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REFRACTIVE INDEX DETERMINATIONS OF GLASS FRAGMENTS— A SIMPLIFIED PROCEDURE

JOHN E. DAVIS

John E. Davis has been in charge of the Oakland Police Laboratory for the last twelve years. He is a graduate of the University of California at Berkeley, following which he served for two years on the laboratory staff of the Missouri State Highway Patrol. Mr. Davis is a member of the California Association of Criminalists and the International Association for Identification.—EDITOR.

Particles of broken glass constitute one of the more commonly found types of physical evidence. Their occurrence results primarily from the fact that glass so frequently serves as the only physical barrier to the criminal bent on burglary, that bottles are frequently used as weapons of assault, and that the automobile is necessarily equipped with glass encased lights in a region most likely to suffer damage on impact. The breakable nature of the material, its tendency to shatter when broken, the tenacity with which particles of it may be held by the usual fabrics, and the apparent ease with which the fragments find their way into pockets or trouser cuffs, all serve to assure its continuing value as physical evidence.

The real value of glass as evidence, however, lies in its physical characteristics— notably density and refractive index—and the fact that both of these characteristics vary over relatively broad ranges, depending upon the composition of the material. Considering the great variety of glasses which are produced, and the manufacturing "tolerances" or unavoidable differences in composition which result from production methods, we are not surprised to find that a given glass has a considerable degree of individuality as judged by density and refractive index determinations.

Fortunately for the criminalist, both density and refractive index can be determined with a rather high degree of accuracy. More important, however, are the still more accurate comparative techniques, wherein a particle of evidence glass may be directly compared with fragments from a suspected source. Methods utilized here (particularly those concerned with density determinations) are capable of distinguishing extremely small variations between samples.

As to refractive index determinations, it cannot be said that the comparative techniques provide a degree of accuracy (as contrasted with absolute values) comparable to that obtained in density determinations, but any comparison of glass fragments must necessarily involve a determination of both density and refractive index before a conclusion of "identity" may be formed.

Although considerable work has been done in recent years in the development of improved procedures and techniques as regards density determinations, little or no improvement appears to have been made in respect to refractive index determinations. It appears that many criminalists do not routinely attempt to determine the absolute refractive index value of glass fragments, and those who do are not too satisfied with their results, even realizing the limitations of any absolute-value method.

The most commonly employed procedure for the determination of refractive index of small glass fragments appears to be the Becke method, although the oblique light technique is regarded as but slightly less sensitive. As to the accuracy of the Becke method, various authors assign it an error of 0.001 to 0.005 as usually performed. Most references to the method, however, are in texts on mineralogy where conditions are not quite the same as usually encountered in glass analyses. Refined procedures for the application of the Becke method are estimated to give an error considerably less than those listed above (to 0.0001) but involve the use of temperature control, a monochromator, and other accessories not generally available in the police laboratory.

From a practical standpoint the Becke method as generally applied, has certain disadvantages. While the basic principle and probable accuracy of the method cannot be improved upon, the procedure involved in its application leaves much to be desired. For example:

(a) It requires the use of a graduated series of calibrated liquids.

(b) It requires that the specimen be placed in one liquid after another until it is found to be "bracketed" by two, after which an intermediate is mixed from the two.

(c) The particle may require washing with acetone or other solvent between steps.

(d) Mixing of the bracketing liquids is sometimes difficult.

(e) Should the liquid be taken for a refractometer reading and a second determination required, another time-consuming mixing process must be performed.

(f) With some liquids, creeping over the slide or cell becomes a problem.

(g) Evaporation of volatile liquids is often a handicap—particularly as regards making a refractometer reading.

(h) Where (as seems to be usual) a 16 mm. objective or even a 44 mm. objective is used, it is essential that the edges of both particles be in the same plane (comparative tests) if the Becke line is to be observed properly. Keeping the particles in position is not always simple.

(i) The appearance of a color halo (Christiansen effect) at the end point is often more of a hindrance than a help, where white light is utilized.

(j) The procedure is generally a tedious one.

(k) As usually performed it is time consuming—averaging perhaps 30 minutes or more for a determination.

(l) Most important of all, as usually performed one has no way of knowing how much higher, or how much lower, a given liquid is than the glass, until it is bracketed by one with a higher N and one with a lower N.

It is to be realized that not all of these objections would be effective in a given case. Modifications in procedure and technique of individual workers would eliminate some of them, and some would perhaps be regarded as "no problem" by others.

These and other shortcomings of the method have seemed to the writer sufficiently important to justify efforts to minimize them. Objections (j), (k), and (l) were regarded as alone calling for some modification in procedure in the hope that they might be eliminated. As a result of work during the past few months, the writer has evolved a procedure which has thus far proved itself considerably superior to

the Becke method as generally followed—particularly where the glass fragments are fairly large. It involves no new principle, but is rather an improved technique or procedure.

THE BASIS OF THE METHOD

The recommended procedure is based on the fact that the dispersion of immersion liquids is greater than that of glass. Thus, when a fragment of glass is immersed in a liquid having the same refractive index for sodium light, it will have a greater index for red light and less for blue. As a result, brightly colored fringes or "halo" effects may be seen at the end point. This is the well-known Christiansen effect, detectable in subdued form in the usual Becke procedure under white light when the refractive index of liquid and glass are the same for yellow light.

In the usual Becke procedure the Christiansen effect is not utilized directly. Its appearance is more or less incidental to the determination, and at most merely indicates that an end point has been roughly reached. Where the sodium lamp is used exclusively in these determinations, the effect is, of course, not utilized at all. Experiments indicate that the Christiansen effect may be utilized most advantageously in refractive index determinations on glass, by providing over a rather broad range an indication of the liquid-glass refractive index ratios, and a recognition of the "end point" within very close limits even under white light.

Basically, the method depends upon the fact that, under the conditions to be described, if the immersion liquid has a refractive index (Nd) considerably higher than that of the glass, the glass will appear amber, golden, or "beer bottle brown." If the liquid has an Nd considerably lower than the glass, the specimen will appear outlined with a "cold" blue or blackish blue line. The colors will appear as stated if the refractive index of the liquid and glass are within 0.1 to 0.05 of each other, depending upon dispersion ratios.

As the liquid and glass Nd approach one another through adjustment of the immersion fluid, pastel colors will appear over a rather broad range, and color halos will be detected at sharp edges which indicate whether an end point has been reached. Throughout the entire range of colors, the analyst can observe indications as to the relative liquid-glass Nd ratio, and be guided as to the direction and degree of alteration in the Nd of the liquid required to produce an end point.

The color observations are made in white light, and if utilized exclusively as a means of reaching the end point, will provide a close approximation of the absolute Nd of the glass. Refractometer readings of the finally adjusted liquid will generally be found accurate to within 0.002 or less. For comparative purposes alone, the colors are most useful, and may serve to indicate differences in dispersion between specimens. Where sodium light is utilized as a final check (utilizing the Becke line), accuracies to within 0.001 may be expected on a reading of the immersion liquid; comparative mesurements will be correspondingly more accurate.

The procedure to be described, utilizing either the color halo or the Becke line, does not vary essentially from other procedures in recognition of the end point. It does, however, offer a more rapid and effective approach to that end point.

MATERIALS AND EQUIPMENT UTILIZED

Immersion liquids Nitrobenzene (N 1.5504) and Xylene (N 1.4939) are used in this laboratory. The dispersion of these liquids appears most satisfactory for the purpose, and the refractive index range available through their use will suffice for the majority of glass specimens. This range can be extended by making use of other liquids or mixtures, but the following descriptions will assume the use of Nitrobenzene and Xylene alone.

All work is performed in a glass cell considerably larger than that usually utilized in such work. It consists of two microscope slides (2″ by 3″) which form a base for the cell. The uppermost slide has a ¼″ hole drilled through it, after which it is cemented to the lower slide with waterglass. This provides a fair-sized cell, with a flat, smooth bottom, designed to contain the glass fragments under examination. Surrounding this depression is a glass ring approximately ¼″ high and ¾″ inside diameter, cemented in place. The completed cell thus consists of a large ring with a clear bottom in the center of which is a depression. The slide is used on a binocular microscope equipped with a 48 mm. objective (32 mm. will work as well), and 10 x oculars. The substage condenser is completely removed, and the plane surface of the mirror utilized alone.

For illumination, two lamps are set before the microscope, side by side. One is a Spencer ♯370 lamp equipped with iris diaphragm and daylight glass. The other is a sodium lamp. The lamps are approximately eight inches from the microscope. A very small aperture is used on the white light lamp (¼ to ½ inch diameter), and the sodium lamp has been equipped with a one-inch aperture fitted with ground glass to diffuse and soften the light.

The immersion liquids are added by means of pipettes drawn from soft glass tubing. They are about the size of an ordinary eye-dropper, but drawn into a long capillary tube at the small end, terminating in an orifice 0.5 mm. to 1.0 mm. in diameter. Three such pipettes are used (one for each liquid and one for mixing), each equipped with an eye-dropper type rubber bulb.

PROCEDURE

(1) Put the questioned particles of glass, preferably wedge-shaped flakes, in the smallest depression of the cell and place it on the microscope stage. Using transmitted white light, bring them into focus in the center of the field. (The entire central depression of the cell should be included within the field of view.)

(2) Place a few drops of Nitrobenzene on the particles, using enough to cover them completely. Adjust the mirror so that the field is evenly illuminated with white light. Note the color of the glass. If it has an amber hue, golden brownish yellow, or similar apparent "body color," the refractive index of the glass is lower than that of the liquid.

(3) Focus upward to where the specimen appears considerably blurred (coarse adjustment), and note that a "white" halo moves outward from the specimen.

(4) Next add about two dozen drops of Xylene to the cell.

(5) Mix the two liquids thoroughly in the cell. This can best be accomplished by use of a pipette reserved for mixing purposes. Steady the fine end of the pipette with

the fingers of the left hand, insert the tip into the large cell along its outer edge, and draw the cell contents into the pipette. Then expel the liquid along the same edge so that it swirls around the cell. Repeat the process four or five times. This should result in a homogeneous mixture of the liquid throughout.

(6) Again examine the particles with the microscope. They will most likely have lost the amber color completely and now appear clear with cold blue edges and "joints." This color effect indicates that the liquid has too low a refractive index. On focusing upward to a point where the specimen is definitely blurred, color halos will appear dark blue, and on focusing downward, a bright yellow.

(7) The problem now becomes one of adjusting the liquid to a point where it has an Nd identical to that of the glass. In this instance, perhaps two to four drops of Nitrobenzene would be added—then mixed as described before, and again viewed. The colors will indicate roughly how much of the liquids to add, and which one is called for. It is only necessary to keep in mind the rough quantities of each used at any given stage, and to remember the halo colors which indicate excessively high or low Nd of the fluid.

When the immersion liquid has a refractive index within perhaps 0.006 of that of the glass, the glass will show considerable color—"pastels" of green, blue, rose, etc. At this point the adjustment to an end point under white light calls for an examination of the color halo on the edges. It is not always necessary to focus up and down for this observation once experience has been gained, but initially it is a distinct aid. At a perfect end point the specimen will almost disappear, but on focusing upward to where it is badly blurred, edges will appear a very light sky blue—almost "fluorescent" in quality. If the instrument is focused below the specimen, the same areas will appear orangish yellow or "burnt orange." At this point the liquid should be within 0.002 of the true end point value, if read on a refractometer.

Two or more specimens may be compared at this point or at other liquid adjustments in this vicinity with considerable accuracy. If the specimens are the same, color fringes will have the same appearance. If on one the halo is lighter than the other, they are definitely different. Comparison between fragments by this means seems to be nearly as sensitive as application of the Becke line with sodium light, although a precise determination of the "end point" is somewhat more subjective.

(8) When the adjustment appears proper, the microscope mirror is switched over to the sodium lamp, and the Becke line sought. There appears to be no need to utilize the 16 mm. objective for this work. The 48 mm. objective used without a substage condenser appears to work quite satisfactorily and is much more convenient where particle size permits. From this point, the usual Becke method of focusing up and then down between liquid adjustments is followed. Here it will be found that the use of the long focal-length objective and the large working distance available facilitates the viewing and mixing operations. Where white light analysis indicated the liquids to be quite close to the glass as regards refractive index, very small drops or droplet additions should be made between mixing and observing.

(9) Adjust the specimen to an end point with sodium light as described. Then switch back to white light (evenly illuminated field) and again examine the specimen to become familiar with the color characteristics at a true end point.

(10) For absolute determinations a quantity of the liquid is drawn up into the· mixing pipette for a refractometer reading. The reading will normally be less than 0.001 removed from a reading of the gross sample of glass on the same instrument.

Once the operator has become familiar with the color characteristics described,. and observed the effect of relative liquid-glass dispersion on those colors (particu-- larly at the end point), the sodium lamp may be dispensed with for comparative purposes. Throughout this work it is essential that the field be evenly illuminated. It is best also if a considerable quantity of liquid is used, such that the large cell is half full or more.

The procedure described here is much more rapidly performed than described. It eliminates all of the objections to the usual Becke procedure listed earlier, besides

TABLE I

COLORS AND WHAT THEY INDICATE WHEN IMMERSED*

Apparent "Body Color" of Glass Fragments	Halo Up-Focus**	Halo Down-Focus**	Indicates Nd of Liquid to be
Brownish black	White	Not apparent	Much too high
Brownish amber	White	Not apparent	Too high
Light amber	"white"	Not apparent	Too high
Golden yellowish with brownish cast	"white"	Not apparent to shadow-like brown	Too high
"Pastel" colors, greens, yellowish greens, blues, rose, etc. notice-able	White with blue cast	Dark burnt orange	Slightly too high
Slight, but pale yellowish with traces of color depending on thickness. Almost invisible	Blue-white or "Fluorescent sky blue" A pale blue but dis-tinctly tinted. If dispersion is low, lighter blue, with greenish and rose lines sepa-rating	Medium burnt orange to a burnt yellow showing color separations	Within 0.002 (Switch to so-dium light and Becke test)
Stronger pastels again visible— more yellows and blues likely, with greens etc.	Darker sky blue	Brighter yellowish	Slightly too low
Less body color. Color restricted more to edges and joints	Gas-flame blue	Bright or lemon yellow	Too low
Generally clear, color visible at edges and joints only	"Cold blue (dark)"	Light yellow to white	Too low
Clear. Edge and joint colors black-ish—little blue detectable	Blackish	White	Much too low

* Where utilizing Nitrobenzene and Xylene at room temperature.

** Colors on up and down focus refer to a given edge. Where "joints" between faces are in-volved, colors will be reversed. Actually one can see both colors at any given time depending on whether observation is made of edges or joints. In any event they will merely reverse "positions" with a change in focus from above to below the specimen.

having advantages not mentioned. The usual determination takes from five to ten minutes—rarely as long as twenty minutes. The use of two ordinary liquids instead of a calibrated series, is a great advantage as is the ease of mixing by the method described. Since the color and color halos indicate both the direction and roughly the degree of alteration required in the immersion liquid, a rapid adjustment is possible. (See Table I.)

Repeated experiments with this method on a variety of glass samples has shown highly accurate results comparatively, and liquid measurements in the neighborhood of 0.001 or less off known value of the glasses tested. While certain glasses would lie outside the range of these two liquids, it appears that the range may be extended by mixing with them other liquids of appropriate values. So long as but two liquids are utilized for the final determination and the dispersion is not too great (or too slight), any reasonable combination should serve.[1]

Since a mixture of Nitrobenzene and Xylene provides a range suitable for most purposes, their use in pure form is recommended for initial tests. Should the specimen appear to have a higher index than Nitrobenzene, Methylene Iodide and Xylene (or Nitrobenzene) may be used. If the glass has a lower index than Xylene, Acetone or Chloroform and Xylene may be utilized. Here, however, the volatility of the liquids may seriously interfere with an absolute determination. For comparative work alone, however, they are convenient where modification of the mixture is obtained by evaporation. Dispersion differences between these liquids and the glass may be slight so that but a short color range is obtained (Pyrex, e.g., in Chloroform and Xylene).

In practice the simplest procedure is to check fragments of the "known" glass in each of two or three of the liquids mentioned. The color will at once indicate what range is required for its analysis. Evidence particles and a known fragment may then be immersed in the cell for comparative or absolute determinations.

The method described here has been applied to a number of clear glass specimens with excellent results. Deeply colored glasses have not been tested, though fragments of a brown beer bottle, and of a fairly deep greenish heat-absorbing glass gave no difficulty. The technique may be learned easily in a short time and is believed more rapid and convenient than the Becke method as generally applied.

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[1] Because the appearance of the color utilized in this procedure depends upon the relative dispersion of the liquid and glass at the end point, certain allowances must be made for a variation in this ratio. At their final end point some glasses will show only sky blue and burnt orange halos, while others will show distinct separation of reds and greens so that neither the orange nor the blue is quite as described here. The blue may be pale, or greenish, while the orange is more of an orange yellow or "burnt yellow." This does not appreciably interfere with the determinations, however, and may even be utilized as an indication of relative dispersions among glasses. Where internal standards are used (calibrated glass samples), relative liquid-glass dispersions may be estimated or roughly calculated on the basis of the color fringes, though it is likely that other liquids would prove more suitable for this determination.