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Forensic discrimination of glass using cathodoluminescence and CIE LAB color coordinates: A feasibility study

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ABSTRACT

Cathodoluminescence (CL) spectroscopy has been shown to be useful for differentiating typical evidentiary glass samples. CL occurs when a surface is bombarded with an electron beam as in scanning electron microscopy and most of this luminescence is in the visible range. In effect, CL imparts color to colorless evidence and as a result, proven methods of forensic color analysis can be applied. In this work, spectral data dimensions were reduced to three and plotted in the CIE LAB color space. This approach allows for incorporation of uncertainties generated principally by intra-sample variation. NIST glass standards were used for method development and validation while potential case applications were studied with collections of window, consumer, and auto headlamp glasses. Using refractive index as the initial grouping variable, all of the window and consumer glasses were differentiated as were 6 of 10 automobile headlamp glasses. The potential advantages of CL include low cost instrumentation, its non-destructive nature, and ease of operation. The current limitations of CL in this context are the lack of databases and standards and the relatively low resolution of typical CL spectra.

1. Introduction

In many forensic laboratories that analyze glass, testing often relies on refractive index (RI) measurements and physical matching. Using calibrated oils and microscopy, RI measurements accurate to the third decimal place are common. Some laboratories utilize automated refractive index measurement instrumentation (Glass Refractive Index Measurement or GRIM) capable of providing 5 decimal places and thus greater discrimination between glasses. However, it is desirable to supplement RI information with other analytical measurements to enhance the evidentiary value of glass. Ideally, the selected methods would be non-destructive and utilize affordable instrumentation.

Many analytical techniques focusing on elemental analysis have been explored and adopted for glass analysis. Selected examples include inductively coupled plasma mass spectrometry (ICP-MS) [1–3], laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [4], scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS) [5], and X-ray fluorescence spectrometry [6,7]. Refractive index has also been combined with elemental techniques for analysis [8,9]. These methods are powerful but as with any instrumental method, each has advantages and disadvantages, and not all will be available to all forensic labs. The procedures and results described here are offered as feasibility study demonstrating that cathodoluminescence (CL) spectroscopy and color analysis can be a cost-effective tool for forensic glass analysis.

CL has many potential advantages that recommend it for forensic work. For laboratories that already own a scanning electron microscope, a CL attachment can be purchased at a cost comparable to other SEM add-ons. In this configuration, it can be combined with the elemental techniques associated with the SEM. For labs that do not have SEM instrumentation, a CL accessory can be purchased for most models of polarizing light microscopes at a cost roughly equivalent to the polarizing microscope itself. Compared to the cost of an ICP-MS instrument (particularly with a laser ablation accessory), this is a significant savings. In this project, CL spectra were utilized to study the bulk characteristics of glass, but CL can also be utilized for spot analysis analogous to XRF and EDS. CL also has a long history of peer-reviewed publication and application, laying the foundation for forensic acceptance. Operation of CL instrumentation requires little training as long as the operator is skilled in techniques associated with the base instrument (i.e., SEM or PLM).

The principle disadvantages of CL in this context are the lack of databases and standards and the relatively low resolution of

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typical CL spectra. Currently, it is not possible to assign bands to structural features such as in IR or Raman spectroscopy. As with XRD and allied methods, CL is essentially a surface technique that requires some attention to sample preparation. The method will also need to be validated in casework alongside of other methods to understand how to best utilize it in forensic laboratories. This report is intended as a first step in that direction.

Cathodoluminescence occurs when material is bombarded with high-energy electrons (10–20 kV), causing the emission of light in the visible, near infrared, and infrared regions of the electromagnetic spectrum. Widely used in geological sciences, CL microscopy has also been applied to determine emission colors of various rare earth element-containing minerals. In the semi-conductor industry, CL is applied to determine thickness variations in quantum wells of semi-conductors as well as determining various impurities that may be present in a semi-conductor [10–13].

There are two main sources of electrons utilized for CL: cold cathode and a hot cathode. Cold cathode CL is commonly performed using an external electron source coupled to an optical microscope [14]. There is no high vacuum involved in cold cathode CL. Therefore, the air that is introduced around the sample serves to dissipate any charge that may build up on the surface of the sample. An advantage of this method is that the sample does not have to be carbon coated and the instrumentation is relatively inexpensive, often sold as an accessory to standard polarizing light microscopes. A disadvantage is the low luminescence response from some materials [15]. Electrons for hot cathode CL are generated by a heated filament under vacuum, which is easily achieved by coupling a CL spectrometer to a scanning electron microscope (SEM). The electron beam is more intense in hot cathode CL and may result in more signal [15]. The present work utilized the hot cathode design.

Palenik and Buscaglia contributed a chapter to a recent book that thoroughly addresses the background of CL in the forensic context [15] and the interested reader is directed to this as an excellent primer. Briefly, electrons in a solid sample can be excited from the valence band to the conductance band when bombarded with electrons. Relaxation of the excited state can follow several paths, leading to different types of luminescence. Intrinsic luminescence results from direct recombination of electron–hole pairs and is generally associated with the lattice of the material being bombarded. Other types of recombinations can occur in the region between the valence and conduction bands. These recombinations are characteristic of activators that may be present in a material, such as rare earth elements, and are termed extrinsic luminescence. Both intrinsic and extrinsic luminescence produces peaks in a CL spectrum. However, unlike Moseley's law for peak positioning in energy dispersive spectroscopy, there is no law governing the position of peaks in a CL spectrum [16] and the wavelength of emission alone typically cannot be used to definitively identify a specific chemical or crystal structure. The energy and width of each peak are dependent on the temperature, pressure, and interaction between the activator ion and lattice ions. Thus, even though a CL spectrum cannot be interpreted in the same way as an EDS or infrared spectrum (where bands correspond to functional groups), the CL spectra may hold sufficient information to facilitate classification. The goal of this project was to determine if CL spectra of glass could be utilized for this purpose.

Glass is an amorphous, non-crystalline material. Synthetic glasses differ in composition from that of natural glass such as obsidian. Synthetic glasses tend to have high alkali levels, which allow the glasses to be produced at a lower temperature. In addition to the alkalis, calcium is often added for stability and durability. Sand is the common source of silica; however, sand also adds in impurities such as Al_2O_3, Fe_2O_3, and TiO_2 [17]. The trace element composition and defect structure of the material itself makes glass an ideal matrix for cathodoluminescence studies.

The CL emissions of glass are often strong in the visible range of ~400–700 nm and in effect, under cathodoluminescent conditions, colorless evidence acquires a color (and a spectrum in the visible range) that depends on the defect structure of the glass. There are several generic methods that can be used for subsequent spectral comparison. As noted above, CL peaks and bands cannot, like peaks in an infrared spectrum for example, be correlated to specific structural features. Spectra can be compared directly and processed by subtraction and other tools to gauge similarity or difference. CL spectra can also be deconvoluted [18–22] in an attempt to reveal the number and nature of underlying peaks. For the present work, a different approach was used, one that has a history of forensic application and one that affords a method of assigning reasonable uncertainties to the spectral measurements.

Quantitative color analysis, based on reflectance spectra obtained in the visible range, has been used as part of trace evidence studies for decades. Examples include classification of fiber evidence [23,24] and inks [25,26]. Quantitative color analysis was first proposed in 1931 by the *Commission Internationale d'Eclairage* (*CIE*). Starting from a reflectance spectrum and tables of weights (provided by ASTM), the spectrum can be converted into three variables that are plotted in an easily interpreted color space; here utilizing the CIE LAB system. In this color space, the L^* value refers to lightness, while a^* and b^* describe the hue of the color in terms of red, green, yellow, and blue. Several review articles are available describing color spaces [27–31]. For purposes of this work, the luminescent spectrum was treated as a reflectance spectrum such as might be obtained from paint, ink, or fibers.

2. Materials and methods

2.1. Glasses

Glass samples were obtained from the Crime Scene Complex (CSC) at West Virginia University and Jordan Auto Parts in Pennsylvania. The CSC is a group of three houses and a garage that are used for crime scene training at West Virginia University. As such, the glass samples obtained there are representative of typical casework samples. The samples gathered there included window and consumer glass. Standard reference glasses were obtained from the National Institute of Science and Technology (NIST, Gaithersburg, MD). Descriptions of glass samples obtained from the CSC and Jordan Auto are included in Tables 1 and 2 and the abbreviations assigned in the Tables will be used throughout the text. A mineral standard composed of 53 separate minerals (SPI Supplies, West Chester, PA) was analyzed for reference spectra. Minerals analyzed were chosen based on the similarity of composition to that of the standard glasses.

Each glass sample obtained from the CSC and Jordan Auto Parts was individually broken with a hammer. Although variable, the size of the fragments used for analysis was on the order of a centimeter in the largest dimension. Smaller samples could be analyzed with the methods described here; the intrinsic limitations lie with the instrumentation. Broken fragments were subject to a cleaning process which included successive five minute sonication intervals of the following: deionized water and laboratory soap, hexane, chloroform, and methanol. With smaller fragments, this cleaning process might have to be further adapted or developed. After washing, no further surface preparation was required; the samples were placed on a conductive SEM sample holder with carbon tape. A double pane window from the CSC was used for a break-in simulation study. The window was

Table 1
Window and consumer glasses.

Glass	RI	ID
Sylvania 50 W reflector bulb	N/A	50 W
4 W night light bulb	1.5100	4 W
Decorative bowl	1.5140	DB
Clear drinking glass	1.5140	DG
Picture frame glass	1.5160	PF
H&H window glass #1	1.5160	HH 1
H&H window glass #2	1.5160	HH 2
Holiday cup	1.5160	HC
Humvee window glass	1.5160	HV
Listerine mouthwash bottle	1.5160	LB