X-Ray Microanalysis of Art Glass Surfaces

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Introduction

In recent years there has been a virtual explosion in the world of art glass. New glass formulations have brought a host of new colors into the marketplace, and the availability of low-cost, high-quality torches and other tools has brought art glass to the hobbyist. In addition to burn risks and possible cutting injury, there are a number of less obvious hazards that should be known to novice glass workers. One of these is the presence of heavy metals in or on glass surfaces and possibly in the atmosphere immediately surrounding the work area, presenting both potential skin contact and inhalation hazards. This study examines the metallic surfaces generated on five glass colors commonly used in art glass jewelry.

Many of the colorants in glass are metallic compounds (oxides, chlorides, etc.). Lead oxide is perhaps the best known glass additive and has been used in "lead crystal" for hundreds of years. It was first used on an industrial scale for crystal production by George Ravenscroft in the mid-seventeenth century [1] and is a mainstay in the fine glassware industry. It does not impart color on its own but rather changes the refractive index and dispersion of the glass, giving cut and polished "leaded" glass its characteristic colorful flash. With the possible exception of long-term storage of acidic foods or liquids, this type of glass is safe for use with foods and for skin contact, presenting no health risk from lead exposure. Minute amounts of gold chloride impart a pink-red color to glass, and iron compounds may lead to the greenish cast often seen in less expensive commercial glasses. Selenium dioxide, while non-metallic, may be used in trace amounts to cancel out the iron-green color yielding a water-clear transparent glass without color cast. Higher amounts of selenium will produce a ruby-red glass distinctively different from the pink-red seen in gold-containing glasses. The chemistry of colored glass is quite complex and is a constantly evolving area of study for manufacturers, with new colors appearing in the marketplace quite often.

One technique commonly used in art glass is the creation of a metallic "reduction" surface. These can be colorful, attractive surfaces and are popular in art glass jewelry. To produce this type of surface, a glass with a relatively high metal content is exposed to a flame with a high fuel-to-oxygen ratio (also known as a reduction flame). This flame chemistry tends to remove oxygen from metal oxides and leave the pure metal on the surface of the glass. The color of this surface is often assumed to indicate the metal in question, and, combined with the names of stock glass colors, end users may reach erroneous conclusions about the actual chemical nature of the surface. Gold-appearing surfaces are often assumed to be gold, silver surfaces silver, etc. Analysis of these surfaces shows that apparent color and stock names may be misleading.

Materials and Methods

Five samples of glass from two different manufacturers were purchased on the open market. Three glass samples from Effetre 456 Rubino Oro, one sample each of Effetre 264 Light Ivory, Effetre 236 Dark Turquoise, Effetre 271 Silver Plum (Effetre Glass, Murano, Italy), and one sample of Kugler 215 Gold Brown (Friedrich Farbglashütte GmbH, Kaufbeuren-Neugablonz, Germany) were used in this study. Each glass type was supplied in 5-mm diameter rod form.

Samples were prepared by making two small, round beads (approximately 8–10 mm) of each glass in a neutral flame. One bead from each pair was kept as a control and the other was treated in such a way as to develop a metallic surface. Three "lollipop" samples of Rubino were prepared by melting the ends of single rods from different batches, flattening the tips, and exposing them to a reducing flame to develop the color-reaction surface. Ivory glass is known to be reactive with metal colorants in other glass colors and was exposed to the torch plume from the Rubino glass. The Silver Plum glass was exposed to a high oxygen flame to develop a metallic surface.

All samples were examined in a LEO 1450 vp scanning electron microscope operated at 20 kV, and images were collected in both secondary electron (SE) and backscatter electron (BSE) imaging modes. X-ray data were collected using a Rontec X-flash X-ray detector and microanalysis software.

Results

When exposed to a high-fuel flame, Rubino glass darkened and developed a surface color ranging from silver to gold. Returning these samples to a hotter neutral flame caused the surface to lose the metallic sheen. It could be recreated by returning the glass to the reducing flame. The three lollipop samples showed similar surface color development, even though the unheated rods had distinctly different levels of color and transparency. Control samples remained an intense transparent pink-red color (Figures 1A and 1B). Scanning electron microscopy (SEM) studies of the reduced surface showed small, bright islands of material in the BSE signal compared to the surrounding surface. Energy-dispersive X-ray microanalysis (EDS) of

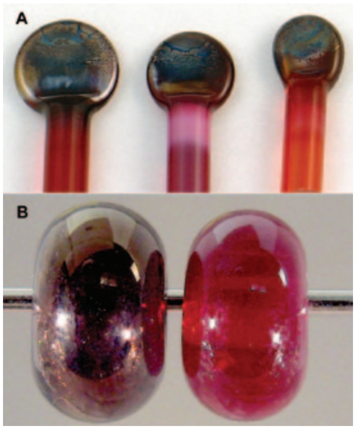

Figure 1: (A) Three color variants of Effetre 456 (Rubino Oro or Gold Pink) shown in rod form with reduced areas of silver and gold on the flattened tips. (B) The left bead shows the darkened metallic surface of the reduced glass whereas the right bead shows the pink-red color of the glass melted in a neutral flame.

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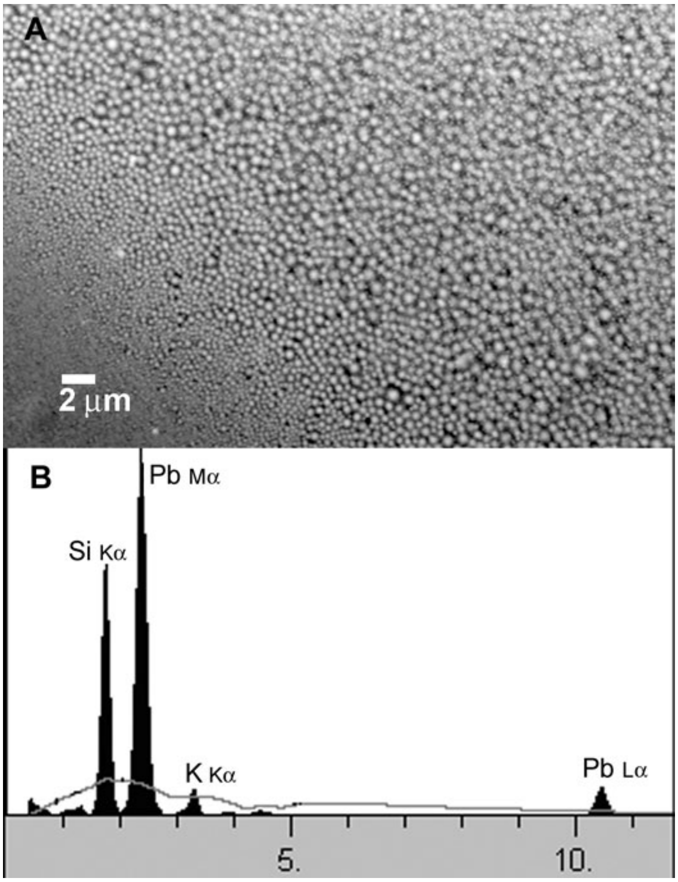

Figure 2: (A) Scanning electron micrograph in BSE mode showing bright islands of material on the reduced glass surface. (B) X-ray spectrum indicating the presence of lead along with silicon on this surface.

these features indicated the presence of lead with silicon in the surrounding glass (Figure 2).

Ivory glass remained a pale tan color when melted in a neutral flame. When exposed to the torch plume downstream from Rubino glass melted in a hot neutral flame, the Ivory glass turned a streaky metallic gray, typical of the reaction of this glass with metals (Figure 3). This process is commonly known as "fuming" and is often used to create a metallic surface on glass using pure metals such as gold or silver.

Dark Turquoise glass remained the color of the unheated rod when melted in a neutral flame. High heating in a slightly reducing flame produced a red color on the surface of this glass (Figure 4). Some metallic silver gray areas were also seen in areas exposed to less heat. The SEM showed small crystalline structures on the red surfaces, and EDS X-ray analysis indicated the presence of copper and zinc. Higher levels of zinc were recorded in the metallic silver gray areas (Figures 5A and 5B).

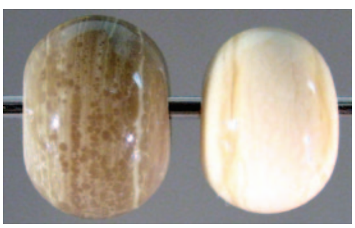

Figure 3: Beads made from Effetre 264 Ivory glass. The left bead was produced in a neutral flame and then exposed to the torch plume from a melted gather of Effetre 456 glass. It turned silvery gray as compared to the normal color of this glass when melted in a neutral flame with no exposure.

Silver plum glass remained very similar in color to the unheated rod when melted in a neutral or slightly reducing flame. Increasing the oxygen in the flame brought a bright silver surface to the glass. The EDS X-ray analysis showed manganese and zinc on this surface (Figures 6A and 6B).

The Kugler Gold Brown developed a bright silver surface. Careful manipulation of this glass in the torch flame can result in colors ranging from dark gold to bright silver. The SEM showed a surface similar to that seen on the Rubino glass, small highly backscattering dots on a darker surrounding surface. The EDS X-ray analysis indicated the presence of lead as well as silver on these surfaces (Figures 7A and 7B).

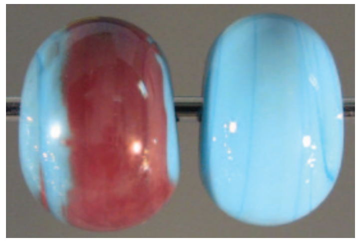

Figure 4: The left bead shows the red and gray reduction colors produced on the surface of Effetre 236 Dark Turquoise glass when exposed to a reducing flame as compared to the color of this glass when melted in a neutral flame.

Discussion

The visual appearance of these reduced glasses would suggest to the layman that the surface might, indeed, be either silver or gold. While both of these elements are heavy metals, they are considered safe for skin contact and are prized as materials for jewelry making. Copper in both pure and alloy form is often used as a jewelry metal as well. Manganese and zinc

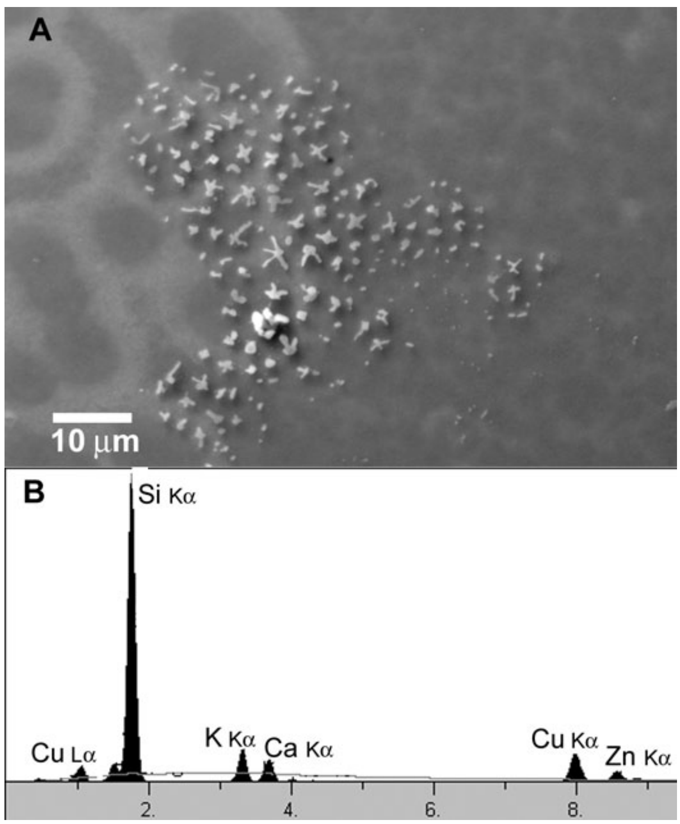

Figure 5: (A) SEM image (SE mode) of crystallization on the reduced Effetre 236 surface. (B) X-ray spectrum indicating the presence of copper and zinc as well as silicon on the glass surface.

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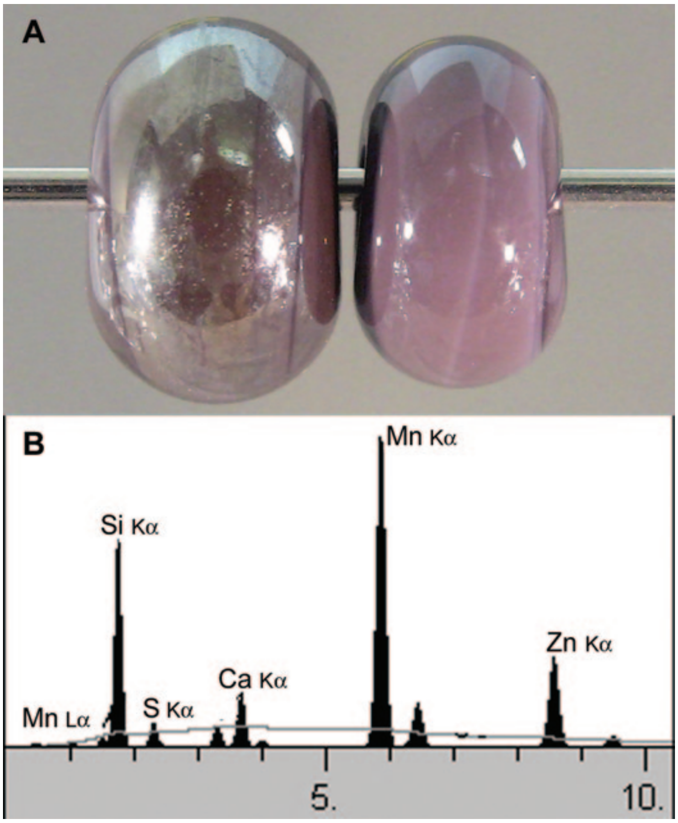

Figure 6: (A) Metallic surface produced on Effetre 271 Silver Plum glass (left) as opposed to the normal color of the glass. (B) X-ray spectrum indicating the presence of manganese and zinc along with silicon on the glass surface.

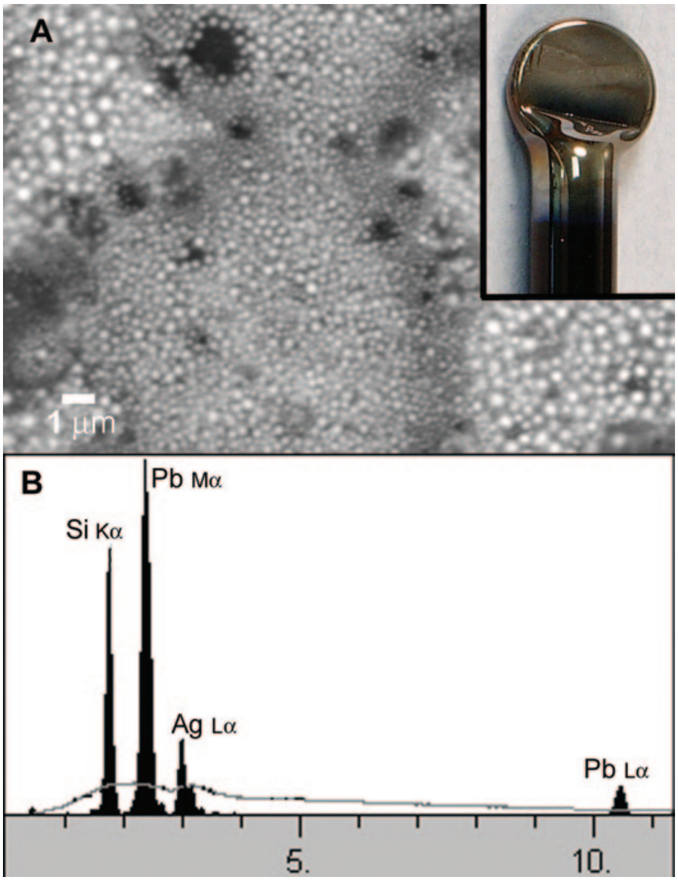

Figure 7: (A) SEM image (BSE mode) of Kugler 215 (Gold Brown) showing bright islands on the surface similar to those observed on Effetre 456 (Figure 1). Inset image shows the silver surface that develops on this glass under reducing flame conditions. (B) X-ray spectrum indicating the presence of lead as well as silver in this glass.

are generally considered safe for skin contact, and compounds of these metals are often used in dermatologic therapies.

Lead, on the other hand, is not considered safe for human contact. It has been banned from use in jewelry production and is currently the subject of restrictive legislation by the Consumer Products Safety Commission [2]. The presence of lead on jewelry surfaces exposes the wearer to potential toxic skin contact. Contact dermatitis reactions to chromium, cobalt, or nickel in jewelry alloys also give a clear demonstration of this type of hazard. Metallic lead on exposed glass surfaces, while not a paint, might be interpreted as a coating and fall under the statutes outlined in the Consumer Products Safety Improvement Act (CPSIA), which limits the lead content of a surface on any material that may be contacted by children under 12 years of age to less than 90 parts per million as of August 2009 [3]. Producing and/or selling items with this type of surface might be interpreted as a violation of the CPSIA.

Many glass workers assume that the disappearance of the metallic sheen from reheated reduction glasses is caused by the metal melting back into the glass. The fuming experiment demonstrates that lead is vaporized from the surface of the reduced glass, and lead vapor is present in the torch plume. Glass workers using inadequate ventilation in their work area will be exposed to varying levels of toxic metal vapors as well as other respiratory irritants in the torch plume. The presence of these elements in this atmosphere underlines the importance of appropriate torch plume capture and exhaust from the immediate work area.

Conclusion

The exact formulas for colored glasses have long been held as closely guarded secrets. In the modern world, however, this information needs to be readily accessible to the end users of raw glass materials as well as consumers of art glass products. Consumers cannot depend on the color name or the surface color of a finished piece to determine the metallic elements present in the glass. Issues related to glass composition include safety and health considerations for the artist and the consumer, as well as possible legal implications for all concerned with the production and sale of these materials. Anyone working with these materials should familiarize themselves with the possible chemical hazards involved and take appropriate steps to ensure safe working conditions. Distributors and consumers need to have more information in order to make informed decisions about the use of art glass products.

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