage phenomena of a glass pane produced by a low-velocity impact. After the application of the force, the glass bulge on the side opposite to the impacting force and radial fractures begin at Point 1. Later, concentric fractures will form at points 2.*

A force applied to a surface will produce compression to the side facing the force and tension on the opposite side. The tension state on the forward side will create radial fractures that will produce at the same time subsequent compression of that side of the glass. This compression will produce further tension on the side originally exposed to the force creating concentric fractures.

Figure 3 shows that radial fractures propagate away from the point of impact and generates ridges that tends to be perpendicular to the opposite side of the impact and parallel to the side of impact.

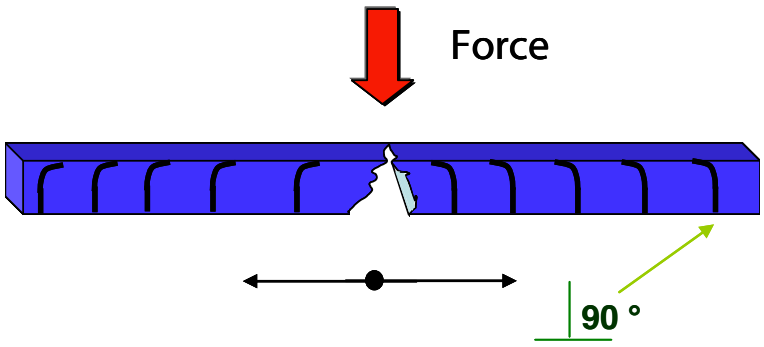

Figure 3. *Diagram of typical ridges on a radial fracture.*

Tempered glass breaks in different patterns than common glass due to the fact that surfaces are under a state of "compression" while the central region is under tension. For this reason, fractures on tempered glass have to be studied separately.

This course does not intent to offer thorough details on the significance of glass fractures. Glass examiners should be aware that interpretation of fractures is influenced by many factors and that comprehensive knowledge of the different factors involved in a glass fracture must be taken into account to avoid misinterpretation of the evidence. The references cited at the beginning of this section are a good source for the reader.

3.3. Physical measurements

The first step in any glass analysis is to identify the glass by physical and optical properties such as hardness, amorphous structure and isotropism. Transparent fine debris commonly found in trace evidence (i.e sand, plastics, etc) could be initially confused with glass. Nevertheless, physical examinations could easily corroborate the presence of glass materials vs other transparent materials.

Physical observations include fracture characteristics, color of the glass, thickness, curvature or flatness, and fluorescence. These observations are made in the preliminary stages of the analysis.

The physical examination of glass can provide important information such as:

a) Type of impact that caused the fracture of glass, e.g. a fracture caused by a gunshot, body impact, or by a hard object such a tool or bat.
b) Direction of the force, e.g. to establish if a window was broken from inside or from outside.
c) Type of material, which may be very useful to corroborate or invalidate alibi, i.e whether the glass is a flat architectural window, a tempered glass, a headlamp, or a container.
d) Source of origin of the glass fragment, e.g physical fit.
e) Glass appearance (fresh vs scratched and dirty pieces may be important to determine whether or not the glass transfer was recent, which is particularly important in the transfer of glass to shoes).

a. Physical fit

A physical fit or physical “match” between two glass fragments that were originally joined is the best case scenario a forensic examiner could have during physical evaluation of glass, but due to the types of fractures generated in glass and the different scenarios for glass transfer, a perfect physical fit is rarely found in real cases.

Such a match requires the edges of one fragment to perfectly fit into an edge of another, much like a jig-saw puzzle. (Almirall, 2001). The match of pieces of glass is three dimensional and the analyst should document the details by aims of photography. The match should also be observed under the microscope in order to determine microscopic match of marks (conchoidal, hackle marks). Figure 4 exemplifies a “physical match” between to pieces originated from the same headlamp.

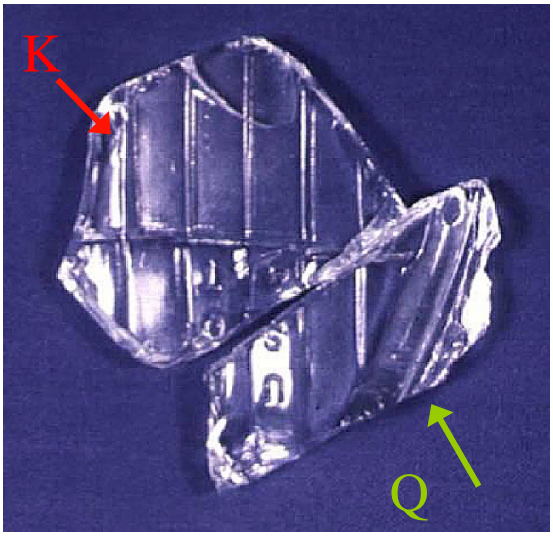

***Figure 4**. Photography of a physical match between a known fragment of glass (headlamp) and a questioned fragment of glass.*

b. Thickness

In cases where glass is recovered as a fragment that present the full thickness (original surfaces), it may be useful to measure the thickness of the glass. The thickness measurements can provide information about the possible type of object from where it comes, i.e. a vehicle side window, tempered glass, beverage bottle. Nonetheless, for comparison purposes thickness measurements provides limited information.

c. Density

Nowadays, density measurements are rarely performed in forensic laboratories since they have been mostly replaced by refractive index measurements, which provide similar information with the advantage of being faster, more accurate and more precise.

Density of glass can be determined using the sink-float method. The determination of density has the disadvantages of involving toxic liquids and requiring at least 5 mg of sample. Another limitation of density measurements is that measurements of small, irregular or dirty fragments of glass may be inaccurate (Koons, 2002).

3.4. Refractive index analysis

Glass examinations are commonly conducted by refractive index measurements. Nevertheless, improvements in the quality control during the manufacture of glass have reduced the range of variation for refractive index values of glass as a population (Buscaglia, 2001) thereby reducing the "informing power" of refractive index as a discrimination tool for glass fragments.

As a consequence, it has become necessary to use additional techniques, such as elemental composition analysis, to enhance the informing power of some comparisons between fragments

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Refractive index provides valuable information and is still the **screening tool** of choice for forensic examinations of glass. Nonetheless, if a "match" is found between two fragments by refractive index, it is recommended to conduct analysis of the elemental composition of the glass to a) further **improve the value** of such association or b) reduce the number of false positive errors.

Refractive index is defined by the Snell's law as the ratio of the wave velocity in a vacuum to the wave velocity in the transparent medium:

$$\mathbf{RI = V_{vacuum} / V_{Glass}}$$

There is an ASTM method for the automated determination of RI for the forensic comparison of glass fragments (ASTM, 2001). Advantages of this method to older versions (i.e Emmons immersion method) are that it is faster, is less tedious for the operator and provides more precise and accurate data.

The Automated Determination of Refractive Index of glass fragments using the oil immersion method with phase contrast microscope is described in the ASTM method for glass samples as small as 300 µg or ~150µm in size. As a reference a typical hair is ~100µm thick.

In this method, the glass fragments is crushed into small pieces and immersed in a micro-drop of oil. The sample is then observed under a phase contrast microscope while the temperature is increased gradually at a controlled rate in a hot stage. The oil is observed in a computer monitor via a CCD camera. The temperature at which the glass disappears (minimum contrast between the glass and the oil) is recorded electronically and the average of the match temperature from both, the heating and the cooling cycle, is converted to refractive index values according to the calibration curve of the oils. This cycles are represented in figure 5.

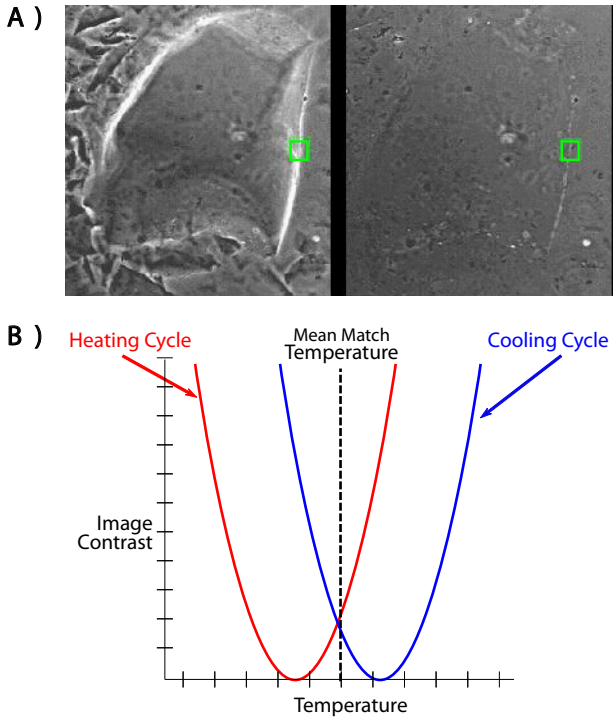

Figure 5. *A. Glass fragment above the matching temperature (left) and at the matching temperature (right). B. Heating and cooling cycle used for refractive index determination.*

This calibration curve is obtained from standard oils and checked with reference glasses. A precision of 0.1ºC is required by ASTM for inter-laboratory comparisons. Usually, a standard deviation in RI of 0.00002 may be expected for a 5h period and a standard deviation of 0.00003 over a 5 day period. Nonetheless, there are different factors that could affect the precision of refractive index measurements, such as natural heterogeneity within a glass object. For instance, there are reported larger variations within patterned glass as well as within float vs non float surfaces (Hammer, 2001). Susuki et al (Susuki, 2000), reported a variation of RI values of 0.001 for containers.

In order to take account for innate heterogeneity of the source, it is important to measure replicates for several edges and fragments. For comparisons, it is recommended to conduct at least 5-10 replicates of the known and the questioned samples.

3.5. Laboratory annealing of glass fragments

Several authors (Curran et al 2000, Locke et al 1982, Locke et al 1984, Marciuiller 1990) have reported the use of annealing methods to distinguish tempered glass from non tempered glass and as a tool to improve the discrimination power from refractive index measurements, mainly for tempered glasses.

The annealing method uses a furnace to heat the samples and remove the “stress” in the glass. The sample is then cooled down at a controlled rate. There are holders with multiple holes specially designed to place control and suspects samples into the furnace at the same time.

Refractive index of glass specimens is measured before and after the annealing process and the refractive index difference (ΔRI) is used either to classify glass as tempered or not tempered, or to conduct further comparisons.

Locke and Hayes reported that an ΔRI value 0.00120 is typical of tempered glass, while values below 0.00060 identify the glass as non-tempered. Nevertheless, there is still an overlapping range between some non tempered specimens.

3.6. Chemical measurements: elemental analysis

Extensive research has been carried out on the use of elemental analysis of glass by radiochemical, spectroscopic and mass spectrometric techniques (Stoecklein, 2001). Elemental analysis have been conducted by Atomic Absorption (Hughes, 1976; Catterick, 1978), X-Ray Fluorescence (Buscaglia, 1994; Koons, 1991), Neutron Activation (Coleman, 1973; Coleman, 1968), Scanning Electron Microscopy (Kuisma-Kursula, 2000), Inductively Coupled Plasma Atomic Amission Spectrometry (ICP-AES) (Koons, 1991) and ICP-MS (Zurhaar, 1990; Parouchais, 1996; Duckworth, 2000).

Each technique has its own advantages and shortcomings but ICP-MS has been shown to be the most effective analytical method for the comparison of trace elements in small glass fragments (Duckworth, 2002). Some of the advantages of ICP-MS over the other analytical techniques include its multi-element capability, excellent sensitivity, high sample throughput and the capability to provide isotopic information.

The isotope dilution (ID) method, when coupled to an ICP-MS analysis, usually provides the best accuracy and precision when the sample size is limited (Smith, 2000).

Although conventional solution ICP-MS (external calibration, EC and isotope dilution, ID) have been proven to be excellent tools for elemental analysis of glass, they have the disadvantage of requiring the dissolution of the sample, thereby destroying the sample prior to its introduction into the ICP-MS.

Newer sample introduction techniques, such as laser ablation (LA-ICPMS) and LIBS, overcome these limitations (Russo, 1998; Watling, 1997; Watling, 1999, Trejos 2004, Trejos 2005, Latckozy 2005, Almirall 2006, Naes 2008).

Module 4 will cover elemental analysis in more detail.

Click on **Module 3 additional material** to learn more about forensic examinations of glass: overview

Module 4. Elemental analysis of glass examinations

This module will be focused on the importance of elemental analysis on glass examinations. Glass examiners may have available a variety of techniques to conduct elemental analysis and therefore the advantages and discrimination power of each method will be described.

Elemental analysis is typically conducted at forensic laboratories by SEM-EDX, µ-XRF, acid digestion ICP-methods (ICP-OES, ICP-MS) or laser-based methods (LA-ICP-MS and LIBS). This module will be focused on the advantages and limitations of techniques that are currently available to forensic examiners and/or have the potential to become a useful tool for glass examinations.

The usefulness of elemental analysis of glass relies on premise that:
a) Regardless of standardization of glass manufacture, **minor variations** in the elemental composition remains **between and within batches**.
b) Variation on the **elemental profile of common sources are smaller than variation within the population** (different sources, different manufacturing plants, different production lots)

The discrimination capabilities of the elemental profile or fingerprint will depend on the capability of the technique to detect —with good precision— elements that are good discriminators.

4.1. SEM-EDS

Scanning Electron Microscopy- Energy Dispersive Spectroscopy (SEM/EDS) is broadly used in forensic laboratories for elemental analysis of glass. Nonetheless, glass examiners must be aware that this technique is less sensitive than other methods that will be discussed in this module.

The lack of sensitivity of SEM-EDS limits the comparison of glass fragments to only elements present at major and minor levels (>0.1%, >1000ppm).

Trace elements can not be detected by SEM-EDS and since they are the most discriminating elements, the discrimination capability of SEM-EDS is lower than other sensitive methods such as XRF or ICP.

SEM uses a focused beam of electrons, at a given accelerating voltage, to interact with the surface of the material. This beam produces a number of species that are collected by detectors capable of analyzing the specific electron, photon or x-ray.

Elemental analysis by SEM is based on the detection and identification of characteristics x-rays generated during this electron beam-target interaction. Detection can be conducted by energy dispersive detectors (EDS) or wavelength dispersive detectors (WDS). The former are the most widely used in forensic laboratories.

SEM is a **“surface” rather than a “bulk” technique** that allow the chemical characterization of minor and mayor elements.
The size of the interaction volume varies with sample and accelerating voltage. Typical penetration depths are between **2-5µm or < 1µm3**
SEM is really more useful for getting x-ray analysis from a smaller area.

Glass is refractory and non conductive in nature, requiring a coating process that is usually made with carbon. The coating step prevents sample "charging", otherwise the sample will built a charge in the interaction volume affecting the ability of the SEM to properly image the sample. Glass can also be measured at low vacuum to avoid the coating process, although still some charging may occur depending on the accelerating voltage applied.

Reeve et al (Reeeve, 1976) first reported in 1976, the use of SEM-EDS to further discriminate glass fragments that were undistinguishable by refractive index and density measurements. The authors found that the discrimination power was enhanced by measuring the elemental intensities ratios of nine different elements to calcium (Ti/Ca, Mn/Ca, Fe/Ca, Cu/Ca, Zn/Ca, As/Ca, Rb/Ca, Sr/Ca and Zr /Ca).

Two years later, in 1978, Andrasko et al (Andrasko, 1978) reported the use of the concentration ratios of Na/Mg, Na/Al, Mg/Al, Ca/K and Ca/Na to better characterize glass evidence.

In 1986 Ryland reported a classification scheme for container and sheet glass samples using the intensity ratios of Ca/Mg (by SEM/EDS) and Ca/Fe (by XRF).

Although the classification of glass fragments into categories is important for forensic examinations of glass, the ability to discriminate between glasses of the same type is even more valuable for comparisons. In this sense, SEM/EDS has some limitations due to the lack of sensitivity for trace elemental analysis. (Almirall 2006)

Other disadvantages of this technique are that precision and accuracy is generally poor. Precision depends on geometry of the sample, quantitative analysis is usually not possible and the amount of elements that can be detected is limited in comparison to other methods.

SEM/EDS has some advantages such as: it is quick, non-destructive of the sample and it can be used in forensic laboratories not only for glass analysis but also for other applications such as gun shot residues and paint analyses. SEM is better at detecting lower atomic weight elements than XRF (i.e, Na, Mg, Si, Al)

4.2. XRF

The X-ray fluorescence methods (XRF) work under similar fundamentals than SEM-EDS, being the main difference the excitation source used (see figure below).

During XRF, when a primary x-ray excitation source (photons) from an x-ray tube strikes a sample, the x-ray can be absorbed by the atom and transfer its energy to a innermost electron (photoelectric effect). If the x-ray had sufficient energy, electrons create vacancies when they are ejected from these inner shells. As the atom returns to its stable condition, electrons from the outer shell are transferred to the inner shells and in the process give off a characteristic x-ray.

There are two basic kinds of x-rays; those that are **characteristic of the atom**, and **continuum x-rays** which are just background and can't be used for identification.
The generated **characteristic x-rays** have energy equal to the **difference in energies** of the associated **electron shells.**

Because each element has a unique set of energy levels, we can get spectra that is characteristic of any particular material or element.

X-rays have a greater penetrating power than electrons. Therefore XRF samples a much **larger volume** than is possible with an electron gun (SEM), (**20 µm3, ~hundreds of µm deep**)
XRF analysis is useful for "**BULK**" analysis

Like in the case of SEM analysis, the separation is on the basis of energy (EDS) or wavelength (WDS). Energy dispersive spectroscopy (EDS) uses the energy of the incoming x-ray photon to characterize its nature. The most common type of detector is the SiLi detector. Other detectors use GeLi . Both operate on the same principle.

EDS systems are very easy to use, especially for qualitative analyses. Other strengths include:

a) Relatively inexpensive
b) Simple system - no moving parts
c) Fast - acquires entire spectrum at once (seconds)
d) Can obtain very good quantitative results in most cases if care is taken.
e) Easy to use

Wavelength dispersive spectroscopy (WDS) uses the principle of diffraction to separate the incoming X-rays. Diffraction is inherently a more precise method of detection than EDS, therefore best quantitative data can be obtained with WDS detectors because they provide better resolution. However, WDS requires a much larger detector involving multiple moving parts and special diffraction crystals and therefore require more maintenance.

WDS systems may use one or up to 3 different detectors including the Scintillation Detector, Xe sealed proportional counter and Ar Gas Flow Proportional Counter. Depending upon the particular element, each detector has a certain range where it performs the best.

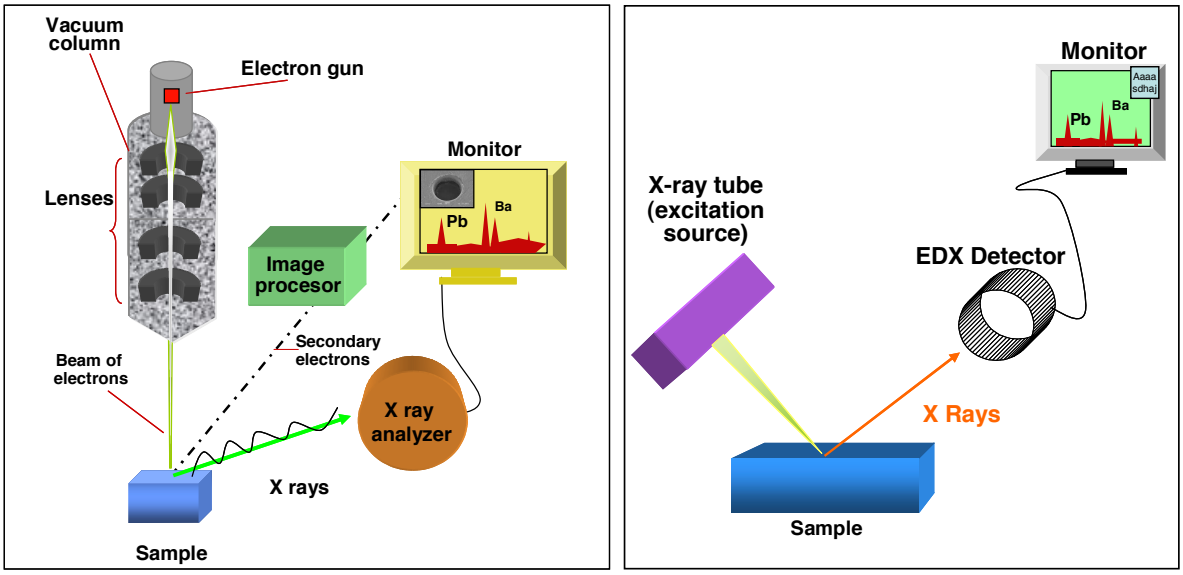

Figure 1. *Comparison of the schematic diagram of a SEM/EDS and a XRF instrument.*

Spurious peaks or artifact peaks can be produced on XRF detection. If two x-rays enter at exactly the same time they are treated as a single x-ray, resulting in Sum Peaks at high count rates.

If a Si x-ray generated within the detector crystal exits and is not converted into e- / e+ pairs, the resulting signal will be low in energy, resulting in a Si-escape Peak.

XRF has been incorporated into forensic laboratories for the analysis of glass fragments and has similar advantages than those obtainable by SEM-EDS: it is considered to be non-destructive, rapid and relatively sensitive. XRF requires relatively small samples (down to ~60µm for some µXRF systems).

XRF has the advantage over SEM of being more sensitive, especially for elements of higher atomic number. As a consequence, XRF is more discriminating that SEM allowing not only the classification of glasses into categories but also a better discrimination among glasses of the same type. Trace elements that are good glass discriminators could be easily detected by XRF methods (i.e Fe, Ti, Sr, Zr)

In addition, XRF has an advantage over SEM in that the sample often can be run in air so there is no need to evacuate a chamber to conduct the analysis. There is now available in the market an x-beam that can be installed in existing SEM units to conduct XRF analysis using the same EDS detector of the SEM instrument. This approach, although requires the use of vacuum, has the advantage of provide elemental analysis by XRF with the added imaging and mapping capabilities provided by the SEM microscope.

Although XRF is limited mainly to semi-quantitative analysis, it has been demonstrated that provides useful information and can be used as a complementary tool for discrimination of glasses.

In 1976, Reeve et al were able to distinguish 97.5% of the glass sources under study. In 1980, Dudley et al were able to distinguish 98% of the glasses originated from a set composed of 50 pair of glasses including window and non window glasses.

In 1991, Koons et al Koons, 1991) analyzed a total of 81 samples originated from tempered sheet glasses in order to evaluate the discrimination capabilities of refractive index, XRF and ICP-AES. Both methods for elemental analysis (XRF and ICP-AES) offered improved discrimination when combined with RI.

In 2008, Naes et al compared the discrimination capabilities of LAICPMS, XRF and LIBS for the elemental analysis of automobile windows. XRF yielded similar discrimination capabilities than the laser-based methods (>99%).

Some disadvantages of XRF are that they require long acquisition times (~30minutes per replicate) to improve signal to noise for trace elements. Nonetheless, they can be run unattended (i.e overnight) and therefore this reduces the time spent by the analyst.

A major limitation of XRF is that geometry of the glass fragment affects the analytical results. The sample must be at the proper location and angle to obtain reproducible data. This necessitates a flat sample at the point of x-ray contact which is not always available in real casework samples. Therefore glass examiners should compare known and unknown fragments of similar geometry and/or use embedding/polishing methods to provide flat surfaces.

4.3. ICP-AES and ICP-MS

Inductively coupled plasma methods (ICP-AES and ICP-MS) are also currently used as standard methods for the analysis of glass samples in forensic laboratories. Since the early 80's, numerous scientists have demonstrated the relevance of the application of ICP's methods to conduct elemental analysis of glass samples. (Koons 1991, Parouchais 1996, Almirall 1998, Suzuki 2000, Duckworth 2000, Montero 2002, Duckwort 2002)

In general terms, ICP instruments are composed of three main parts: the sample introduction system, the ionization source and the detector. The most common sample introduction system introduces liquid samples into the torch by the aim of two key components: the nebulizer and the spray chamber. The nebulizer, produces an aerosol of liquid particles, which are then selected according to their size in the spray chamber. Only the liquid particles that are small enough will pass from the spray chamber to the torch, the rest will be drained to the waste.

The plasma is produced in the ionization source that is comprised of the torch assembly and the load coil. The torch is the device that contained and shapes the plasma, consists of three concentric quartz tubes through which argon gas flows. The outermost tube serve to isolate the heat from the outer components of the torch, the intermediate tube is the one responsible to transport the stream of gas that will generate the plasma and the innermost tube serves as carrier gas for the sample.

The plasma is generated by injecting electrons from a Tesla coil into an argon mixture in the presence of a radiofrequency field. After the plasma is generated it is sustained by a process known as "inductively coupling". The plasma reaches high temperatures (5000-10000K) at which the sample becomes desolvated, atomized, excited and ionized.

The formed ions then travel into the detector (AES or MS). In Atomic Emission Spectrometry (AES), the emission of spectral lines can be detected and measured simultaneously.

In Mass Spectrometry (MS), the ions are extracted into an interface, which works at low-vacuum, and then they are focused and transmitted to the mass spectrometer by aid of lenses. Once in the mass spectrometer, the ions are selected according to their mass to charge ratio and finally detected.

During glass analysis by ICP-AES or ICP-MS, glass fragments are rinsed and dried, then the samples are crushed and weighed (approximately 5 to 8 mg for AES and 2mg for MS). The glass samples are then digested using a mixture of acids (HF, HCl and HNO_3). Ultrasonic baths are used to aid the digestion process and then the sample is taken to dryness at 80°C. Samples are then reconstituted in nitric acid solutions in order to be analyzed and quantified. The sample preparation scheme for glass analysis by ICP is time consuming and destructive of the sample, which are considered the main drawbacks of the technique. Nonetheless, it has been shown that its multielemental capabilities, precision and sensitivity made ICP-AES worth it, since the discrimination power is significantly improved (Koons, 1991).

The main advantages of ICP-AES are the relatively low cost and complexity, large linear dynamic range and the ease of use; the main advantages of ICP-MS are high increased multielement capability and isotopic information. ICP-MS usually provides 10 to 100 times the sensitivity of ICP-AES, allowing less sample consumption during the analysis and element detection at ultra-trace levels. ICP-MS is recognized as the most powerful technique for elemental analysis of glass.

The main disadvantage of the conventional ICP methods is that it is destructive of the sample. Fortunately, this limitation has been overcome by alternative sample introduction systems, such as laser ablation.

In the early 80's Hickman first reported a scheme for classifying glass samples as container, sheet, tableware and headlamp using RI and ICP-AES. He was able to properly classify 91% of the glass fragments from a set of 349 samples. In 1988, Koons et al (Koons 1988) were able to classify all but 4 samples from a set of 182 glass fragments originated from container and sheet glasses.

Several studies later demonstrated the superior informing power of ICP-AES over other elemental analysis techniques available at that moment for forensic analysis if glass (Koons et al 1991, Buscaglia 1994, Almirall et al 1998).

The use of ICP-MS for forensic examinations of glass was later the focus of several investigations (Zurhaar et al, Suzuki et al, Duckworth). This technique combines the strengths of ICP-AES with the added advantages of providing isotopic information and higher sensibility (up to 100 times more sensitive).

Although conventional analysis by ICP-MS follows a similar digestion procedure as for ICP-AES, the improved sensitivity decreases the consumption of sample, which is often limited in real casework. The enhancement in detection limits made also possible to combine ICP-MS with other sampling techniques such as laser ablation (LA), where the destructiveness of the sample is negligible.

In addition, the isotopic information allows the application of isotope dilution methods (ID) that improve the accuracy and precision of the results, which translates in better discrimination between glass samples (Smith 2000, Montero 2003). However, the sample preparation time is almost doubled when the isotope dilution method is used instead of the external calibration method. (Montero, 2003).

4.4. LA-ICP-MS

A Laser Ablation (LA) system enables the introduction of the products from the direct sampling of solids into the plasma. A typical LA-ICP-MS setup consists of a laser, an ablation cell and the ICP-MS, which is used as an ionization source and analyzer. A solid sample is placed inside the ablation cell and a laser beam is focused on the surface of the.

When the laser is fired, the high-energy interaction between the laser and the sample surface produces a cloud of very small particles and micro-droplets. These particles are removed from the sampling cell by a carrier gas, usually argon or helium, and are swept into the ICP plasma for atomization, ionization and subsequent analysis (Russo, 1998).

The ablation cell is provided with a quartz window. The sampling cell is mounted in a translation stage, providing X-Y positioning control for laser targeting on the sample and is under computer control. The Z axis of the translation stage is used to focus the laser via a CCD camera viewing system.

LA-ICP-MS has many advantages over the solution ICP methods. When the analysis is carried out using laser ablation, minimum sample is consumed during the analysis (aprox. 280 ng), spectroscopic interferences due to solvent are minimized. LA does not involve acid solutions, minimizing the problems linked to oxide or hydride formation, which are mainly due to solvent water. The background signal for a "dry" plasma is lower than the conventional HNO_3 blank used in solution analyses.

Since little or no chemical preparation is required, the time of analysis is reduced and, more importantly, the potential for contamination from reagents and airborne particulate material is also greatly reduced. This advantage is particularly significant when determining low analyte concentrations as such contamination can potentially mask a unique feature that may facilitate differentiation.

The elimination of the digestion and solution step not only reduces the cost of high quality reagents and standards but also eliminates the health risks associated with handling hazardous materials such as HF.

Several authors have reported the analysis of glass samples by LA. Features of forensic interest such as discrimination power, accuracy, precision and reproducibility of LA-ICP-MS have been documented to assist its incorporation into courtrooms. (Trejos et al 2004) Performance of the method has been compared versus the traditional ICP-MS solution methods of external calibration and isotope dilution in terms of time and ease of analysis, repeatability, precision, accuracy and discrimination power. (Trejos et al, 2003)

Laser ablation provided discrimination power comparable to the external calibration and isotope dilution methods. For a set of 1035 pairs of automobile glass samples, using only elemental composition by laser ablation, 99.3 % of the samples were distinguishable. When the results of elemental composition were combined with refractive index, 99.7% of the samples were discriminated. (Trejos et al, 2003)

The disadvantages to LA sample introduction include the fact that the optimization of laser parameters changes depending on the matrix, making the method development matrix dependent. The quantification is less straightforward than with solution analysis due to the lack of solid calibration standards, particularly matrix-matched standards. Matched standards are necessary for elemental analysis because the amount of mass ablated may vary according to the sample matrix.

4.5. LIBS

The use of Laser Induced Breakdown Spectroscopy (LIBS) for elemental analysis was first reported in 1962 (Brech, 1962). Laser-induced breakdown is defined as “the generation, by the end of the pulse, of a practically totally ionized gas” (Weyl, 1989). The plasma excites the substrate’s atoms, then light is emitted, and this emission spectrum is used to determine the elemental components of the sample.

The use of laser-induced plasmas and commercial instrumentation has begun to increase over the past several years (Rusak 1998). LIBS can be used to analyze many different types of samples of gases, liquids, and solids (Majidi 1992).

LIBS have the advantage if being a non destructive technique, which is a desired feature for forensic applications. In addition to speed and versatility, other advantages of LIBS are minimal sample preparation, affordability in comparison to LA-ICP-MS and portability. Moreover, LIBS is easier to operate than ICP-based methods.

There are disadvantages associate to LIBS and these include interference effects, detection limits that are typically not as good as those for ICP-MS solution work and LA-ICP-MS and the technique is less mature than other ICP-based methods. Nonetheless, LIBS has demonstrated to have a great potential for comparisons of glass fragments with good precision and discrimination capabilities similar to the gold-standard technique, LAICPMS, and therefore could become the technique of choice in the near future (Naes, 2008).

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Click on **Module 4 additional material** to learn more about elemental analysis of glass

Module 5. Sampling strategies for glass examinations

This module presents some recommendations for sampling glass fragments at the scene as well as recovery of glass fragments at the laboratory.

At the crime scene, examiners and investigators are encouraged to be critical in deciding how to sample glass fragments. Some recommendations about recovering glass fragments are: (Almirall, 2006)

1. Sample as many fragments as practical from the known source because it is important to characterize well the source for comparisons.
2. Fragments originated from laminated glass, i.e. windshields, should be collected separately and labeled to indicate the outer or the inner panel.
3. Pieces removed from a frame should be collected and packaged separately from broken fragments found at the scene.
4. Whenever is possible, identify the outer and inner surface of a glass fragment.
5. Due to the nature of glass transfer, the clothing of suspects and victims, as well as their heads are important sources of glass fragments. Combing the hair and recovering of the debris on a clean paper is recommended.
6. Tools or materials suspected from having a direct impact on the glass surface may also contain traces of glass (bat, rocks, metallic tools, bullets).
7. Glass fragments from different areas should be packaged separately and labeled properly.
8. Do not shake the garments during the collection from the suspect or victim nor during the packaging, since glass fragments can be lost.
9. It is necessary to collect and submit all items as soon as possible to the laboratory since the length of time affect the efficiency of recovery.
10. It is important to be aware of secondary transfer and avoid any cross contamination during the collection of glass evidence from the scene, suspects and victims.

At the laboratory, there are different techniques available for collection of glass fragments. These include hand picking with tweezers, scrapping, vacuuming, taping and shaking the garment over a large metal cone. The method selected depends upon the experience and criteria of the examiner as well as the nature of the sample.

The scrapping method is also used in many laboratories, and consists of using a spatula to scrap the surface of the clothing and recover the debris in a clean sheet of paper that is later inspected under the stereomicroscope. This technique is useful for particulate materials, nonetheless trace examiners must consider whether or not this method could increase the risk of contamination of other trace elements such as fibers. (Almirall, 2006).

Module 6. Introduction to Statistics for Evaluation of Glass Comparisons

This module will cover some aspects of transfer and persistence of glass literature, as well as basic terminology for descriptive statistics and match criteria.

6.1. Statistics and match criteria

Several methods for data analysis are used in many areas of forensic science to assist the interpretation of evidence. Examinations such as elemental analysis and refractive index generate quantitative data that may permit the application of statistical tools for a better characterization of evidence, to measure associations between variables, to calculate confidence intervals, estimate systematic or random errors, to assign discrimination values and to present the data in a more understandable manner. (Almirall, 1999)

There are many statistical software packages such as SYSTAT, Excel and Minitab, to mention some, which greatly simplify the statistical analysis of data.

a. Descriptive Statistics

For data reduction, it is very useful to describe the sample sets by the arithmetic mean, the standard deviation and relative standard deviation. The arithmetic mean for a set of data can be estimated using the equation (Miller, 2000):

$$\bar{x} = \frac{\sum_{i=1}^{n} xi}{n} \quad (1)$$

The standard deviation for the entire set or population is calculated as:

$$s = \sqrt{\frac{1}{n}\sum (xi - \bar{x})^2} \quad (2)$$

For practical reasons a small representative sample is used instead of the entire population and the standard deviation is approximated using the following equation:

$$s = \sqrt{\frac{1}{n-1}\sum (xi - \bar{x})^2} \quad (3)$$

The variance is another important value that measures the dispersion of the data about the mean; it is defined as the squared of the standard deviation:

$$s^2 = \frac{1}{n}\sum (x_i - \bar{x})^2 \quad (4)$$

The relative standard deviation and the percentage of relative standard deviation is a value commonly employed to estimate the precision of a set of measurements and is calculated using the standard deviation and mean values. The only difference between RSD and %RSD is that 100 multiply the latter:

$$\%\,\mathrm{RSD} = \frac{s}{\bar{x}} \times 100 \quad (5)$$

Individual comparisons of a pair of glass of samples can be performed using different approaches, some of them are described bellow:

b. Range overlap

Range overlap is a simple match criteria criterion which determines if the overall range of the control and recovered samples overlap. If so, the samples cannot be distinguished.

c. Confidence interval (± 2s, 3s or 4s)

Another method consist in calculating mean and standard deviations of both the comparison samples. If the **mean value of the recovered sample** is within the **mean value of the control plus or minus "X" standard** deviations, they are considered to match or originate from a common source. Typically, 2, 3 or 4 standard deviations are used for comparisons.

d. Student t-test

A further statistical criterion consist in using Student t-statistic not assuming equal variances according to the equation (Miller, 2000):

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \quad (6)$$

With the degrees of freedom estimated as:

$$df = n1 + n2 - 2 \quad (7)$$

Whenever the calculated t value is larger than the critical value it can be stated that the control and recovered fragments does not originated from a common source.

The t critical value and/or the p-value is displayed in the output of most of the statistical programs (i.e. SYSTAT, Excel and Minitab) for a given number of replicates of the known (K) and the questioned fragments (Q), or it can be obtained from tables in textbooks of statistics. One advantage of the t test comparison is that the statement of match or not match can be supported with a significance or probability value. Student t-test can be used at different confidence values (i.e 95%, 99%)

e. Analysis of variance

This method is used for multiple comparisons – comparisons of more than two samples (Miller, 2000). The results of an ANOVA, however, only indicate whether these multiple means differ significantly without identifying which of the means are significantly different. The Tukey's post hoc test is useful to determine which pairs of means differed significantly. (Almirall, 2006)

This test is very useful for estimating the discrimination power of a technique, where sets of large number of pair comparisons are required. The Tukey's test defines confidence values based on the mean square error (MSE) within "k" groups of "n" replicates. A further explanation of this statistical tool can be encountered in the literature (Almirall 1998; Kleinbaum 1978).

f. Hotelling's T test

HT-test is generalization of the T-test that is used in comparison of more than one variable (multivariate analysis). The limitation of this approach is that requires at as many replicates per sample as n+1, where n is the number of variables measured (i.e number of elements analyzed), therefore it may be time consuming and not practical, depending of the technique used for analysis and the amount of sample available.

g. Bayesian approach

Several authors have reported the use of the Baye´s theorem to assist the interpretation of evidence (Curran et al 2000, Evett 1990, Walsh 1996) The Bayesian approach uses likelihood ratios to reverse conditional probabilities or obtain probability of contact given the evidence from probability of the evidence given contact

This method is particularly popular within the forensic community in Europe. Information regarding the transfer, persistence and recovery of glass is necessary to estimate the likelihood ratios. For example, information that may be needed from the case includes

a) number of particles transferred -related to breaking scenario
b) persistence of particles after "short "period of time -related to time lapse and post-incident activity
c) presence of glass on clothing prior to incident -requires population information

d) retention properties of clothing
e) type of glass involved in the case

6.2. Informing power of analytical methods: forming the opinion

Informing power or discriminination capabilites of the analytical methods have been reported in the literature. Many papers are available that support the fact that the elemental profile of glass offers a very discriminating tool for comparison of glass fragments and complementary information to that obtained by refractive index analyses. (Buscaglia, 1994; Koons, 1991; Koons, 2002; Montero, 2003; Parouchais, 1996).

There is agreement in the forensic community that refractive index remains the screening tool of choice for glass comparisons and that the method provides valuable information. Nevertheless, when a match is suspected between two glass fragments, it is strongly recommended to apply sensitive elemental analysis methods to improve the value of the association and to reduce the number of possible false associations.

In general he increasing order of discrimination power of techniques is as follows:

SEM <<< XRF, LIBS < ICP-OES < ICP-MS, LAICPMS

Although ICPMS methods are regarded as the most powerful discriminating tools in glass comparisons, similar discrimination capabilities could be obtained by XRF, LIBS and ICP-OES in cases where the sample size, geometry and sample type is adequate. XRF, LAICPMS and LIBS could provide similar discrimination capabilities for the comparison of glass samples (>99%, depending on the set under study) (Naes, 2008). LAICPMS and LIBS have the capabilities to discriminate between glass fragments that have been produced in the same manufacturing plant just few weeks apart (Almirall, personal communication). Similar studies within a single manufacturing plant have not been conducted yet for XRF.

An interesting survey of the variation of RI and elemental composition in a single plant for a period of 4.5 years as well as variation between 36 different manufacturing plants within the United States showed that the variation of RI is very limited while elemental analysis can distinguish small differences in glass composition even from glass originating from the same plant over short periods of time. (Montero, 2002, Almirall, 2006)

Another study has shown that for a set of 45 headlamps originating from different sources, refractive index was able to discriminate only 90% a of the headlamps, while the combination of RI with elemental analysis enhanced those values to 100% (Trejos, 2003)

Click on **Module 6 additional material** to learn more about statistical analysis for glass comparisons

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