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Elemental Analysis of Waste Glass by X-Ray Fluorescence Spectrometry (U)

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ELEMENTAL ANALYSIS OF WASTE GLASS BY X-RAY FLUORESCENCE SPECTROMETRY*

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ABSTRACT

An X-ray fluorescence (XRF) technique is reported which shows promise for the elemental analysis of low-level mixed waste glasses. This technique can be used for both quantitative laboratory analysis and in process control. The glass-forming melts are cast into graphite molds and the resulting disks are annealed and polished. The disk is then analyzed with a wavelength dispersive X-ray fluorescence spectrometer and the elemental intensities are converted into concentration with a fundamental parameters routine without the use of matrix-matched standards. The precision of the elemental determinations are all better than one percent relative standard deviation. The XRF analysis has been compared with a reference method utilizing conventional wet chemical dissolution techniques followed by atomic spectroscopic determination. The results show that there is no significant difference between these two techniques, however, the XRF technique is much simpler and faster than the wet chemical methods.

INTRODUCTION

X-Ray Fluorescence (XRF) Spectrometry is a widely-used technique for the routine quantitative elemental determination of ceramics[1] and ordinary glass[2] but it has received little application in the field of waste glass analysis. This is unfortunate since XRF is one of the most precise and potentially accurate analytical techniques available. There are several reasons why analysts in the vitrification arena have stayed away from XRF. High-level waste glasses produce large background count rates due to their inherent radioactivity. This, however, may not be such a problem with low-level mixed waste glasses.

Another problem facing waste glass analysis has been the difficulty in quantifying the elemental composition from the spectral line intensities. The line intensities are not only a

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function of the analyte content but also depend on the presence of other species in the sample due to their matrix effects. These effects include absorption of the incoming and outgoing X-rays. Another matrix effect, enhancement, results when an element with a higher atomic number than the analyte element are excited and their resulting secondary X-rays in turn cause additional fluorescence from the analyte. Empirical calibration curves must be developed by first determining empirical coefficients relating one element's matrix effects on another. This is only accomplished with the use of many standards whose compositions closely match that of the samples. This becomes impractical with waste glass samples which have complex and widely variable compositions often containing more than 20 elements. Several studies on waste glass analysis have been reported using this tedious method of empirical coefficients with numerous standards. The XRF analysis of non-radioactive, surrogate high-level waste glass was reported in 1978 by Slates.[3] This method was laborious and was limited to only a few of the many elements present. Sodium, iron, aluminum, and calcium could not be quantified and the procedure required the use of numerous matrix-matched standards. A recent XRF procedure for determining iron and cerium in waste slags has been reported by Carney[4] but the results were reported to be only semi-quantitative. This procedure also required the use of forty matrix-matched glass standards were prepared. In addition, glass samples were analyzed as powders thus reducing the accuracy and precision and increasing the sample preparation time. A truly useful analytical technique should provide the composition of all the major elements present because the major elements will affect the chemical durability of the final waste form.

An alternative approach for XRF quantification, called Fundamental Parameters (FP), uses mathematical equations with fundamental constants to convert the element intensities into composition.[5] In this analysis no standards are required but the accuracy depends upon knowledge of the individual fundamental constants for each element such as absorption coefficients and fluorescence yields. The method was developed for XRF by Criss and Birks in 1968[6] but it was of limited value due to the scarcity of accurate data on these fundamental constants. As measurements of these constants improved, so did the accuracy in the calculation of the elemental concentrations. This FP method is now in widespread usage for XRF analysis because of this improved accuracy and because it does not require standards.

Another reason that XRF has not been applied to high-level borosilicate waste glass analysis has been the difficulty in analyzing light elements such as lithium, boron, fluorine, and sodium. The fluorescent yields from these elements are diminished and their corresponding X-rays have greatly reduced penetrating power. As a result, the light element intensities are typically very low resulting in poor measurement precision. Developments in instrumentation and in the analyzing crystals have resulted in remarkable improvements in recent years in the analysis of fluorine and sodium.[7] Recent XRF measurements on borosilicate waste glasses showed that sodium line intensities could be determined with a high degree of precision but the boron intensity was still too low to be quantifiable.[8] Boron, then, would have to be determined by difference. However, if the concentration of all the other species in the glass are accurately determined then boron could be determined by difference. This is the approach that will be employed in this study to determine boron.

In previous work in this laboratory, a rapid glass sampling technique was developed.[8] It was reported that samples could be taken directly from the crucible or melter tank and prepared for analysis within 30 to 45 minutes. The intensities from replicate samples were measured and the precision was found to be better than one percent relative standard deviation. This paper reports the quantitative elemental analysis of waste glass samples using a wavelength dispersive XRF spectrometer and the FP method. These results are then compared to results from a reference analysis utilizing conventional wet chemical glass dissolution techniques and atomic spectroscopy.

EXPERIMENTAL

Glass Preparation

Six silicate glasses were prepared by a procedure described elsewhere.[9] Each melt was cast into graphite molds to produced three disks 40mm in diameter by about 5 mm in height. The disks were then annealed at 450°C for 30 minutes and then polished using 1000 grit SiC paper on a Buehler polishing wheel. Next, the glass was carefully abraded manually using 600 grit paper, first in one direction, then orthogonal to the original direction to ensure that each disk had a similar 600 grit finish.

Glass Analysis

The reference analysis of these glasses was performed by wet chemical dissolution techniques and followed by flame emission spectroscopy (FES) or inductively coupled plasma-emission spectroscopy (ICPES) by Corning Engineering Laboratory Services of Corning, New York. Three separate digestion techniques were employed to dissolve the glasses. Sodium was then determined by FES following digestion in hot hydrofluoric acid. Boron was determined by ICPES following digestion in cold hydrofluoric acid. The remainder of the elements were determined by ICPES following digestion with a fusion technique. Instrument calibration was carried out with matrix-matched standards to compensate for matrix interference. Each determination was carried out in triplicate and averaged.

The XRF analysis of the disks was performed with a Rigaku Model 3271 wavelength-dispersive XRF spectrometer using 30 mm sample apertures and the instrument conditions listed in Table I. Samples were rotated at 30 revolutions per minute. An end window X-ray tube with a Rhodium target was used to generate the X-rays.

Conversion of the elemental intensities into concentration was carried out by an FP procedure developed by Rigaku. Element sensitivities were determined from Glass Sample #MMHO using the wet chemical results from Corning Laboratories.

TABLE I. XRF Instrument Parameters[a]

Element Line	Crystal[b]	Detector[c]	Angle, 2θ	Collimator	Time, sec.
B K_α	RX70	PC	50.060	Coarse	n/a
Na K_α	RX35	PC	26.175	Coarse	20
Al K_α	PET	PC	144.965	Coarse	20
Si K_α	RX4	PC	144.650	Coarse	20
Ca K_α	LiF(200)	PC	113.200	Coarse	20
Fe K_α	LiF(200)	PC	57.570	Coarse	20
Ni K_α	LiF(200)	PC	48.705	Coarse	20
Ba L_α	LiF(200)	PC	87.350	Fine	20
Pb L_α	LiF(200)	SC	33.965	Coarse	20

[a] All elements were analyzed at 50kV, 50mA under vacuum.

[b] 160 Å Mo-B4C multilayer crystal; 60 Å W-Si multilayer crystal; 45 Å W-Si multilayer crystal.

[c] PC = Flow Proportional Counter; SC = Scintillation Counter.

RESULTS and DISCUSSION

The precision in the XRF analysis of these waste glasses was determined by comparing the measured elemental intensities from three replicate glass disks. The relative standard deviations (RSD) for each element from each of six glasses are shown in Table II. Boron intensity data were not included because it was too low to be quantifiable. The results show that the RSD is less than 1.0 percent for all measured elemental intensities. This level of precision for quantitative elemental determination is far better than is normally achievable with either ICPES or AA techniques.[2] The precision reported here is representative of both the sample preparation technique and instrument data collection. Such a high degree of precision reduces the number of replicates necessary for an accurate quantitative analysis. In fact, this high degree of precision suggests that one sample might be sufficient for the elemental analysis of waste glass carried out in a process control environment, if the glass sample is drawn from a homogeneous melt.

TABLE II. Percent Relative Standard Deviations of XRF Intensities from Three Replicate Disks

Glass	Na	Al	Si	Ca	Fe	Ni	Ba	Pb
MID1	0.93	0.12	0.22	0.01	0.04	0.04	0.10	0.16
1,2MMH	0.19	0.12	0.27	0.07	0.12	0.06	0.09	0.52
2MMM	0.13	0.10	0.23	0.08	0.28	0.06	0.04	0.21
3MMM	0.19	0.22	0.47	0.04	0.10	0.15	0.20	0.37
2HHH	0.45	0.13	0.26	0.12	0.01	0.10	0.26	0.36
MMHO	0.48	0.27	0.18	0.05	0.04	0.13	0.13	0.16

The accuracy of the elemental analysis of these silicate waste glasses by XRF has been assessed by comparison with a reference method. The reference method employed here involved several wet chemical dissolution techniques, depending upon the analyte of interest, followed by one of several atomic spectroscopic techniques. The XRF analysis involved the measurement of X-ray intensities from each element with a sequential wavelength dispersive spectrometer. The element intensities were then converted into weight percent composition with a fundamental parameters routine utilizing a single standard (Glass *MMHO*) to determine the element sensitivities. The composition of the standard was also determined by the wet chemical procedure.

The results of the elemental analyses from XRF are compared to the analyses from the reference method in Table III. Boron could not be analyzed directly due to the low intensities, therefore, its composition was calculated indirectly by difference. The agreement between the reference and the XRF analysis is very good. The results with B_2O_3, Al_2O_3, SiO_2, CaO, and Fe_2O_3 all agree within 0.65 percent of the reference values. Furthermore, Na_2O, NiO, BaO, and PbO all agree within 0.10 percent. It is clear from these results, that the elemental analysis of these wastes glasses determined by this XRF technique are in excellent agreement with the results from the more conventional wet chemical method.

TABLE III. Comparison of the XRF and Reference Elemental Analysis of Waste Glass Samples (Oxide Weight Percent)

Glass / Analysis	Na_2O	Al_2O_3	SiO_2	CaO	Fe_2O_3	NiO	BaO	PbO	B_2O_3[a]	Total
2MMM										
XRF	13.77	7.58	46.98	12.10	5.00	2.24	4.49	3.19	4.47	99.82
Reference	13.70	7.71	46.80	12.10	4.85	2.19	4.48	3.17	4.31	99.31
3MMM										
XRF	15.08	8.04	20.99	12.74	31.74	1.63	3.45	2.35	3.81	99.82
Reference	15.10	8.11	20.90	12.70	32.00	1.65	3.41	2.37	2.02	98.26
1,2MMH										
XRF	17.99	14.55	32.82	15.72	5.01	2.14	4.33	2.95	4.32	99.82
Reference	17.90	14.50	32.50	15.50	4.80	2.07	4.29	2.89	3.54	97.99
MMHO[b]										
XRF	15.36	1.18	34.27	13.82	19.96	2.01	4.20	2.94	6.09	99.82
Reference	15.30	1.18	34.20	13.80	19.90	2.00	4.19	2.93	6.32	99.82
MID1										
XRF	14.79	6.85	32.05	13.10	20.75	1.96	4.09	2.84	3.38	99.82
Reference	14.80	6.98	*31.70*	13.10	*20.50*	1.89	4.04	2.79	*2.95*	98.75
2HHH										
XRF	17.70	14.49	36.81	7.81	4.94	2.14	4.36	3.04	8.53	99.82
Reference	17.60	14.80	36.50	7.77	4.74	2.07	4.30	2.97	8.30	99.05
2LOO										
XRF	9.60	0.46	57.37	16.67	5.11	3.31	4.66	3.31	0.38	99.82
Reference	9.51	0.48	57.00	16.80	5.04	2.29	4.78	3.36	0.03	99.29

[a] XRF analysis for boron was computed by difference.

[b] Sample #*MMHO* was used to develop the element sensitivities.

The time required to perform the XRF analysis and FP calculations was considerably shorter than that for the wet chemical reference analysis. The analysis of each sample required only 10 minutes while the reference wet chemical methods required many hour of lab work. Instrument calibration which involved the determination of elemental sensitivities using sample *MMHO* also took only 10 minutes, as well. The reference wet chemical method, on the other hand, required that each sample first be milled to a powder and then subjected to three separate digestion procedures. Each of the three resulting digestates was then analyzed by either ICPES or FES. Furthermore, separate calibration curves were developed for each digestate from each glass from a set of matrix-matched standard solutions. This wet chemical analysis was both labor and time intensive.

Potential limitations of this XRF technique are discussed briefly here. Actual waste glass samples will likely differ from these surrogate glasses in several ways. Waste glasses may likely contain more than the nine oxides in these test species, and concentrations of some species will be below one percent. The analysis of more complex matrices including trace elements should still be achievable with XRF but further work is required to demonstrate this capability. Furthermore, mixed waste glasses will contain one or more radioisotopes which may affect background count rates. An example of a low-level mixed waste scheduled for vitrification is the wastewater treatment sludge currently in storage in M-area at the Savannah River Plant in Aiken, SC.[10] The resulting waste glass will include about 20 oxides ranging from boron through uranium.

This XRF technique should be capable of quantifying all elements from sodium through uranium. Elements lighter than sodium present special problems due to their inherently low count rates. Further testing is required before the precision and accuracy of fluorine analysis can be established. Only certain specialized wastes, however, are likely to contain fluorine. Oxygen does not need to be calculated if one assumes all cations to be present as the oxide and the oxidation states are known. For determination of elements lighter than oxygen, direct analysis appears unlikely and quantification must be carried out indirectly by difference. This study has demonstrated that boron can be quantified if it is the only light element present. If the glass contains lithium as well as boron, as is the case with certain high-level waste glasses, then this method would not be capable of distinguishing between the two. Lithium, however, is a very expensive flux and not likely to be chosen as an additive for low-level or mixed waste vitrification.

Radioisotopes, present in low-level mixed wastes, could potentially cause spectral interference due the intrinsic radiation from the glass itself. Defense wastes can contain a variety of radioisotopes including ^{90}Sr, ^{99}Tc, ^{137}Cs, ^{238}U, and ^{242}Pu. Further testing needs to be carried out in order to determine the maximum tolerable radioactive levels in glass without adversely affecting the analysis.

XRF could play an important role in vitrification quality control. It is known that chemical durability is largely a function of glass composition. Composition limits for the glass product would be predetermined and then compared to the actual product composition to ensure product durability. In all likelihood, trace oxides would not play a role in product acceptability because of the minimal effect that they would have on chemical durability.

The actual chemical composition of the glass product could be determined periodically by XRF and then compared to the predetermined limits with the aid of statistical process control charts.[11] The key steps in the elemental determination will include the following:

1) rapid, consistent glass sampling;
2) precise measurement of X-ray intensities; and
3) accurate determination of glass composition from X-ray intensities using FP.

The glass product could be sampled directly as it flows from the melter by collection in a graphite mold. In this way the sample would be ready for analysis within 30 to 45 minutes. Even though the glass disks were polished in these experiments, previous studies on waste glass have shown that precision does not greatly suffer when disks are analyzed without prior polishing.[8] The quantitative chemical analysis could then be available within one hour from the time the glass flows from the melter.

CONCLUSION

This study demonstrates that rapid, precise, and accurate XRF analysis can be obtained for waste glasses containing Al_2O_3, B_2O_3, SiO_2, Fe_2O_3, Na_2O, CaO, NiO, PbO, and BaO. Replicate sample precision is better than one percent relative standard deviation for all elements except boron which must be determined by difference. But even the boron analysis is within one percent absolute by weight. The accuracy in this XRF procedure is as good as the wet chemical methods traditionally employed. This technique can potentially be used for both laboratory quantitative chemical analysis or as a tool in vitrification process control by providing elemental analysis of the glass shortly after it flows from melter.

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