Screening of Ceramic and Leaded Contaminants in Glass Recycling Streams via Handheld X-Ray Fluorescence (HHXRF) Analyzers

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Abstract

Material recovery facilities (MRFs) typically use magnetic and optical sorting systems to separate glass cullet from recycled glass. However, these systems are not effective at screening glass ceramic and leaded constituents from cullet streams. These contaminants lower the value of glass cullet to glass manufacturers, as they represent manufacturing and safety concerns. Handheld X-ray fluorescence (HHXRF) analyzers are widely used in various recycling and manufacturing settings to quickly provide chemical composition on a variety of elements, even to the range of 1–10 ppm. We compare HHXRF analysis of prepared glass samples to laboratory assayed glass standards used by MRFs and glass manufacturers. Our results show that HHXRF can detect even small quantities (<100 ppm) of ceramic elements in glass and glass cullet streams in situ. Our results also show HHXRF detection of leaded contaminants and coloring agents (Fe, Cu, etc.) in cullet streams. We also demonstrate that the same technique can be applied to in-line monitoring systems to analyze material streams for the same constituents.

1. Introduction

Sorting strategies in glass recycling have undergone many evolutions in recent decades, thanks to advances in scanning techniques and automation. One important development is the reduction of contamination caused by non-glass material in glass cullet. These contaminants reduce the yield and economic viability of using recycled glass in glass production. A variety of techniques are used to sort out various kinds of material based on their physical characteristics, such as metals through magnetic sorting techniques and plastics/papers through density sorting techniques (e.g., vibrating screens). However, one class of materials—ceramic glass—poses a particular set of challenges.

Ceramic glasses have become more ubiquitous in recent decades in various products, such as cookware and manufactured goods [1]. Glass ceramics are also key in the manufacturing of personal electronic devices—for example, smartphone screens. Ceramic glasses can possess many of the same physical properties as normal glass, which can make visual and manual sorting difficult. However, because of the higher melting points and unique chemistry of these materials, they can pose various problems when introduced into the glass manufacturing process. Ceramic materials build up in and damage furnaces, increasing costly shutdown and maintenance times. These ceramic constituents also have the potential to damage cutting and separation implements as they can remain intact in molten glass. Finally, the presence of even small fragments of...
ceramic glass can damage or cause defects to casted glass products, such as jars and bottles (Figure 1).

![Figure 1. Ceramic inclusion (zirconia) defect in amber glass bottle [2]](image)

Sorting out these materials has proven to be a difficult challenge for visual and manual sorting. Most ceramic glass separation is done through a combination of automated and manual visual sorting. While some ceramic glasses are discernible owing to their opacity or color, several resemble normal glass cullet. As such, techniques such as spectroscopy have been explored to perform sorting based on chemical differences. Adapting spectroscopy techniques in the sorting process is not a new concept. Visual laser-based spectroscopy has shown some promise, but still has difficulty in handling various glass pigmentation (green, amber, etc.) and obtaining positive IDs of ceramic in glass products [3].

Performing direct measurement of the X-ray fluorescence of elements unique to ceramic glass products—titanium (Ti), zinc (Zn), strontium (Sr), and zirconium (Zr)—is explored in this paper. Additionally, detection of other elements—lead (Pb), iron (Fe), and copper (Cu)—is also explored for other sorting needs, such as the removal of leaded glass from process streams. These various elements (with the exception of Fe and Cu) are not typically found or desired in high quantities in soda glass, which makes up the majority of recycled glass cullet, so they should serve as useful indicators of ceramic/leaded contamination. Using X-ray-based systems has been explored in the past, but typically in the context of imaging as opposed to fluorescent spectroscopy [4].

2. X-ray fluorescence spectroscopy

X-ray fluorescence spectroscopy has been an effective technique for quantization of elemental chemistry for several decades. Exciting matter with X-rays produces secondary radiation through scatter and photoelectric absorption and re-emission. Photons ejected from excited matter that were generated by photoelectric excitation have energies and wavelengths that are characteristic to the atom that emitted them. This phenomenon, referred to as fluorescence, can be measured to determine compositional information.

The first XRF systems were created in the early 20th century based on the work of Henry Mosely in 1912 [5]. These initial systems used diffraction gradients to separate spectra lines based on wavelength. As such, the method used by these devices was dubbed
wavelength dispersive spectroscopy (WDS). In subsequent decades, with the advancement of semiconducting materials from 1947–1960, spectra could be distinguished based on photonic energy, thus removing the need for diffracting gradients and allowing for a greater compacting of optics for spectra generation. The method employed by these systems was referred to as energy dispersive spectroscopy (EDS) [6].

Handheld XRF (HHXRF) systems began to arise in the late 20th century. These systems were EDS-based due to size, portability, and power requirements for portable systems. Additionally, these first systems used isotope sources because of power restrictions with the X-ray tube. Modern handheld systems now use low-power X-ray tubes as their excitation sources. These advancements, along with improvements in portable computing and spectral processing, enabled the development of handheld systems capable of generating results comparable to laboratory results in many applications.

2.1 Equipment

An Olympus Vanta™ handheld XRF analyzer (model: VCR, serial number: 800212) was used for this experiment. This instrument uses a 40 keV capable X-ray tube and a silicon drift detector (SDD) for its spectra generation and acquisition. Of the available calibration modes on the analyzer, the “soil mode” calibration was used and adjusted to work with glass samples. This method was selected for the following reasons: first, it uses a computation technique known as Compton normalization, which is an effective technique for measuring trace levels of heavier elements (i.e., elements whose primary emission line is >4 keV) in a lighter element matrix [7]. As the mode’s name suggests, it is primarily used in the analysis of soil samples, which are largely silica-based (SiO$_2$). This translates well to glasses, which are also largely silica-based. Second, soil mode offers various X-ray excitation conditions, enabling a user to select the ideal conditions for exciting their elements of interest. Finally, soil mode enables users to create custom calibration factors using their own certified samples, meaning the method can be adjusted to different sample types, giving the method quasi-empirical capabilities. This feature was used to adjust the HHXRF analyzer’s calibration to various certified samples. However, it is important to note that Compton normalization calibrations are generally ineffective at measuring concentrations >10%, owing to the increased prevalence of interelemental interferences and matrix effects. As such, results whose readings are considered greater than >10% in our testing will simply be reported as “>10%” by the analyzer.

The HHXRF analyzer was secured in an Olympus Vanta™ Work Station to ensure consistent sample presentation to the analyzer, as well as to provide adequate shielding for longer exposure tests. The instrument is controlled using the manufacturer’s PC software application.
2.2 Samples

Certified NIST samples—NIST 610 and NIST 612—were selected for initial instrument calibration, along with a certified quartz glass blank. The XRF analyzer was adjusted for the various elements of interest using these samples. In addition to these, several ceramic/leaded glass fragments were provided by a supplier for analysis. Fragments were selected to represent different forms of contamination (Figure 2). These samples were independently analyzed using inductively coupled plasma mass spectrometry (ICP-MS) to verify their chemistry and to serve as a point of comparison for XRF accuracy. Samples were tested using XRF on the center of one of their flat surfaces. Additionally, smaller (<3 mm diameter) fragments of these samples were separated for analysis to investigate size/shape effects of XRF analysis and to mimic typical inclusion sizes in mixed cullet.

3. Experiment

The initial analyzer calibration was performed using the NIST samples. To better account for thickness biasing effects, two copies of each sample were stacked and shot simultaneously to obtain comparable thickness to later samples (~6 mm). Each sample was analyzed five times using 30-second exposures for beams 1 and 2 of the soil method (60 seconds total per analysis). Each beam is 40 keV, but they are under different filter
conditions to better excite different groups of elements. Results from these tests were used to generate calibration factors to apply to future testing. The NIST samples were retested using these settings to verify performance (Table 1).

<table>
<thead>
<tr>
<th>Element</th>
<th>Assay</th>
<th>+/- 2σ (XRF ppm)</th>
<th>+/- 2σ (ppm)</th>
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<tbody>
<tr>
<td>Ti*</td>
<td>437</td>
<td>30</td>
<td>496.8</td>
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<tr>
<td>Zr[8]</td>
<td>440</td>
<td>2</td>
<td>445.4</td>
</tr>
<tr>
<td>Zn*</td>
<td>433</td>
<td>4</td>
<td>428</td>
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<tr>
<td>Pb</td>
<td>426</td>
<td>1</td>
<td>427</td>
</tr>
<tr>
<td>Cu</td>
<td>415</td>
<td>29</td>
<td>443</td>
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<tr>
<td>Fe</td>
<td>458</td>
<td>9</td>
<td>447.4</td>
</tr>
<tr>
<td>Sr</td>
<td>515</td>
<td>0.5</td>
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NIST 612

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<tr>
<td>Sr</td>
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<td>0.2</td>
<td>83.2</td>
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</tbody>
</table>

Table 1. Certified assay values and average Vanta XRF results on NIST 610 and 612 after calibration factors (* = Reference or informational values)

4. Results and discussion

Chemistry results and spectra for the samples are shown in Table 2 and Figure 4, respectively. Table 2 shows the average result for each exposure time. An example of spectra for beam 2 is shown in Figure 4 as it is the ideal beam for analyzing first-order transition metals, and most of our elements of interest belong in that category.
Table 2. XRF results of various glass contaminants under different test times (units in PPM unless noted)

While larger concentrations (> 500 ppm) are detected across multiple test conditions, the accuracy of quantification does not appear to be ideal. There are several possible explanations for some of these readings. One aspect may be sample thickness effects. While we attempted to calibrate to the sample thicknesses using the NIST samples, some of these samples are noticeably thicker than what we used in calibration (> 6 mm). That said, readings from the XRF analyzer are largely consistent for all test time variations, indicating that accuracy is likely not to suffer from faster testing, which would be necessary for automated testing. However, test precision would be impacted due to the reduction in sampling time and loss of the associated statistical confidence that come with longer test times.

With regards to the Ti readings in sample 1, ICP results also indicate a sizeable amount of barium (Ba) present in the sample (~9%), which is likely interfering with Ti measurement. There exists a spectral overlap of the Ba L-alpha line with the Ti K-alpha line, which can cause issues with regards to peak deconvolution.

Even if quantitative analysis struggles in some areas, the spectra collected for these tests and subsequent chemistry calculation demonstrate the effectiveness of XRF for the qualitative analysis of these samples (Figure 4). Spectra collected show very prominent peaks for the various detected elements for all test times. The results of these peaks indicate that detection of the presence/absence of these elements should be possible, thus making sorting of the material possible. Results from the small fragments were comparable to their larger counterparts.
3. In-line system

The EDS technique used by the XRF handheld system can also be implemented in larger scale automated systems. One such system, the X-STREAM™ in-line series of products produced by BT-Wolfgang Binder GmbH, uses the same EDS technique as the Olympus Vanta™ handheld XRF analyzer [10]. However, instead of a single excitation source and detector, several arrays of each are used to increase the effective excitation area as well as the total fluorescent yield from the samples, which are typically a further distance from the detector than with handheld systems (Figure 5).

Figure 4. Beam 2 spectra of sample 1 for both the main sample and the small sample fragment (3-second test time)

Figure 5. CG diagram of X-STREAM EDS sample presentation and excitation system (courtesy of BT-Wolfgang Binder GmbH)
4. Conclusion

Detection of ceramic elements in glass cullet samples is possible using HHXRF in fragments as small as 1 mm in size with at least 3σ confidence. While effective quantitative analysis is also possible, it requires substantial sample preparation and instrument calibration, and such tasks would be difficult in the context of rapid sorting. However, qualitative testing using HHXRF or in-line systems is possible and is presently performed in automated and manual sorting systems. As such, XRF can be an effective tool in the sorting of various ceramic contaminants that are difficult to sort using other methods.

Acknowledgments

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References and footnotes


