Elemental Analysis of Glass

Scientific Working Group for Materials Analysis (SWGMAT)

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1. Scope

1.1. This guideline describes methods for determining the concentrations of major, minor, and trace elements in glass fragments. The methods described may be used to measure either absolute or relative element concentrations in glass fragments ranging in mass from gram(s) to less than one microgram.

1.2. The analytical considerations for the use of scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), X-ray fluorescence spectrometry (XRF), inductively coupled plasma-optical emission spectrophotometry (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS) are described. Other analytical techniques, such as atomic absorption spectrophotometry may also be used but are not specifically included in this guideline because they are not as widely used as those listed.

1.3. Several of the analytical methods described are destructive. Therefore, all nondestructive examinations must be completed and legal considerations concerning the destruction of evidence must be satisfied prior to conducting these measurements.

1.4. This guideline does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this guideline to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

1.5. This guideline provides general considerations, rather than detailed instrumental operating instructions. Measurement of element concentrations in glass fragments can be reliably obtained using any of many makes and models of instruments, each with its own specific instructions. The examiner should use this guideline in conjunction with instructions provided by the manufacturer of the particular instrument being used and with validated internal laboratory procedures for the characterization of glass evidence.

2. Reference Documents

2.1. Scientific Working Group for Materials Analysis Documents

Trace evidence recovery guidelines
Quality assurance guidelines

2.2. American Society for Testing and Materials Standards

D1193 *Specifications for Deionized Water*
E50 *Reagent Purity*
E135 *Standard Terminology Relating to Emission Spectroscopy*

2.3. Environmental Protection Agency Test Method

Method 200.7 Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

3. Terminology

Analytical blank is a solution containing all reagents in the proportions used to prepare glass samples, processed in the same manner as a glass sample without the presence of the glass.

Analytical curve is the functional relationship between instrument response and analyte concentration.

Analytical sample is that portion of a specimen analyzed.

Calibration standards are a series of known standards used for calibration of the instrument (i.e., preparation of the analytical curve). A calibration standard containing zero added concentrations of analytes is referred to as a calibration blank.

Calibration verification standard is a single-element or multielement standard of known concentrations, obtained from a different source than those used for the calibration, used to monitor and verify instrument performance on a daily or case-by-case basis.

Classification is the placement of a specimen into a particular product-use or manufacturer source category based upon the comparison of measured attributes with a database of known attributes for each category. Examples of classes include sheets, containers, light bulbs, tableware; or Libby-Owens-Ford, Pilkington, Corning; or float line A, float line B from a given manufacturing plant.

Dead time in X-ray spectrometry is the amount of time that a detector is receiving a signal that is not being counted.

Discrimination is the ability to distinguish between two glass objects in the same class based on comparison of their measured attributes.

Escape peak in energy dispersive X-ray spectrometry is a spurious peak whose energy is equal to the difference in energies between an analyte element's characteristic X-ray and a detector photon, such as SiKα.

Internal standard is an element or isotope either inherent in or added to samples and calibration standards at a known concentration. It is used to correct for differences in sensitivity between samples or among samples and standards.

Limit of detection (solution methods) is the analyte concentration equivalent of a signal that is equal to three times the standard deviation of a series of ten replicate measurements of an analytical blank signal.

Limit of detection (X-ray methods) is the analyte concentration equivalent of a signal that is equal to three times the square root of the background in the energy region of the spectrum for the analyte of interest.

Linear dynamic range is the concentration range over which the analytical curve remains linear.

Relative standard deviation (RSD) is the standard deviation divided by the mean.

Sensitivity is the slope of the analytical curve (i.e., the increase in analytical response corresponding to an increase in one unit of analyte amount, either in mass or concentration units). Units of response and analyte amount must be stated.

Specimen is a portion of a glass object available for examination.

Take-off-angle in X-ray spectrometry is the angle formed between the surface of the specimen and the line from the average point of origin of fluorescent X-rays to the center of the detector.

4. Summary of Guideline

4.1. This guideline describes several techniques for determining selected major, minor, and trace elements in glass fragments. Each technique described may either be used to determine the concentrations of elements in a glass fragment or to determine the concentrations of several elements relative to each other. A brief introduction to the principles, analytical methodologies, uses, and advantages and limitations of scanning electron microscopy-energy dispersive X-ray spectrometry, energy dispersive X-ray fluorescence spectrometry, inductively coupled plasma-optical emission spectrophotometry, and inductively coupled plasma-mass spectrometry in forensic glass examination is presented. The reader is encouraged to see the cited references and bibliography for more specific information.

5. Significance and Use

5.1. The concentrations of certain elements in glass serve to chemically characterize its source. The concentrations of several elements are intentionally controlled by the manufacturers to impart specific end-use properties to a particular glass product, and in some instances can be used to identify the product type of a recovered glass fragment. However, even individual glass objects that have major element concentrations within the manufacturer's acceptable ranges display variations that can be measured and provide useful points for a forensic comparison. Glass manufacturers generally do not control the concentrations of trace elements, except as needed to impart color or to keep them below levels that would impart undesirable physical or optical properties to the glass. The differences in concentrations of manufacturer-controlled elements or uncontrolled trace elements may be used to differentiate sources when the variation among objects exceeds the variation within each object. Element concentrations may be used to differentiate among glasses made by different manufacturers, glasses from different production lines of a single manufacturer, specific production runs of glass from a single manufacturer, and in some instances individual glass objects produced at the same production facility.

5.2. The discrimination potential of element concentrations in glass was documented as early as 1973. Several instrumental methods have been used by forensic scientists including neutron activation analysis (Coleman and Goode 1973), flameless atomic absorption (Hughes et al. 1976), inductively coupled plasma-optical emission spectrophotometry techniques (Hickman 1987; Koons et al. 1988), energy dispersive X-ray fluorescence spectrometry (Andrasko and Machly 1978; Reeve et al. 1976), scanning electron microscopy-energy dispersive X-ray spectrometry (Ryland 1986), and inductively coupled plasma-mass spectrometry (Haney 1977; Parouchais et al. 1996).

5.3. Comprehensive reviews of the literature on the application and advantages and limitations of several of the analytical techniques used for the elemental analysis of forensic glass samples have been reported (Almirall 2001; Buscaglia 1994).

Several factors that can be considered in selecting the appropriate analytical method for the analysis of glass in the forensic laboratory are shown in the following table.

Table 1: Analytical Methods for Glass Analysis

Click here to see Table 1

6. Sample Handling

6.1. Sample Preparation

The selection of a sample preparation technique will depend on the particular method to be used for analysis, fragment size and shape, and the purpose of the examination.

6.2 Sample Cleaning

All samples must be cleaned prior to elemental analysis to remove surface contamination or residual material from previous analytical determinations. Cleaning may include washing samples with soap and water, with or without ultrasonication, and rinsing in water, followed by rinsing in acetone, methanol, or ethanol, and drying. Soaking in various concentrations of nitric acid for 30 minutes or longer and rinsing with deionized water and ethanol prior to analysis removes most surface contamination without affecting the measured concentrations of elements inherent in the glass. For very small fragments sampled by laser ablation, preablation may substitute for cleaning (see Section 6.5 in the *Scientific Working Group for Materials Analysis Collection, Handling, and Identification of Glass*).

6.3. In order to assess the variability within each glass source, multiple analytical samples should be selected wherever possible. The size and number of samples selected for analysis will depend upon the analytical technique, interpretive criteria, and size of the fragments available for analysis. In general, measurement precision decreases with decreasing sample size.

7. Analysis

7.1. Scanning Electron Microscopy with X-Ray Spectrometry

7.1.1. Instrument description and operating principle

7.1.1.1 In scanning electron microscopy, a focused electron beam is scanned over the surface of a sample, causing, among other things, the emission of X-rays. The wavelengths or energies of the detected X-rays are used to identify the elements, and the intensities of the X-ray peaks in the measured spectrum correlate with the quantities of each element present in the sample area exposed to the electron beam.

7.1.1.2. Two methods of X-ray detection can be defined by the manner in which the data are collected and displayed. The methods described are wavelength dispersive X-ray spectrometry (WDS) and energy dispersive X-ray spectrometry (EDS).

7.1.1.2.1. Wavelength dispersive X-ray spectrometry sorts the generated characteristic and background X-ray emissions by their wavelengths using a crystal monochromator. Wavelength dispersive X-ray spectrometry offers the best spectral resolution of all of the X-ray emission methods. Due to the high resolution and low background, the lowest levels of detection and most reliable quantitation are attainable. Cost and complexity of instrumentation have limited its use with scanning electron microscopy in forensic science laboratories.

For this reason, scanning electron microscopy-wavelength dispersive X-ray spectrometry is not discussed in further detail in this guideline.

7.1.1.2.2. Energy dispersive X-ray fluorescence spectrometry sorts the generated characteristic and background X-ray emissions by their energies. Energy dispersive X-ray fluorescence spectrometry offers fast, simultaneous data collection, and the cost of instrumentation is significantly lower than that of wavelength dispersive X-ray spectrometry. Energy dispersive X-ray spectrometry is most commonly used with scanning electron microscopy in forensic laboratories.

7.1.1.3. Because a scanning electron microscope can scan a focused electron beam over a small area, scanning electron microscopy-energy dispersive X-ray spectrometry has the ability to detect the presence of elements in a small sample, such as a questioned glass fragment.

7.1.2. Uses of scanning electron microscopy-energy dispersive X-ray spectrometry in glass examination

7.1.2.1. In most published studies, scanning electron microscopy-energy dispersive X-ray spectrometry measurements of element intensity ratios have been applied to classification of glass types (Ryland 1986; Terry et al. 1982). An analytical scheme that combines measurement of Ca/Mg intensity ratios obtained using scanning electron microscopy-energy dispersive X-ray spectrometry with Ca/Fe ratios obtained using X-ray fluorescence spectrometry has been used with good success by several forensic laboratories to classify glass fragments into sheet and container categories (Keeley and Christofides 1979; Ryland 1986).

7.1.2.2. For discrimination among glass sources, a scanning electron microscopy-energy dispersive X-ray spectrometry protocol was reported for determining the ratios of the intensities of Na/Mg, Na/Al, Mg/Al, Ca/Na, and Ca/K in glass fragments (Andrasko and Machly 1978). Measurement of these ratios by scanning electron microscopy-energy dispersive X-ray spectrometry was incorporated into a scheme with refractive index, density, and emission spectrography. Thirty-eight out of 40 window glasses analyzed by this scheme were found to be distinguishable. The variation in the measured element intensity ratios by scanning electron microscopy-energy dispersive X-ray spectrometry was found to be consistent across a new sheet, an old sheet, and within a single fragment of glass.

7.1.3. Analytical considerations

7.1.3.1. Sample preparation

7.1.3.1.1. Samples should be cleaned and dried according to Section 6.2. prior to embedding. Small irregularly shaped samples may be analyzed, but flat sample surfaces are recommended whenever possible and are particularly important when accurate, precise quantitative results are desired. This may be achieved by embedding the sample in a resin that is subsequently cured and polished to provide a flat surface. The embedded sample may need to be coated with a thin conductive layer, such as carbon, to reduce charging from the electron beam. The glass sample is altered and partially consumed during the embedding and polishing process.

7.1.3.2. Scanning electron microscopy-energy dispersive X-ray spectrometry measurements are made on individual fragments of glass. The beam current and magnification used will depend on sample size and instrument capabilities. Magnifications on the order of 1,000X are adequate for most samples, but magnifications up to 10,000X can be used.

7.1.3.3 An accelerating voltage of 10 to 20 kilovolts is typically used.

7.1.3.4. The scan area used should be as large as possible to obtain representative spectra from the sample. The magnification, scan area, and operating parameters should be consistent among known and questioned specimens being compared.

7.1.3.5. The operating current should be adjusted for optimal count rates so that analytical time is not excessive. It should be noted that Na migration could occur at high operating currents. Na migration is evidenced by a significant drop in
NaK_{α} intensity with time.

7.1.3.6. The detector-to-specimen distance and the takeoff angle should be optimized for each instrument.

7.1.3.7. Acquisition times are selected based on sample size and count rate. These can be either based on a fixed time during which the detector is acquiring data (e.g., a specified number of live seconds) or on achieving a specified intensity for a selected X-ray energy (e.g., acquiring spectral data until the intensity of the Ca K_{α} peak reaches 50,000 counts). The advantage of using the latter method is that it aids in normalizing the data and yields similar precision for samples of different sizes and shapes.

7.1.3.8. Spectra should be acquired from replicate samples in order to obtain a measure of the variability within the sample and specimen. The most frequently used methods of data interpretation are spectral comparison by simple overlaying of X-ray spectra of two fragments or by calculating the element intensity ratios.

7.1.3.9. Full quantitative analysis is possible but requires calibration with matrix-matched standards embedded in each stub along with the analytical samples under identical operating conditions.

7.1.4. Advantages of scanning electron microscopy-energy dispersive X-ray spectrometry for glass examinations

7.1.4.1. The most significant advantages of scanning electron microscopy-energy dispersive X-ray spectrometry for determining element concentrations in glass fragments are that it is nondestructive, applicable to very small samples, and readily available to many forensic laboratories.

7.1.4.2. Scanning electron microscopy-energy dispersive X-ray spectrometry, when combined with energy dispersive X-ray fluorescence spectrometry, permits product-use classification of glass samples.

7.1.4.3. Scanning electron microscopy-energy dispersive X-ray spectrometry is useful in forensic laboratories as a rapid, screening method that can add some discrimination capability to optical and physical measurements.

7.1.5. Limitations of scanning electron microscopy-energy dispersive X-ray spectrometry for glass examinations

Several characteristics of scanning electron microscopy-energy dispersive X-ray

spectrometry have limited its widespread application in forensic laboratories for the comparison of glass fragments.

7.1.5.1. The irregular shape of some small glass fragments makes precise and accurate quantitative determination of element concentrations difficult. Variations in fragment surface orientation contribute to relatively poor precision and accuracy of results obtained by scanning electron microscopy-energy dispersive X-ray spectrometry compared with other methods of analysis.

7.1.5.2. The compositional differences distinguishable by scanning electron microscopy-energy dispersive X-ray spectrometry will, in most instances, manifest themselves in readily distinguishable refractive index and/or density values.

7.1.5.3. The detection limits on a concentration basis of scanning electron microscopy-energy dispersive X-ray spectrometry are poor, typically in the 0.1 percent range; and therefore, the number of elements that can be determined is limited. Many elements, such as Ba and Sr, which are useful for both classification and source discrimination, are present in most glasses at levels that are not detectable using scanning electron microscopy-energy dispersive X-ray spectrometry.

7.1.5.4. The detection limits for scanning electron microscopy-energy dispersive X-ray spectrometry are approximately an order of magnitude poorer than for scanning electron microscopy-wavelength dispersive X-ray spectrometry.

7.2. X-Ray Fluorescence Spectrometry

7.2.1. Instrument description and operating principles

7.2.1.1. X-ray fluorescence spectrometry is an elemental analysis technique based upon the measurement of characteristic X-rays emitted from a sample following excitation by an X-ray source. The energies or wavelengths of the detected X-rays are used to identify the elements, and the intensities of the X-ray peaks in the measured spectrum correlate with the quantities of each element present in the sample area exposed to the X-ray beam.

7.2.1.2 As with X-ray methods associated with scanning electron microscopy, two X-ray fluorescence spectrometry methods, wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence spectrometry are also defined by the manner in which the data are collected and displayed.

7.2.1.2.1. Wavelength dispersive X-ray spectrometry (see Section 7.1.1.2.1. for a description) offers the best spectral resolution of all of the X-ray fluorescence methods. The glass manufacturing industry for quality control purposes uses wavelength dispersive X-ray spectrometry extensively. However, in addition to the high cost of instrumentation, wavelength dispersive X-ray spectrometry requires relatively large, flat samples, both of which severely limit its forensic use. Wavelength dispersive X-ray fluorescence spectrometry is not discussed in further detail in this guideline.

7.2.1.2.2. Energy dispersive X-ray fluorescence spectrometry (see Section 7.1.1.2.2. for a description) methods are considered nondestructive, surface or near surface techniques. Fluorescent X-rays that reach the detector typically originate from a glass sample region no deeper than about 100µm. To analyze small, irregularly shaped fragments common to

forensic casework, micro- and capillary X-ray fluorescence spectrometry techniques are appropriate. In these techniques, the beam is collimated down to micrometer size beam diameters, typically 100 to 300µm for forensic glass analyses.

7.2.2. Uses of energy dispersive X-ray fluorescence spectrometry in glass examination

7.2.2.1. Energy dispersive X-ray fluorescence spectrometry has been used to classify unknown source glass samples as to their product-use types (Dudley et al. 1980; Howden et al. 1977; Ryland 1986).

7.2.2.1.1. Energy dispersive X-ray fluorescence spectrometry is capable of distinguishing glass samples of different product-use type whose refractive indices are indistinguishable (Dudley et al. 1980).

7.2.2.1.2. Using element intensity ratios determined by energy dispersive X-ray fluorescence spectrometry, sheet and container sources were correctly classified in 93 percent of the cases tested (Ryland 1986). A combined energy dispersive X-ray fluorescence spectrometry and scanning electron microscopy-energy dispersive X-ray spectrometry procedure was reported to be useful for classification of modern sheet and container glasses. These samples could not be separated by scanning electron microscopy-energy dispersive X-ray spectrometry determination of Ca/Mg alone. Using a 35 kilovolts accelerating voltage in energy dispersive X-ray fluorescence spectrometry, a low Ca/Fe ratio is indicative of sheet glass and a high Ca/Fe ratio indicates a container or tableware source. Some samples had intermediate values and were unclassifiable with this technique.

7.2.2.1.3. Energy dispersive X-ray fluorescence spectrometry was used to measure the concentrations of 10 elements as ratios to Ca in 50 pairs of window (nonfloat) and nonwindow glasses having refractive indices that are indistinguishable in the fourth decimal place (Howden et al. 1977). When element intensity ratios were used, 95 percent of the individual glass specimens were correctly classified as to source type. The classification rules were made using only refractive index, As, Fe, and Mg as points of comparison.

7.2.2.2. Discrimination among sources of glass may be accomplished by energy dispersive X-ray fluorescence spectrometry using both qualitative and semiquantitative methods.

7.2.2.2.1. Some glasses contain elements, such as As, Rb, and Mn, which are readily measured by energy dispersive X-ray fluorescence spectrometry but are not present at detectable levels in all glasses. In such instances, discrimination of samples may be attained by a qualitative comparison of the spectra. Exclusion cannot be made based on the absence of element(s) in one sample that are present at or near the limit of detection in the other comparison sample (Dudley et al. 1980).

7.2.2.2.2. Semiquantitative analysis of the energy dispersive X-ray fluorescence spectra can be used to discriminate among glass samples of different origins. Energy dispersive X-ray

fluorescence spectrometry using element intensity ratios successfully discriminated all but two of 81 window glass samples in one study (Reeve et al. 1976). These two samples were distinguishable from each other by optical properties.

7.2.2.2.3. The addition of energy dispersive X-ray fluorescence spectrometry measurements of Si/Ca, Fe/Ca, and Sr/Zr to an analytical scheme improved the source discrimination capability among automobile side window glasses over the use of refractive index measures alone (Koons et al. 1991). In this study, energy dispersive X-ray fluorescence spectrometry was slightly more discriminating than refractive index but not as discriminating as inductively coupled plasma-optical emission spectrophotometry.

7.2.2.2.4. One study (Dudley et al. 1980) evaluated the ability of energy dispersive X-ray fluorescence spectrometry measurements to discriminate glass sources with indistinguishable refractive indices, in addition to assessing its classification capability. Using element ratios to Ca, the glasses from 49 of the 50 pairs of samples of window and nonwindow origin were distinguished.

7.2.3. Analytical considerations

7.2.3.1. Sample preparation

7.2.3.1.1. Samples should be cleaned and dried according to Section 6.2. prior to sample mounting or analysis.

7.2.3.1.2. The selection of a sample mounting technique depends on the sample size, beam collimator size, X-ray fluorescence spectrometry sample chamber design, availability of mounting material and polishing instrumentation, and the purpose of the examination. The following is a list of some methods that have been used successfully for mounting glass samples in the sample chamber: placing directly over the aperture with no support; using a plastic support; suspending over the aperture by thread; affixing on X-ray film followed by inverting; suspending a particle of glass over the aperture by super-gluing the back side to a small diameter high-purity graphite spectrographic electrode (with pointed tip); and embedding in a resin that is subsequently cured and polished to provide a flat surface. Flat sample surfaces and thick samples are recommended whenever possible but are essential when accurate, precise quantitative results are desired. When attempting to compare irregularly shaped samples without polishing, precision may be improved by selecting known samples of similar shape and size to the questioned samples.

7.2.3.2. Energy dispersive X-ray fluorescence spectrometry measurements are generally made on individual fragments of glass using a beam collimator of 3mm or less, depending on sample size and instrument capabilities.

7.2.3.3. An accelerating voltage of 35 kilovolts can be used for end-use classification purposes, and a fixed setting in the range of 35 to 50 kilovolts is suitable for discrimination purposes.

7.2.3.4. The operating current should be adjusted as needed to obtain good count rates, optimally less than 50 percent detector dead time.

7.2.3.5. Acquisition times can be selected based on sample size and count rate, as

with scanning electron microscopy-energy dispersive X-ray spectrometry. See Section 7.1.3.7. for more details.

7.2.3.6. Quantitative concentrations are routinely determined with energy dispersive X-ray fluorescence spectrometry on comparatively large, flat samples. For the most accurate quantitative determinations, calibration with matrix-matched standards is required. Standardless quantitative mathematical models for calibration do exist; however, they may result in poorer accuracy. Because primary and fluorescent X-rays do not reproducibly penetrate the small size and the irregular shape of forensic glass fragments, quantitative elemental concentrations generally cannot be determined with adequate precision and accuracy without sample preparation to provide a flat surface. However, ratios of the intensities of two X-ray lines of similar energies are reasonably constant. Therefore, comparison of the elemental compositions of glass fragments of varying masses and shapes can be performed with good precision using intensity ratios. Intensity data for selected elements should be ratioed after baseline subtraction and escape peak corrections have been performed. Like scanning electron microscopy-energy dispersive X-ray spectrometry spectra, energy dispersive X-ray fluorescence spectra are best compared either by overlaying spectral images or by comparing calculated peak intensity ratios.

7.2.4. Advantages of X-ray fluorescence spectrometry for glass examinations

7.2.4.1. The most significant advantage of any of the X-ray techniques is that they are nondestructive. They are rapid, fairly sensitive, and can be performed with minimal sample preparation.

7.2.4.2. Energy dispersive X-ray fluorescence spectrometry analysis is less spatially discriminating than scanning electron microscopy-energy dispersive X-ray spectrometry due to its larger analytical beam size and the greater penetration depth of X-rays compared to electrons. However, the limits of detection of energy dispersive X-ray fluorescence spectrometry for most elements are generally better than for scanning electron microscopy-energy dispersive X-ray spectrometry. Specifically, the higher energy excitation typical of energy dispersive X-ray fluorescence spectrometry yields better sensitivity for higher atomic number elements than scanning electron microscopy-energy dispersive X-ray spectrometry. Thus, energy dispersive X-ray fluorescence spectrometry has better analytical capabilities for several good glass source-discriminating elements, such as Mn, Sr, and Zr. Significantly better peak-to-background ratios can be obtained using energy dispersive X-ray fluorescence spectrometry compared with scanning electron microscopy-energy dispersive X-ray spectrometry, particularly with instruments that allow the incident X-ray beam to be collimated to a small spot size.

7.2.5. Limitations of X-ray fluorescence spectrometry for glass examinations

7.2.5.1. Most of the disadvantages pertaining to quantitation of element concentrations in small irregularly shaped particles are more pronounced in energy dispersive X-ray fluorescence spectrometry than they are in scanning electron microscopy-energy dispersive X-ray fluorescence spectrometry.

7.2.5.2 The greatest limitation of energy dispersive X-ray fluorescence spectrometry is the necessity to employ matrix-matched multielement standards in order to obtain accurate quantitative results.

7.2.5.3. Disadvantages of wavelength dispersive X-ray spectrometry compared to

energy dispersive X-ray fluorescence spectrometry are that the instrumentation is more expensive and that larger samples are required.

7.2.5.4. The operation of X-ray tubes at high powers may cause the discoloration of some glass samples.

7.3. Inductively Coupled Plasma-Optical Emission Spectrophotometry

7.3.1. Instrument description and operating principles

7.3.1.1. In most inductively coupled plasmas, an electrical discharge is initiated in a flowing stream of inert gas, usually argon, and then sustained by a surrounding radio frequency field. The resulting stable discharge, or plasma, has the appearance of a small continuously glowing flame, with temperatures in the range of 7,000-10,000K. When a sample is introduced into the plasma, extensive atomization, ionization, and excitation of the sample atoms occur.

7.3.1.2. As the ions and atoms present in the sample enter cooler portions of the plasma and drop to lower excited states, they emit light at characteristic wavelengths. In an inductively coupled plasma-optical emission spectrophotometer, this emission is dispersed with a spectrophotometer and its intensity is measured. Comparison of the emission intensities of a sample with those of standard solutions is used to determine the concentration of the elements in the sample.

7.3.1.3. Glass samples can be introduced into the plasma either by dissolving them and nebulizing the resulting solution or by direct solid sampling. Only solution methods are discussed in the inductively coupled plasma-optical emission spectrophotometry portion of this guideline. Direct solid sampling is outlined in the inductively coupled plasma-mass spectrometry portion of the guideline because solid sampling is more commonly used with mass spectrometry than with optical emission spectophotometry.

7.3.2. Use of inductively coupled plasma-optical emission spectrophotometry in glass examination

7.3.2.1. The initial inductively coupled plasma-optical emission spectrophotometry methods developed for glass analysis were primarily designed for purposes of classification. An inductively coupled plasma-optical emission spectrophotometry analytical method was developed to determine the concentrations of Mn, Fe, Mg, Al, and Ba in glass fragments (Catterick and Hickman 1981). Over the next several years, the concentrations of additional elements in glass by inductively coupled plasma-optical emission spectrophotometry were determined, and 6 to 10 element classification schemes based on comparison with a glass database divided into nine product categories were developed (Hickman 1981; Hickman et al. 1983). Currently, the protocol most widely used for casework was developed for determining the concentrations of 10 elements (Al, Ba, Ca, Fe, Mg, Mn, Na, Ti, Sr, and Zr) with excellent analytical precision in milligram-sized glass fragments (Koons et al. 1988). A combination of five of these elements was shown to provide good classification into the two categories of sheet and container glass. Inductively coupled plasma-optical emission spectrophotometry has also been used to associate food containers to the manufacturing plants in which they were made and to identify sources of contaminant glass in cases involving product tampering (Wolnik et al. 1989).

7.3.2.2. In further studies, the distributions of up to 22 elements, most measured by

inductively coupled plasma-optical emission spectrophotometry, in various glasses were shown to provide excellent discrimination capability among sources within a product class (Hickman 1983; Hickman et al. 1983). In a study measuring the concentrations of 10 elements in automobile side-window glasses, the probability that two glasses from different vehicles would be indistinguishable was reported to be one in 1,080, compared with one in five for refractive index alone and one in ten for energy dispersive X-ray fluorescence spectrometry analysis alone (Koons et al. 1991). Studies have shown that using inductively coupled plasma-optical emission spectrophotometry sheets of glass produced within minutes of each other in a single float-glass production line can be differentiated. In a recent study using statistical analysis of samples collected in casework, it was reported that inductively coupled plasma-optical emission spectrophotometry measurements provide very high discrimination capability. The probability that two glass fragments from different sources will have indistinguishable concentrations of ten elements is extremely small (Koons and Buscaglia 1999).

7.3.3. Analytical considerations

7.3.3.1. Prior to analysis, each fragment must be washed to remove surface contamination and residual fluids from refractive index and density measurements. Typically, this is done by soaking in HNO_3, rinsing repeatedly with deionized water, then ethanol, followed by drying.

7.3.3.2. Fragments, typically weighing 0.2 to 8mg, are obtained by crushing the specimen between sheets of clean plastic. Prior to dissolution, analytical samples must be weighed to the nearest 0.01mg, or better, on a microbalance, whose calibration is checked immediately preceding each use.

7.3.3.3. Dissolution procedures involve the use of high purity HF, HNO_3, and, in some cases, HCl (Catterick and Hickman 1981; Koons et al. 1988). A typical procedure consists of the digestion of glass fragments in polypropylene tubes by the addition of concentrated HF and other mineral acids, taking the solution to dryness (to remove all residual HF) by heating the tubes, and complete redissolution of the residue in a strong acid, such as HCl. This dissolution procedure typically requires several days. The complete removal of HF is required to prevent deterioration of glass or quartz spray chambers, nebulizers, and torches present on most inductively coupled plasma instruments.

7.3.3.4. An internal standard, usually scandium, must be added to each sample and standard solution in order to correct for minor differences in analytical sensitivity among samples and among samples and standards.

7.3.3.5. The analytical curve for each element is prepared using a minimum of four calibration standards, including a calibration blank. Multielement calibration standards containing the internal standard and the diluting acids in the same concentration as the sample solutions are used. The concentration ranges for each analyte element must span the concentrations in the sample solution.

7.3.4 Advantages of inductively coupled plasma-optical emission spectrophotometry

7.3.4.1. Analytical characteristics of inductively coupled plasma-optical emission spectrophotometry instruments include the capability to determine a wide

range of elements, long linear response ranges, a limited number of spectral and matrix interferences, low detection limits for many elements of interest, and ease of automation of data handling.

7.3.4.2. The detection limits of this method vary slightly from day to day. Typical values are 0.01 to 0.1µg/g in the glass. For samples smaller than 5mg, these detection limits are raised somewhat because of increased dilution factors. Precision measurements for all elements when present in the middle of their respective concentration ranges are generally better than two percent relative standard deviation.

7.3.5. Limitations of inductively coupled plasma-optical emission spectrophotometry

7.3.5.1 The dissolution of glass fragments is destructive, requires the use of corrosive acids and high purity reagents, and sample digestion is time-consuming compared to sample preparation for X-ray methods.

7.3.5.2. In comparison to most forensic laboratory equipment, inductively coupled plasma-optical emission spectrophotometry instrumentation is costly, requires more extensive operator training, and, to date, a limited number of forensic applications for it have been found.

7.4. Inductively Coupled Plasma-Mass Spectrometry

7.4.1. Instrument description and operating principles

7.4.1.1. The inductively coupled plasma torch is an excellent ionization device. Instruments made by coupling inductively coupled plasma with mass spectrometry as an ion isolator and detector have shown improved analytical capabilities suitable for glass fragment analysis. Mass spectrometry instruments may be of quadrupole, time-of-flight, or magnetic-sector design with single or multiple electron multiplier detectors.

7.4.1.2. The useful features of inductively coupled plasma-mass spectrometry compared with inductively coupled plasma-optical emission spectrophotometry are a smaller and better-defined set of spectral interferences, detection limits roughly 1,000-fold lower, longer linear working ranges, and more rapid scanning capability. The better sensitivity of mass spectrometry compared to optical emission spectrophotometry permits use of a smaller sample size and the quantitative determination of some trace elements not detectable by inductively coupled plasma-optical emission spectrophotometry. Using solution inductively coupled plasma-mass spectrometry, approximately 40 elements can be determined in a 1mg glass fragment.

7.4.1.3. Another characteristic of inductively coupled plasma-mass spectrometry is that samples need not be introduced as solutions. The rapid scanning speed of the mass spectrometer allows measurement of transient signals, such as those produced with laser ablation of solid samples used to sweep a vapor into the plasma for analysis (Montaser et al. 1998).

7.4.2. Uses of inductively coupled plasma-mass spectrometry in glass examinations

7.4.2.1. The first reported studies of the use of inductively coupled plasma-mass spectrometry for the forensic comparison of glass fragments indicated an ability to quantitatively determine the concentrations of 40 to 62 elements in glass fragments as small as 500µg (Parouchais et al. 1996; Zurhaar and Mullings 1990). For any given glass, approximately 40 of these elements are likely to be present at detectable concentrations.

7.4.2.2. More thorough studies have been aimed at developing reliable analytical procedures and determining which elements provide the best discrimination capability. Reported analytical precisions for sample introduction in solution are typically better than 10 percent relative standard deviation for elements present at concentrations greater than a few parts per billion (Duckworth et al. 2000).

7.4.3. Analytical considerations

7.4.3.1. The dissolution procedures for inductively coupled plasma-mass spectrometry are similar to the procedures used for inductively coupled plasma-optical emission spectrophotometry, except that HNO_3 is preferred over HCl for the final analytical solution to minimize or eliminate interferences from polyatomic chlorides. Because of the high sensitivity and low detection limits of inductively coupled plasma-mass spectrometry, it is essential that contamination from such sources as digestion reagents and the laboratory environment be controlled. The range of major, minor, and trace element concentrations in glass digest solutions is so great that most inductively coupled plasma-mass spectrometry protocols require analysis of multiple sample dilutions to measure the concentrations of all analyte elements.

7.4.3.2. Internal standards must be added to all sample and standard solutions and used in the calculation of element concentrations when making inductively coupled plasma-mass spectrometry measurements. Internal standards consist of 10 to 100µg/L concentrations of elements not present at high concentrations in the glass (e.g., Rh, In, Y, Tl).

7.4.3.3. Standard concentrations are different than those used with inductively coupled plasma-optical emission spectrophotometry because of the higher sensitivity of mass spectrometry over optical emission spectrophotometry and the greater number of elements measured. Although the linear dynamic range of inductively coupled plasma-mass spectrometry is greater than that of inductively coupled plasma-optical emission spectrophotometry, the linearity is so good that only two or three standard concentrations are typically required for each element. The number and combination of elements present in each standard solution must be selected based on chemical compatibility at the mg/L to ng/L level, the presence of contaminants in stock solutions, and ultimately, on the discrimination power afforded by each element for the comparison of glass fragments.

7.4.3.4 Sample introduction for inductively coupled plasma-mass spectrometry may also be made by direct vaporization of a solid sample, for instance, by laser ablation and passing the vapors directly into the plasma. Problems associated with the solubilization of glass fragments, such as reagent contamination, dilution of the sample, and incomplete digestion are avoided when using laser ablation-inductively coupled plasma-mass spectrometry.

7.4.4. Advantages of inductively coupled plasma-mass spectrometry

7.4.4.1 Inductively coupled plasma-mass spectrometry can be used to perform fast, multielemental analysis similar to inductively coupled plasma-optical emission spectrophotometry but with greater sensitivity and better detection limits, allowing for the analysis of smaller fragments and additional elements. The additional elements can provide more points of comparison, potentially improving discrimination capability, and can be used to detect specific elements present in some products, such as Ce when it is added as

a decolorizer.

7.4.4.2. Inductively coupled plasma-mass spectrometry can also be used for measuring multiple isotopes of the same element. Isotopic measurements may potentially be used for improved accuracy of element quantitation (isotope dilution method) or for detection of isotopic variations among sources.

7.4.4.3. Laser ablation-inductively coupled plasma-mass spectrometry provides a means for rapid, direct determination of element concentrations in solid samples with minimal sample destruction and contamination.

7.4.5. Limitations of inductively coupled plasma-mass spectrometry

7.4.5.1. The higher sensitivity and multielement capabilities of inductively coupled plasma-mass spectrometry relative to other elemental analytical techniques requires that strict contamination control of analyte elements be maintained during sample preparation and analysis.

7.4.5.2. Interferences when using a quadrupole instrument, though generally well known, in some instances are not easily corrected and prevent accurate quantitation of a few elements. Removal of some interference effects, particularly isobaric mass overlaps, can be accomplished using a high-resolution spectrometer or by collision cell technology, both at added cost and complexity of instrument operation.

7.4.5.3. Limitations to the implementation of inductively coupled plasma-mass spectrometry technology in forensic laboratories are the high cost of instrumentation and laboratory support, the high level of operator training required, and the large time requirements for sample and standard preparation and analysis.

7.4.5.4. Historically, it has been difficult to obtain quantitative results using solid sample introduction because of the inability to add an internal standard to a solid material. However, for some glass types, such as soda-lime glass, this limitation has been overcome by using a matrix element (silicon) as the internal standard for quantification. An external standard (e.g., NIST SRM) should be used for quantitative analysis of solid sampling by laser ablation.

7.4.5.5. The precision of inductively coupled plasma-mass spectrometry is poorer than that of inductively coupled plasma-optical emission spectrophotometry under optimum conditions. The inductively coupled plasma-mass spectrometry precision measurements for all elements when present in the middle of their respective concentration ranges are generally 10 percent or better relative standard deviation.

8. Considerations

8.1. Elemental analysis methods are used when other methods of comparison fail to distinguish two glass fragments as having different sources. The amount of additional discrimination provided by element concentration regardless of the method of determination depends upon the number of elements measured and the precision of the measurements.

8.2. Replicate measurements must be taken to assess the extent of element concentration variations within the specimens.

9. References

Almirall, J. Elemental analysis of glass fragments. In: *Trace Evidence Analysis and Interpretation: Glass and Paint.* B. Caddy, ed. Taylor and Francis, London, 2001, pp. 65-83.

Andrasko, J. and Maehly, A. C. The discrimination between samples of window glass by combining physical and chemical techniques, *Journal of Forensic Sciences* (1978) 23:250-262.

Buscaglia, J. Elemental analysis of small glass fragments in forensic science, *Analytica Chimica Acta* (1994) 288:17-24.

Catterick, T. and Hickman, D. A. The quantitative analysis of glass by inductively coupled plasma-atomic emission spectrometry: A five element survey, *Forensic Science International* (1981) 17:253-263.

Coleman, R. F. and Goode, G. C. Comparison of glass fragments by neutron activation analysis, *Journal of Radioanalytical Chemistry* (1973) 15:367-388.

Duckworth, D. C., Bayne, C. K., Morton, S. J., and Almirall, J. Analysis of variance in forensic glass analysis by ICP-MS: Variance within the method, *Journal of Analytical Atomic Spectrometry* (2000) 15:821-828.

Dudley, R. J., Howden, C. R., Taylor, T. J., and Smalldon, K. W. The discrimination and classification of small fragments of window and nonwindow glasses using energy-dispersive X-ray fluorescence spectrometry, *X-Ray Spectrometry* (1980) 9:119-122.

Haney, M. A comparison of window glasses by isotope dilution spark source mass spectrometry, *Journal of Forensic Sciences* (1977) 22:534-544.

Hickman, D. A. A classification scheme for glass, *Forensic Science International* (1981) 17:265-281.

Hickman, D. A. Elemental analysis and the discrimination of sheet glass samples, *Forensic Science International* (1983) 23:213-223.

Hickman, D. A. Glass types identified by chemical analysis, *Forensic Science International* (1987) 33:23-46.

Hickman, D. A., Harbottle, G., and Sayre, E. V. The selection of the best elemental variables for the classification of glass samples, *Forensic Science International* (1983) 23:189-212.

Howden, C. R., German, B., and Smalldon, K. W. The determination of iron and magnesium in small glass fragments using flameless atomic absorption spectrophotometry, *Journal of the Forensic Science Society* (1977) 17:153-159.

Hughes, J. C., Catterick, T., and Southeard, G. The quantitative analysis of glass by atomic absorption spectroscopy, *Forensic Science* (1976) 8:217-227.

Keeley, R. H. and Christofides, S. Classification of small glass fragments by X-ray microanalyisis with the SEM and a small sample XRF spectrometer. In: *Proceedings of Scanning Electron Microscopy,* SEM, AMF O'Hare, Illinois, 1979, Part I, pp. 459-464.

Koons, R. D. and Buscaglia, J. The forensic significance of glass composition and refractive index measurements, *Journal of Forensic Sciences* (1999) 44:496-503.

Koons, R. D., Fiedler, C., and Rawalt. R. C. Classification and discrimination of sheet and container glasses by inductively coupled plasma-atomic emission spectrometry and pattern recognition, *Journal of Forensic Sciences* (1988) 33:49-67.

Koons, R., Peters, C., and Rebbert, P. Comparison of refractive index, energy dispersive X-ray fluorescence and inductively coupled plasma atomic emission spectrometry for forensic characterization of sheet glass fragments, *Journal of Analytical Atomic Spectrometry* (1991) 6:451-456.

Montaser, A., Minnich, M. G., McLean, J. A., Liu, H., Caruso, J. A., and McLeod, C. W. Sample introduction in ICPMS. In: *Inductively Coupled Plasma Mass Spectrometry.* A. Montaser, ed. Wiley-VCH, New York, 1998, pp. 194-218.

Parouchais, T., Warner, I. M., Palmer, L. T., and Kobus, H. The analysis of small glass fragments using inductively coupled plasma mass spectrometry, *Journal of Forensic Sciences* (1996) 41:351-360.

Reeve, V., Mathiesen, J., and Fong, W. Elemental analysis by energy dispersive X-ray: A significant factor in the forensic analysis of glass, *Journal of Forensic Sciences* (1976) 21:291-306.

Ryland, S. Sheet or container? — Forensic glass comparisons with an emphasis on source classification, *Journal of Forensic Sciences* (1986) 31:1314-1329.

Terry, K. W., van Riessen, A., and Vowles, D. J. Elemental analysis of glasses in a SEM, *Micron* (1982) 13:293-294.

Wolnik, K. L., Gaston, C. M., and Fricke, F. L. Analysis of glass in product tampering investigations by inductively coupled plasma atomic emission spectrometry with a hydrofluoric acid resistant torch, *Journal of Analytical Atomic Spectrometry* (1989) 4:27-31.

Zurhaar, A. and Mullings, L. Characterisation of forensic glass samples using inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry* (1990) 5:611-617.

10. Bibliography

Bertin, E. P. *Principles and Practice of X-Ray Spectrometric Analysis.* 2nd ed. Plenum, New York, 1975.

Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Lyman, C. E., Fiori, C., and Lifshin, E. *Scanning Electron Microscopy and X-Ray Microanalysis,* Plenum, New York, 1992.

Janssens, K. H., Adams, F. C. V., and Rindby, A. *Microscopic X-Ray Fluorescence Analysis.* Wiley, Chichester, 2000.

Kubic, T. A. Forensic applications of scanning electron microscopy with X-ray analysis. In: *Industrial Applications of Electron Microscopy.* Z. R. Li, ed. Marcel Dekker, New York, 2002, pp. 279-329.

Montaser, A. *Inductively Coupled Plasma Mass Spectrometry.* Wiley-VCH, New York, 1998.

Newbury, D. E., Joy, D. C., Echlin, P., Fiori, C. E., and Goldstein, J. I. *Advanced Scanning Electron Microscopy and X-Ray Microanalysis,* Plenum, New York, 1986.

Thompson, A. and Walsh, J. N. *Handbook of Inductively Coupled Plasma Spectrometry,* 2nd ed. Blackie, Glasgow, 1989.