# Methods for Determining Metal Ion Leaching from Glass Cullet using Flame Atomic Absorption Spectroscopy

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## ABSTRACT

Glass cullet (recycled or broken glass) has been proposed to replace dredged sediment in beach and river recovery processes after severe weather events. Dredging of the ocean floor to replace lost sediment on beaches has led to many negative environmental impacts, such as disturbance of marine ecosystems, notably the death of both animal and plant life near coastlines. The majority of cullet that has been proposed for replacement of dredged sediment is float glass, not bottle glass that could be obtained from a recycling center. This research project focused on developing an efficient method of quantitatively measuring leaching of metal ions from recycled bottle glass cullet, which is the main concern with long-term use of these materials. A standard concentration of brine was used to incubate the glass cullet, with sample aliquots removed at different exposure times. Flame Atomic Absorption Spectroscopy (FAAS) was used to determine the concentration of metal ions leached out of green cullet from multiple samples. An average concentration of 23.43 ppm of chromium ions was detected after green glass cullet was exposed to 3.5 wt% NaCl solution for five weeks.

## Introduction and Background

While natural coastal erosion occurs daily, it has become a global issue as climate change causes more frequent severe weather events. The continual rise of sea levels has led to rapid transport of coastal sediment and erosion (Badineaux 2012). Man-made dams and levees have also inhibited the flow of sediment from rivers into oceans that naturally would replenish beach sediment. Human-engineered shoreline replenishment programs that locally dredge offshore sediment for beach replenishment have provided only short-term solutions with adverse environmental impacts (Badineaux 2012).

The battle against coastal erosion encouraged a diverse approach of hard and soft methodologies to keep natural coastal sediments in situ. Examples of hard techniques, which proactively prevent localized erosion, include construction of sea walls, longshore barriers, and jetties. However, because these techniques are designed to prevent sediment flow, this could lead to increased erosion of sediment down drift from the structures (Speybroeck et al. 2006; Houston and Dean 2014).

In contrast, soft techniques, which temporarily replace eroded material, include methods like dredging or sediment infill, but these have been stop-gap measures because the cause of the heavy erosion in the area remains. Dredging, the most cost-effective and widely used soft technique, is detrimental to the local biota. Large amounts of offshore sediment, which provides homes for marine organisms, have been excavated and resettled above water on the beach, destroying the biological community of those organisms (California State Conservancy 2002).

Glass cullet, a granular material made of crushed glass, has been used as a compatible beach replenishment supplement for silica sand. The main source of glass cullet is from industrial float glass, which is primarily used for windows and is tempered or colored during the production process. These compositional and structural changes make it difficult to reuse or recycle float glass. An alternative to using float glass could be recycled bottle glass, which is produced via a molding process. This approach is promising because, as long as bottles are separated by color, they are theoretically infinitely recyclable. The abundance of glass in the United States also makes this a realistic achievement. Unfortunately, only 33% of the U.S. recycles glass because of the low demand for glass cullet (Jacoby 2019). For example, the city of Fort Smith, Arkansas no longer recycles glass (City of Fort Smith 2021). With further research, the implementation of glass cullet as a technique to combat coastal erosion and the effects of sea level rise may help give scientists a fighting chance while giving recycled glass a new purpose.

Previous research investigated the impact of using glass cullet as sand replacement on nesting megafauna, such as sea turtles. In a study published in 2008, the turtles did not distinguish a difference between natural sand and sand-sized glass cullet (Milton et al. 1997; Makowski & Rusenko 2007; Makowski et al. 2008; Makowski et al. 2011; Makowski et al. 2013; Fisher et al. 2015). However, the environmental impacts of using bottle glass cullet have not been thoroughly investigated. One concern is the possibility of the heavy metal ions used in the bottle coloring process leaching out through weathering and exposure to heat and UV light. Elements including cobalt, cadmium, nickel, chromium, iron, manganese, copper, and sulfur are used as coloring agents in glass production (Sturgeon 2008; Kut'in et al. 2018).

We approached the environmental concerns of leaching from a chemistry-based perspective. This project is novel because it explored using "home-made" glass cullet from house-hold bottles. For methodology development, we placed green glass cullet in a brine environment (to mimic coastal conditions) with the goal of determining if chromium ions leached from the green glass were detectable via Flame Atomic Absorption Spectroscopy (FAAS).

## Methods

A calibration curve was created for the Flame Atomic Absorption Spectrometer (Buck Scientific 210VGP) using concentrations of 1, 5, 10, 15, 20, and 25 ppm (Figure 1). These solutions were generated from a 1000 ppm stock of chromium (CENCO Central Scientific Company, USA) with 2% (v/v) $HNO_3$.

**Figure 1.** Students running calibration samples on the FAAS.

Green bottles of unknown various ages were collected. All bottles were sterilized by washing them in hot soapy water and then placed in a 70% isopropyl bath for 30 minutes to limit bacterial growth during incubation in brine solution. The bottles were pulverized into approximately gravel-sized pieces, then polished to round out sharp edges using a rock tumbler and polishing media (Central Machinery Tumbler Media Ceramic Polishing Abrasive). After polishing, the cullet was rinsed, separated by size using an automated sieve with a range of 0.079 inches to 2.5 inches (Gilson USA Standard), as seen in Figure 2.

**Figure 2.** Green bottle glass cullet after polishing in rock tumbler.

For each methodology experiment, one hundred grams of glass cullet was placed into a clear 1 L glass jar containing 3.5 wt% sodium chloride in deionized water. A jar of deionized water with no glass was used as a control. All samples were left to incubate at room temperature, ~71°F. Aliquots of water were removed after 5 weeks. The aliquots were analyzed by FAAS to determine the concentration of leached chromium metal ions. The samples tested were compared to the calibration curve of chromium ions. Deionized water was used as a control to zero the instrument. The aliquots were run through the FAAS and the absorbances of each were recorded. For every cullet jar, three aliquots were removed. Each aliquot sample was "sipped" by the FAAS three times and an average value of absorbance was recorded. This was repeated a total of three times per aliquot. This gives three average values for a total of nine sample "sips." Those three values were then averaged together to get a final absorbance value from the sample jar. Linear regression analysis was applied to the calibration standard data to create a proposed model that best represents the relationship between chromium ion concentration and measured absorbance. Using the final average absorbance of the cullet samples and the generated linear equation, the concentration of the chromium ion in the cullet was calculated.

## Results and Discussion

Calibration standards were used to obtain the data points (circles) and regression line shown in Figure 3. The equation obtained from the linear regression was $y = 0.0018x + 0.0019$. The absorbance obtained from the sample was 0.04407, which led to a calculated concentration of 23.43 ppm (black square), as seen in Figure 3.

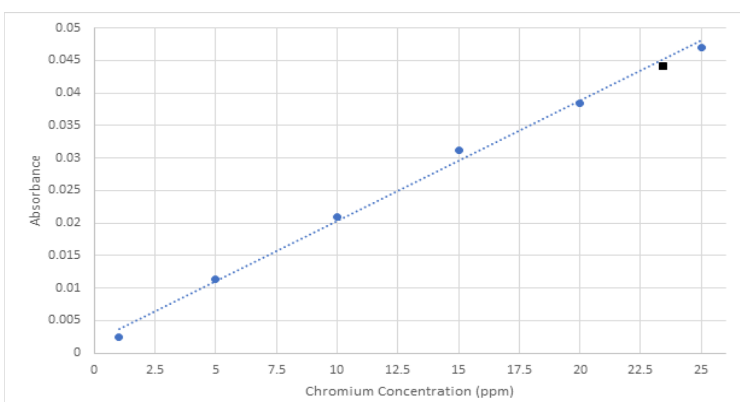


**Figure 3.** Chromium concentration of calibration standards (circle) and sample from bottle glass cullet leachate (black square).

Based on the calculated concentration, chromium was detected in the leachate from the cullet in the deionized water sample. This result shows the validity of the methodology that was developed. While this concentration could be considered high, there are multiple factors to take into consideration when looking at the use of glass cullet in long-term shoreline restoration applications. For example, in realistic applications, there would be a significantly larger volume of fresh or seawater that the chromium could leach into as opposed to the 1L of water in the laboratory sample, making the concentration much lower. For this experiment, the age of the bottles varied, and the chromium concentration used in the initial coloring of glass could have changed over time, which is likely to be the case in real-world applications and will be addressed in future work. Additionally, the charge of the chromium ion can change based on environmental factors. In terms of human exposure, the bioavailability of chromium can also fluctuate, with gastrointestinal absorption estimated as less than 5% for chromium (VI) (EPA 1998).

## Conclusion

This preliminary work was conducted to determine if chromium leaching from glass cullet could be detected using FAAS. Based on the result from our “proof-of-principle” experiment with green glass cullet, this methodology could be applied to other colored cullet samples. Bottle glass comes in many colors that come from the elements used as colorants. This novel experimental setup could be used to determine the concentration of sulfur (amber glass), cobalt (blue glass), cadmium or lead (yellow glass), manganese (purple glass), and many others. This initial result sets the foundation for future work, which will include investigation of other metal leachates. Our future plans also include expanding our protocol to include samples that have been placed in a 3.5 wt% brine solution and then introduce changes in temperature, agitation, and UV light exposure to better mimic a marine environment. This will allow us to understand the effects of these parameters on metal ion leaching.

## Limitations

We recognize that when performing linear regression analysis, more data points are preferred. Multiple experiments could be run simultaneously to allow for collection of additional data. We are aware there are more advanced instruments (ICP-MS) that could be used for this purpose, but they are typically out of the financial reach of small, teaching-focused, primarily undergraduate institutions (PUIs). Flame atomic absorption spectroscopy was chosen because these instruments are readily available at most PUIs, since they are often used in teaching labs. FAAS is an affordable, low maintenance, widely used analytical instrument. While other methods have been used to determine metal ion leaching from glass cullet, FAAS has not been utilized for this purpose. As a methodology note, the green bottle color can also arise from iron oxide used as a colorant, however, chromium oxide is used to color “emerald” green glass, which is what was used for this project.

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