Glass Refractive Index Determination

Scientific Working Group for Materials Analysis (SWGMAT)

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1. Scope

This document describes guidelines for measuring the refractive index of forensic glass samples. Refractive index can be measured by a number of different techniques including Emmons double variation, automated or manual temperature variation, dispersion staining, and other immersion methods.

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 Standard

E1967 *Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase-Contrast Microscope*

2.3. Association of Analytical Chemists Method

973.65 Emmons Double Variation

3. Terminology

Annealing is the process of reducing residual strain in glass by controlled heating and cooling.

Becke line is the bright halo near the edge of a transparent particle immersed in a medium. The halo moves with respect to that edge as the focal plane of the microscope is changed.

Becke line method is a method for determining the refractive index of a transparent particle relative to its surrounding medium by noting the direction that the Becke line moves when the distance between the objective of the microscope and the preparation is changed. The Becke line will always move toward the higher refractive index medium when the distance is increased and will move toward the lower refractive index medium when the distance is decreased from the point of critical focus.

Dispersion is the change in refractive index with a change in wavelength of illumination. Commonly referred to as V, relative dispersion is a measurement of the difference between the refractive index at different wavelengths of light, typically n_C(486nm), n_D(589nm), and n_F(656nm), mathematically expressed as $V=(n_D-1)/(n_F-n_C)$.

Hartmann net is a graphical representation containing a series of parallel lines representing the refractive index versus wavelength relationships at fixed temperatures for an immersion liquid, where the refractive index scale is linear, and the wavelength scale is approximately logarithmic.

Match point is any combination of temperature and wavelength, at which two media have indistinguishable refractive indices. At the match point, the glass will exhibit minimum contrast and visibility.

Phase-contrast microscope is an interference microscope in which contrast is enhanced by altering the optical path of the diffracted ray with respect to the direct ray. This is accomplished by the action of a phase-shifting element, which results in retarding one of the rays relative to the other.

Polarized light microscope is a microscope equipped with two polarizing elements, one (polarizer) located between the light source and the sample and the other (analyzer) between the sample and the observer.

Refractive index (RI) for a particular transparent medium is the ratio of the speed of light in one media compared to another, mathematically expressed as $n_i = v_1 / v_2$, where refractive index = n_i at a specific wavelength i, and the speed of light in each media are v_1 and v_2. For glass analysis, v_1 is the speed of light in a vacuum.

Temperature coefficient of refractive index variation (dn/dT) is the change in the refractive index relative to a change in temperature.

Thermal history is the last set of conditions under which a glass has been cooled from its softened state. Refractive index and density are a function of thermal history.

4. Summary of Guideline

This guideline covers the measurement of refractive index of glass for forensic examination by a variety of techniques to suit the capabilities of a wide range of laboratories. This guideline also describes the process of laboratory annealing.

5. Significance and Use

Refractive index is the most commonly measured property in the forensic analysis of glass. Refractive index is a function of the composition and thermal history of the glass. Several methods for measuring refractive index, along with their advantages and limitations and the procedure for laboratory annealing, are presented in this guideline.

6. Sample Handling

6.1. Material recovered should be examined to determine if it is glass and, if so, prepared for further analysis, as outlined in the *Scientific Working Group for Materials Analysis Collection, Handling, and Identification of Glass*.

6.2. Glass fragments may be crushed to produce sharp edges. There are various methods of crushing glass. Large fragments may be crushed using a mortar and pestle or a glass crusher. Small fragments may be placed on a slide in a small drop of immersion liquid and crushed in situ using the tip of a tungsten probe.

6.3. Fragments of glass are mounted in the appropriate immersion liquid on a glass slide and covered with a glass cover slip. Slides and cover slips should be cleaned prior to use. This can be done using solvents, such as acetone, ethanol, or methanol, with a low-lint or lint-free wipe ensuring the solvent has evaporated before mounting the samples.

7. Analysis

7.1. Emmons Double Variation (see Association of Analytical Chemists Method 973.65 for a detailed description for conducting this technique).

7.1.1. Materials

7.1.1.1. Phase-contrast microscope.

7.1.1.2. Hot stage that can be controlled for heating and cooling with a precision of ± 0.2 degrees Celsius or better.

7.1.1.3. Monochromator calibrated to ± 1nm, capable of providing light in the wavelength range from 460nm to 680nm.

7.1.1.4. Immersion liquids such as Locke silicone oils, DowCorning 710 silicone oil for soda-lime-silica glass (e.g., flat glass), Dow Corning 550 silicone oil for borosilicate glass (e.g., headlamps), and Dow Corning F/6/7024 for glasses with a refractive index above that of the common soda-lime glasses. The immersion liquid selected must have a dn/dT on the order of 10^{-4}. It must also be stable across the temperature range of interest.

7.1.1.5. Hartmann net calibrated for the immersion liquid used.

7.1.1.6. Calibrated glass standard(s).

7.1.2. Procedure

7.1.2.1. Place the slide containing glass fragments mounted in the immersion liquid on the hot stage.

7.1.2.2. Focus and align the microscope, including the substage condenser.

7.1.2.3. Adjust the phase rings, using the centering screws, until the rings are superimposed.

7.1.2.4. Set the hot stage temperature to a value within the immersion liquid's stable range and adjust the wavelength of the light until the match point is reached. The match point and temperature are noted. Repeat this procedure for at least two other temperatures in the liquid's stability range.

7.1.2.5. Refractive index measurements are typically recorded at the sodium D line (589nm, yellow), and hydrogen C and F lines (656nm, red, and 486nm, blue, respectively). These values may be calculated or graphically determined.

7.1.2.5.1. Lines representing the immersion liquid at known refractive index versus wavelength values for various temperatures may be plotted on a Hartmann net. The wavelength at the match temperature for a glass fragment may then be plotted upon the net, and the refractive index read off the graph. Graphical determinations allow for the assessment of measurement error through an observation of the linearity of the plot of the data.

7.1.2.5.2. Linear equations representing the immersion liquid at known refractive index versus wavelength values for various temperatures may be calculated from standards. The wavelength and match temperature may then be placed into the equations to solve for the refractive index. Linear regression programs may then be used to assess the linearity of the data.

7.1.2.5.3. If the questioned sample has an original surface, then it is recommended that a surface sample of the known glass also be measured.

7.1.2.6. Analyze a reference glass sample of known refractive index prior to each use to ensure that the instrument is operating within acceptable parameters.

7.1.2.7. Results are typically reported to the nearest 0.0001.

7.1.3. Advantages

7.1.3.1. This method provides a rapid means to measure the refractive index of glass at multiple wavelengths.

7.1.3.2. The precision of the method is approximately 0.00004 to 0.00006 (Cassita and Sandercock 1994), which is typically better than the measurable variation of a glass object. The expected variation within a single float source is in the range of ± 0.00004 for annealed glass and ± 0.00016 for tempered glass (Locke 1985).

7.1.4. Limitations

This method will not differentiate between glass samples from different sources with refractive index differences less than 0.0001.

7.2. Automated Glass Refractive Index Measurement (see American Society for Testing Materials Standard E1967 for a detailed description for conducting the method).

7.2.1 Materials

7.2.1.1. Phase-contrast microscope.

7.2.1.2. Hot stage that can be controlled for heating and cooling with a precision of +/- 0.2 degrees Celsius or better.

7.2.1.3. Narrow bandwidth (10nm, centered on the wavelength of interest +/- 5nm) light filters. Typically 488nm, 589nm, and 656nm wavelengths are used.

7.2.1.4. Video camera system.

7.2.1.5. Processing unit for match-point detection.

7.2.1.6. Immersion liquids, such as Locke oils, Dow Corning 710 silicone oil for soda-lime-silica glass (e.g., flat glass), Dow Corning 550 silicone oil for borosilicate glass (e.g., headlamps), and Dow Corning F/6/7024 for glasses with a refractive index above that of the common soda-lime glasses. The immersion liquid selected must have a dn/dT on the order of 10^{-4}. It must also be stable across the temperature range of interest. If drift is noted in the measured value of the reference, the immersion liquids may be heat treated to remove residual traces of monomer and thus increase their stability and shelf life. This is done by bubbling dry nitrogen through the liquid while it is heated on a water bath in a lightly corked conical flask or by heating an individual slide on the hot stage for several minutes prior to analysis (Locke Scientific, Hampshire, United Kingdom).

7.2.1.7. Calibrated glass standards.

7.2.2. Procedure

7.2.2.1. A slide containing glass fragments mounted in an immersion liquid is placed on a hot stage.

7.2.2.2. Focus and align the microscope, including the substage condenser.

7.2.2.3. Adjust the phase rings, using the centering screws, until the rings are

superimposed.

7.2.2.4. Calibrate the instrument for the liquid and wavelength of interest using glass standards. The instrument should be recalibrated when the measured value of the glass standard is no longer within operating parameters, when a different liquid is used, or when the instrument is serviced.

7.2.2.5. Adjust the temperature so that the refractive index of the liquid is higher than the glass sample. Allow the temperature to equilibrate before analysis. Upon starting the analysis, the instrument lowers the temperature of the preparation through the match point for the glass. The contrast between the fragment and the liquid is monitored, and the match point, defined as the temperature at minimum contrast, is noted. This process is repeated as the temperature is then raised through the match point. These values are recorded as the match temperature on cooling and the match temperature on heating, which are averaged to give the match-point temperature for the sample. The refractive index of the sample is automatically calculated from the calibration data.

7.2.2.6. A glass sample of known refractive index should be analyzed prior to each use to ensure that the instrument is operating within acceptable parameters.

7.2.3. Advantages

7.2.3.1. The precision of the method is typically better than the measurable variation of a glass object. The manufacturer reports that repeat measurements can produce results with a standard deviation of 0.00003 over a five-day period, with results typically reported to the nearest 0.00001. The expected variation within a single float source is in the range of ± 0.00004 for annealed glass and ± 0.00016 for tempered glass (Locke 1985).

7.2.3.2. Operator fatigue does not affect the precision or accuracy of the method.

7.2.3.3. The refractive index is automatically generated and electronically recorded.

7.2.3.4. The interoperator reproducibility is better than with the manual method.

7.2.4. Limitations

7.2.4.1. The hot stage, glass slides, and microscope must be kept scrupulously clean. Traces of liquid transferred from the glass slides to inside surfaces of the hot stage have been shown to produce anomalous results, such as a gradual change in apparent match temperature.

7.2.4.2. Determination of refractive indices at various wavelengths (dispersion) for individual particles is time-consuming.

7.2.4.3. This method will not differentiate between glasses whose refractive indices differ by less than ± 0.00003.

7.3. Immersion Methods: Dispersion Staining and Becke Line

7.3.1. Materials

7.3.1.1. Microscope.

7.3.1.2. Calibrated refractive index liquids.

7.3.1.3. Dispersion-staining objective (dispersion-staining method only).

7.3.1.4. Wavelength filter to produce monochromatic light, usually 589nm, optional (Becke line technique only).

7.3.2. Procedure

In both techniques, the fragment is immersed in a refractive index liquid. The difference between the refractive index of the glass fragment relative to the liquid is observed. In dispersion staining, this observation is made using a dispersion-staining objective and noting the colors of the corona of the particle. In the Becke line method, a bright halo (Becke line) is observed around the particle. Movement of the Becke line with respect to the particle on changing the microscope focus indicates refractive index of the particle relative to the immersion oil. The amount of contrast between the particle and the immersion liquid indicates the magnitude of the difference in refractive index. The fragment is then removed from the liquid, washed, and placed in another liquid with a refractive index closer to the match point. This process is repeated until the refractive index of the match point has either been reached or bracketed by two oils. When the match point is approached, the results can be plotted on Hartmann dispersion nets, which allows for the extrapolation of the results between liquids.

7.3.3. Advantages

7.3.3.1. The advantages of these techniques are that they require only a microscope, calibrated liquids (and the means to calibrate them, either a refractometer or calibrated glass beads), and a dispersion-staining objective for the dispersion-staining technique. A wavelength filter to produce monochromatic light, nominally 589nm, is typically used but not necessary for the Becke line method.

7.3.3.2. Becke line and dispersion-staining techniques provide for rapid sorting of very different glass sources.

7.3.4. Limitations

7.3.4.1. Extensive training in the use of dispersion staining is desirable for this technique, as the reliability of the results is dependent on the skill of the analyst.

7.3.4.2. It is often difficult to recover the glass fragment of interest and to adequately clean it between liquids. Consequently, evidence can easily be lost or liquids mixed resulting in errors in the measured indices.

7.3.4.3. Results can be reported with certainty only to the 0.001 under the best conditions but are typically less reliable. These techniques often do not provide good discrimination between sources.

7.3.4.4. The refractive index of the liquids can vary with the temperature of the liquid. If each liquid is not calibrated over a range of laboratory temperatures or if laboratory temperature is not maintained at a fixed value, error can be introduced to the measurement.

7.4. Laboratory Annealing

7.4.1. Materials

7.4.1.1. A furnace, preferably programmable, capable of maintaining a temperature of at least 600 degrees Celsius.

7.4.1.2. Suitable sample holder.

7.4.2. Procedure

7.4.2.1. When questioned glass is not distinguishable in refractive index from the known glass, both may be annealed to determine whether or not they have similar thermal histories. One method that can be used for annealing is described for the "short schedule" by Locke and Hayes (1984).

7.4.2.2. Where sample size permits, glass fragments should be broken, and one portion annealed while the original sample is analyzed for refractive index measurement. Smaller fragments may be annealed after initial refractive index measurements are completed. However, this technique alters the original sample. A glass chip is removed from the slide, cleaned with a solvent, and then annealed. Annealing should be done on multiple chips; however, it is recognized that some fragments may be too small to retrieve without the risk of losing them.

7.4.2.3. After laboratory annealing is completed, the refractive indices of the fragments are measured again using the same method as was used originally.

7.4.2.4. The magnitude of the change of the refractive index is calculated by subtracting the preannealing value from the postannealing value.

7.4.2.4.1. Using the "short schedule", a magnititude of the change of the refractive index of more than approximately $+1x10^{-3}$ is considered indicative of tempered glass.

7.4.2.4.2. Using the "short schedule," the magnitude of the change of the refractive index of
less than $+8x10^{-4}$ is considered indicative of annealed glass.

7.4.2.4.3. The use of longer annealing schedules can result in higher values of the magnitude of the change of the refractive index than those obtained using the "short schedule."

7.4.2.4.4. A negative value for the magnitude of the change of the refractive index is indicative of an almost perfectly annealed glass, such as optical glass.

7.4.2.4.5. Upon annealing, heat-strengthened glass and some windshield glass have a magnitude of the change of the refractive index intermediate between that of annealed and tempered glass.

7.4.2.4.6. A glass with a known magnitude of the change of the refractive index should be included in each annealing measurement process to verify the annealing program.

8. Considerations

8.1. Glass samples exhibit a range of refractive index values. Refractive index is a function of the chemical composition of the glass and its thermal history. The composition of a glass sample can be measured by a variety of techniques. Thermal history is typically assessed through a measurement of either refractive index or density.

8.2. The variations in either refractive index or density at fixed values of the other indicate that even with precise measurement of one property, the other is capable of providing some degree of additional discrimination. If density and refractive index are used in conjunction when one parameter is measured, the

second gives an improvement in discrimination capability of approximately twofold (Koons et al. 2002; Stoney and Thornton 1985).

8.3. Because there is a high correlation between density and refractive index, a limited amount of additional significance can be placed on an association based on the combination of these techniques.

8.4. The variation in refractive index across a pane of sheet glass is reported to be between $2.2x10^{-5}$ and $2x10^{-4}$ in n_D (Andrasko and Maehly 1978; Dabbs and Pearson 1972; Koons et al. 2002). Variations in n_D for container glass have been reported to be $5 X 10^{-5}$ to $3 x 10^{-4}$ (Locke 1985). These variations are small but measurable by several of the techniques described in this guideline, providing a useful tool for the characterization and discrimination of glass objects.

8.5. Replicate measurements must be taken to assess the extent of refractive index variation within the specimens.

8.6. Surface fragments may have a different refractive index than the bulk glass refractive index.

8.7. Samples that are distinguished by refractive index did not originate from the same source.

9. References

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