The Color-Induction Effects of Gamma Radiation on 19th and 20th Century American Glass

By Rod Elser

This project was initially conceived in 2004 as a combined effort of the New England Society of Open Salt Collectors (NESOSC) and the Open Salt Collectors of the Atlantic Region (OSCAR). It was presented to the Board of the national Open Salt Collectors at their 9th Convention in 2005 where it was authorized and funded. The results of this project were first presented on June 9, 2007 at the 10th National Open Salt Collectors Convention which was held in Indianapolis, IN.

Background: This experiment was funded by Open Salt Collectors to learn more about and assess the potential impact commercial irradiation sites could have on the hobby of collecting glass open salts. The concern is that the increasing number of commercial irradiation sites, which are commonly used now for not only the sterilization of medical supplies but also for imported fruit, vegetables and meats, will make it easier for unscrupulous individuals to induce color changes in collectible glass items, potentially "transforming" common items into rare ones. While this is a concern for collectors of early lacy items, which were often produced in a wide variety of colors, it is also of concern to collectors of other early non-lacy pieces as well as glass items made in the second half of the 19th century and into the 20th century.

Members of the project team were (in alphabetical order): Ed Berg; Ed Bowman; Rod Elser; Mike Kump; Jim & Judy Royer; Lesley Solkoske; and Mike Zagwoski. Collectively this team executed the project plan, which began with a review of prior research, then proceeded to collecting and inventorying a large number and wide variety of glass open salts, exposing them to irradiation and then analyzing the results.

We wanted to make this as scientific an experiment as possible. To that end, a wide variety of open salts were collected, inventoried, identified as best possible by manufacturer and time period of production, cross checked against reference books, photographed, tested for specific gravity—to determine the composition of the glass formula, basically whether it was made with a lead-based or soda/lime formula—and then finally exposed to radiation to determine the results. They were also photographed after the exposure to document the results on an individual basis. In total over 300 salts were collected for this project—well over 100# worth as we learned from the shipping costs! Individuals who donated salts included: Lorraine Ayers; Carolee Baker; Glenn Black; Ed Bowman; Rod Elser; Judy Johnson; Mary Kern; George Kullgren; Mike Kump; Bob Miller; Debi Raitz; Lesley Solkoske; and Donna Wolfe. We had salts that were made from the lacy period up to and including some that were made into the 1980's. Most, however, were obviously made during the peak period of early American pressed glass from 1860 until the 1890s. There were 18 lacy salts, including two opalescent and one sapphire blue, and a nice mixture of flint and non-flint table salts and many soda/lime individuals. Some had already started to turn "sun purple" and we even had one canary (Vaseline) glass salt. With such a large number of salts we ended up with a number of duplicates which further allowed us to see whether there would be differences among salts of the same pattern.

During this process we also ketp in contact with individuals we knew had a shared interest in this subject from both Art Reed (Sweet Water Glass) and Jeff Evans (Jeffrey S. Evans Auctions), to Michael Olsen, Department of Chemistry, Colorado State University and Dr. Robert Brill at the Corning Museum. Additionally Dwayne Anthony has done similar experiments with glass insulators (none of which date back to the lead-based glass formula period) and Arch Doty, Jr. had conducted a very interesting experiment with glass cup plates, all of which would date to the lead-glass period.

It was already known that some glass naturally turns a lavender color ("sun purple") after prolonged exposure to direct sunlight. This is a chemical reaction between the sunlight and the manganese that was occasionally used to manufacture glass. It was also known that starting in the 1970s some individuals started exposing clear glass items to irradiation (using equipment in medical, educational and research facilities), often resulting in the glass turning color, typically but not always purple. By the late 1980s older glass items (such as Lalique pieces and collectibles such as glass insulators and canning jars) started to appear in colors not previously recorded. This caused a growing concern among collectors about the authenticity of certain "rare" pieces. This situation was greatly complicated in the 1990s when large commercial irradiation sites were being built, primarily to sterilize imported foods but were also available to irradiate pallet-load quantities of glass. As previously noted, Dwayne Anthony and Arch Doty, Jr. conduced some experiments with irradiation on, respectively, glass insulators and cup plates that showed that some normally "rare" colors could be induced in clear glass by exposing them to irradiation. No experiments, however, had been done with open salts and there was a question about whether collectors of these items should be concerned or not.

The irradiation was done by Sterigenics, a commercial radiation company with multiple locations throughout the U.S. We had three fairly large boxes of salts that were give a strong dose of gamma radiation. Gamma radiation is approved by the FDA for sterilization as it kills all microorganisms by attacking their DNA. It has deep penetration even with very dense objects, results in very little temperature change and has no residuals, meaning the item irradiated can be safely handled immediately. The salts were sent through a containment chamber where they passed through 12 steps at each of which they were exposed to gamma radiation for 9 minutes.

> From a technical perspective, gamma radiation is often referred to a "pure energy" and it results in an alteration at the atomic level of the item being exposed. Specifically, color is reflected light and is dependent upon outermost shell of electrons (valence electrons) of the item—some wavelengths of light are absorbed, while some pass through and others are reflected. The valence electrons have one stable state and one or more "excited" states, each of which reacts differently to light. The irradiation results in these "excited" states and alters the glass at the atomic level; different chemicals in the glass react differently, often resulting in what we perceive as a color change.

Before getting to the results, let's review some of the "numbers". We started with 335 open salts, nearly all made in the 19th century but also a few later examples from as late as the third quarter of the 20th century. Of this number, 168 were table salts (more commonly called *master salts*), 18 of which were lacy; 162 were individual-size salts and 6 were what open salt collectors would refer to as mid-sized.

Jim & Judy Royer determined the SG for each of the 335 salts used in this experiment! This was a critical step as it allowed us to differentiate between salts made with a lead-based formula versus those made with a soda-lime formula as well as giving us a general idea as to the relative age of each of the salts.

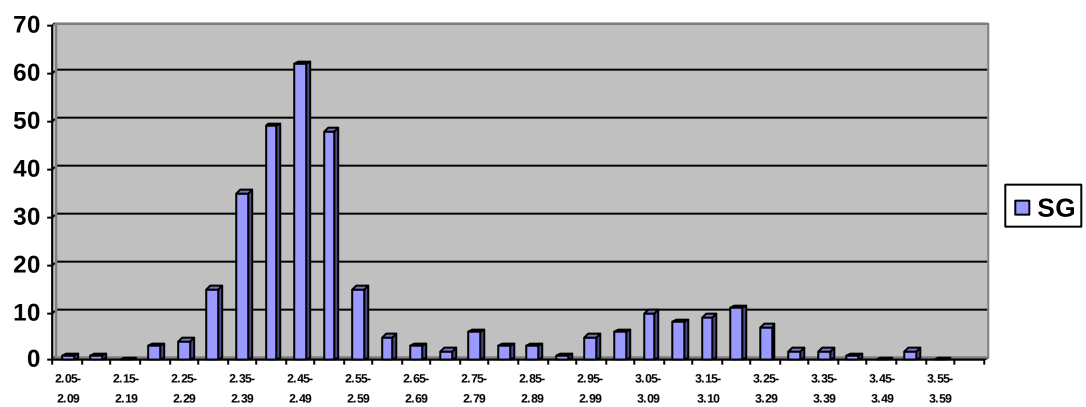
> **Specific Gravity:** Some of you may be wondering what "Specific Gravity" really is and what it has to do with this project. To answer this question, let's turn to an article Jim Royer did recently for the #22 Issue (Spring 2012) of the National Newsletter of the Open Salt Collectors: "Specific Gravity (SG) is a ratio of densities and is a dimensionless quantity. Substances with a SG of 1 are neutrally buoyant in water. Those with a SG greater than 1 are denser than water and thus will sink, and conversely, those with less than 1 will float." So the denser an item is, the higher its specific gravity (SG). The SG of an item can calculated relatively easily by comparing its weight when in water to its weight outside of water; the ratio of these two weights yields the SG. Back to Jim's article: "*But why is this relevant to open salt collectors?* Since the 1500's most glass falls into one of two categories: flint glass (also called "lead crystal" or just lead glass) or soda-lime glass. Glass manufactured before the late 1860s was nearly all flint as it produced the clearest products and gave this 'flint glass' its distinctive ring when tapped. However, it was somewhat more difficult to manufacture and definitely expensive because of the lead that was used. Most glass produced after the early 1870s was made with the new soda-lime formula. This glass was easier to produce and was significantly less

> expensive to make as well so it was quickly adopted by nearly all manufacturers. It therefore becomes informative for a collector to use SG as a means of dating his glass. It is not, however, a definitive age test; it simply indicates whether the sample tested is either flint or soda-lime, which in turn can be used with other information to help date the piece."
>
> Flint glass generally has a SG equal to or greater than 3.0 while soda-lime runs in the neighborhood of 2.5 to 2.7. As with many things though, there is a grey region (in our case salts that might have been made with a mixture of flint and soda-lime glass) where only a chemical analysis will suffice. . . . . .and since this is both an expensive and a "destructive" test (requiring a small sample of the glass itself), it is generally not the kind of test we want to use on a rare piece or to commission on an inexpensive salt. But remember that the SG test is only indicative, not definitive, when it comes to age, and as Popeye used to say "I *yams what I yam.*"

Of the 168 table salts, 52 or about 30% had a Specific Gravity (SG) over 3.0, which would typically indicate a lead-based formula. 98 or nearly 60% had an SG less than 2.75, generally indicating that they were made using a soda-lime formula. The remaining 10 table salts had a SG greater than 2.75 but less than 3.0 and we couldn't fully explain why this would be. Of course it could be an error in our measurements, but it might also indicate that, for example, the batch of glass used to produce these items was intended to be soda-lime but might have had some lead-based cullet inadvertently mixed in.

Of the 162 individual salts, 146 or 92% had a SG that would indicate the soda-lime formula while only 7 or 4% had an SG in the lead glass range and 6 fell in the "in-between" range. Certainly most individual open salts were produced until after the 1860's so it was expected that nearly all would have used the soda-lime formula. All this, though, is to indicate that we had a good mix of both lead-based and non-lead bases open salts—roughly 50% of each.

<u>Specific Gravity Distribution on Irradiated Open Salts</u>
<u>Number of salts by specific gravity range</u>



As can be seen in graph, there are two specific gravity "groupings"—one clearly in the 2.25 to 2.75 range, representing salts made with a soda-lime formula; and the second in the 2.95 to 3.30 (and slightly above) range, representing salts made with a lead-based formula.

We were also able to identify at least 30 different manufacturing companies, based on design or pattern. hoping perhaps that we might find this of significance as we analyzed the results.

So, what did we see? Of the 335 open salts, <u>334 changed color</u> (99.7%!), nearly all of them significantly. Most of the salts, however, came out a "dirty" brown, definitely not a color that would be commercially produced and one not likely to fool even a modestly experienced collector. Having said that, though, a significant number of the salts did change to a more natural color, most commonly various shades of blues, purples and browns to even a border-line green. Without trying to go "Martha Stewart" on you, there were deep blues as well as purple blues, steel blues and light blues; deep purples, bluish purples, light purples as well as amethyst. The browns varied from a rich root beer color to what could be called a very unattractive dirty brown (as previously noted) and there were a number that I would call more of a dark, smoky color than anything else. A color classification system for the resulting colors was developed—but it was done in a subjective, non-quantative manner—and the identification of 9 "standard" colors resulted. (To be precisely classified by color, however, each of the salts would need to be processed through a spectrograph, a piece of equipment not readily available.) Interestingly, though, the majority of the irradiated salts were—again, based on my eye alone—able to be associated with 6 of the 9 identified "standard" colors with only a few falling into each of the other 3 "standard" colors.

Only 26 salts, about 8%, had an irradiated color that was classified as "special" or "unique"—interesting though, all of the Sandwich glass salts, with the exception of the 4 Stag Horn salts, were classified as "special" or "unique. In what is certainly one of the more significant mysteries, the only salt that didn't change color at all was a sapphire blue lacy in the Mt. Vernon design.

Shown below are photos of a sample of the salts that were irradiated, in most cases with a "before" photo on the left and an "after" photo on the right. With these you can see for yourself some of the more interesting colors that resulted from the irradiation. (Note that the photos were taken with relatively bright lights and that in most cases, the color of the salt wouldn't be as easily seen in normal indoor lighting.)

Before/After Slide/Photos

All of the lacies, with the exception of the 4 Stag Horn design ones, came out more or less unique, as did about an equal number of non-lacy ones. All 4 of the Stag Horn design salts turned a nearly identical shade of purple blue. It is interesting to note that each of these 4 salts also had a Specific Gravity that was well within the normal range of soda-lime glass. This fact raises the question as to whether these "lacy" salts really date to the same period as more traditional lacy salts—although it could also be that they were all made in Europe, despite the American attribution in the Neal book on lacy salts to the more common forms, whether during or after the lacy period. There were two opalescent lacy salts and they both came out a light root-beer opalescent—definitely not a color description seen in any reference book on lacy salts.

Obviously the results indicate it doesn't matter whether an item is made with a lead-based or soda-lime formula—all changed color with the exposure to gamma radiation. We tried, however, with mixed results, to determine whether there was any correlation between the resulting color and whether the glass was lead or soda-lime. The sorting I did—<u>and again using an imprecise methodology</u>—placed most soda-lime items into 4 of the "standard" color categories; this represented about 72% of the soda-lime total. Interestingly, only 3 of the lead glass salts (about 5%) fell into one of these same 4 color categories so there does seem to be some connection here that justifies further investigation. For the lead glass salts, roughly one third fell into the same color class with the rest scattered across the other categories. So there does seem to be some correlation between the resulting colors and the nature of the glass formulation, but it certainly isn't absolute and perhaps, with the exception of soda-lime glass, not really indicative.

We were unable to determine whether any correlation exists between manufacturer and the resulting color change; despite our initial efforts, in the end the sample size by company was just too small.

Aside from what was noted earlier about the Stag Horn salts, there were a few other interesting results to note. Eight of the salts were, to one degree or another, a light shade of amethyst, often called "sun" purple, going into the experiment. Two of these were lead glass and the others were soda-lime. Research indicates that this lavender hue is most likely the result of the natural radiation in sunlight reacting with manganese that was used in the original glass formula to help made the glass clearer. As such, I would have expected these 8 salts to come out of the gamma radiation with a similar color—actually the opposite was closer to reality. The range of colors was similar to all the other salts.

As I noted earlier, our sample also included a number of sets of identical salts, all the way from pairs up to sets of 6 and even 8. In most, but certainly not all cases we noted a range of induced colors. I doubt if there is just one explanation of why the colors weren't closer within such sets, but a possible partial explanation is that a number of them were of a generic design or shape and though superficially identical, could easily been made by multiple companies over a range of years.

This brings us to the most fundamental question, which is whether open salt collectors should be concerned about irradiated salts negatively impacting our hobby. While time alone will provide a definitive answer to this question, based on this study my opinion would be that it won't. The most common color that resulted from the irradiation was a "dirty brown," a color that realistically no one would find attractive. And while it might seem profitable to irradiate a large number of inexpensive, common salts in hopes that a few would come out in beautiful—and possibly high-priced—colors, enough documentation exists about these salts that these "unique" colors would stand out as not being authentic and would not likely be able to be sold for any large premium. The fact that only one of the irradiated lacy salts came out a *potentially* believable color indicates that there would also not be much financial advantage in irradiating clear lacy salts in hopes that a high-priced color might result. All in all, experienced collectors should indeed be concerned, but certainly not overly so. As we have always heard, if something seems too good to be true, it probably is!

Lastly, where do we go from here? As noted previously, Dr. Brill at the Corning Museum has been closely involved with this project from the initiation. In 2008 he offered to work with us to do a spectral analysis as well as full chemical analysis for both qualitative and qualitative purposes on a small number of selected samples. The samples needed to include both irradiated and comparable non-irradiated examples for comparative purposes. This testing, however, is a fairly expensive process, costing as much as $900/salt; hence the need to work with only a small number of examples. Dr. Brill thought he could work this testing into his own research budget, spreading the cost over two budget years . We enthusiastically agreed with this offer and in December of that year the selected samples were mailed to him at Corning. This set of samples consisted of 6 irradiated salts together with 4 samples of naturally colored (i.e. not radiated) glass. The 6 irradiated salts were:

1. MV1b, Mount Vernon lacy table salt, cobalt blue; #14 in project (this was the only salt that didn't change color with the irradiation)
2. H&J3260, hexagonal footed table salt, originally colorless; #65 in project
3. SN1, Stag Horn lacy table salt, originally colorless; #94 in project
4. H&J2677 (but clear), round individual salt with 6 panels, originally colorless; #107 in project
5. H&J2670, round individual salt, originally colorless; #164 in project
6. OL16, oval lacy table salt, originally colorless; #193 in project

And the 4 non-radiated pieces of glass were:

1. Small scent bottle (donated by Jeff Evans)—dark blue/purple; second-half of 19th century
2. Rectangular table salt—c1860; purple
3. Dark amber individual, hexagonal; early 20th century; H&J546

4. Light amber individual, round; late 19^{th} century; H&J558 but light amber

Concurrent with the above activity, Dr. Brill asked for specific objectives for the testing. This is what was established:

Objectives for Spectral and Chemical Analysis:

1. What colors would be expected to result from irradiation and what is the relative frequency of each?
2. Are the induced colors noticeably different from factory-produced colors from the same period?
3. Is there a meaningful difference in induced colors between lead-based and soda-lime formula glass?
4. Is there an easy, practical way to tell if color has been induced through irradiation?
5. Is irradiation-induced color change able to be reversed using heat? If so, what is required to effect this reversal and would it be a practical test?
6. Do "sun-purple" open salts react consistently when irradiated?

Unfortunately before Dr. Brill could get started with the actual work, the economic recession resulted in his budget being slashed. While he has been able to make some progress with the spectral analysis of the samples, the more important chemical analysis has yet to begin.

One final update is that approximately two thirds of the salts irradiated were destroyed in early 2012 to eliminate the potential for their ever getting into the market. It was not practical to indefinitely retain all 336 of the salts irradiated so a representative subset has been retained for future analysis (or display) and the rest destroyed the 'old-fashioned' way—with a hammer.

The study numbers of the salts destroyed were recorded and since there are before and after photos of each individual salt on file, full information on each salt is still retained even though the salt itself has now been destroyed.