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QUANTITATIVE SEM/EDS ANALYSIS OF HIGH-LEVEL WASTE GLASSES

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Silicate glass will be used to stabilize high-level radioactive wastes (HLW) for disposal in a geological repository. The chemical durability of waste glass in the repository will be determined by the nature and progress of the glass-water (underground water) reaction. Aqueous corrosion of HLW glasses is known to result in the chemical alteration of the glass surface and the formation of secondary phases. Accurate quantitative analysis the altered glass surface and the reaction products that form is important for understanding the reaction kinetics and mechanism of glass corrosion.

SEM/EDS is a powerful tool to study the alteration of waste-disposal glasses through quantitatively characterizing the reaction products. It is able to detect trace elements at concentrations less than 1 wt.%: for example, Fig. 1 shows the uranium peaks detected by SEM/EDS of a typical simulated waste glass, which contains 0.25 wt.% uranium in the matrix glass according to ICP/MS analysis. Nickel (0.44 wt.%) and chromium (0.47 wt.%) peaks are also clearly distinguishable in the spectrum (see arrows in Fig. 1). However, quantitative analyses of glass compositions are complicated by the lack of well-characterized reference samples having known and homogeneous compositions for candidate waste glasses, which may contain a combination of more than 20 different elements in one matrix. It has been proposed[1] that unreacted glasses with known compositions could satisfactorily serve as standards for quantitative analysis of waste-disposal glasses and the secondary phases. The main advantage of using such standards is that they contain all the elements to be analyzed in the homogeneous vitreous matrices. In this paper, we evaluate several reference waste glasses with respect to their suitability as standard samples for quantitative SEM/EDS analysis. The precision and accuracy using such standards for quantitative analysis are also discussed. All the experiments were carried out on a Topcon ABT 60 SEM operating at 20 kV.

The degree of homogeneity was evaluated by analyzing 10 specimens randomly selected from a 100-300 particle (100-200 mesh) specimens for each glass. Analysis of the elements of interest using no standards (standardless) in random order demonstrates the precision of standards since errors caused by instruments are generally much less than 1%. The results indicate that the homogeneity differs from glass to glass, and also differs from element to element within one glass (see Fig. 2). SRL 131 glass was the most homogeneous glass, where the standard errors for major elements (i.e., those percentages at > 5wt.%) were less than 1% and for minor elements (i.e., those percentages at <5wt.% but >1wt.%) were less than 4% (see Fig. 2a). However, standard errors as high as 4% were observed for major elements and 40% for minor elements for SRL 202 glass (see Fig. 2b). The homogeneity for trace elements was not evaluated since the counting statistics for these elements were poor.

Quantitative EDS analysis was carried out by using the PROZA routine in the Voyager system supplied by NORAN. The PROZA routine is a refined ZAF process that takes into account the escape depth of the light element x-rays. Table 1 compares the results of the analyses with and without standards for the same spectrum acquired from a simple waste glass. As expected, the concentrations obtained from the analyses with standards are close to the values entered for the standard's compositions. On the other hand, the standardless analysis seems to underestimate the weight concentration for light elements, such as Al, Si, and Ca. This indicates that standardless analysis is not reliable for analysis of peaks located at low energy ranges, particularly when these peaks tend to overlap. The results for sodium were more erratic and varied with locations within the same specimen, probably due to the migration of sodium under the electron beam[2,3]. Table 2 shows the results for a complicated waste glass which contains more minor and trace elements than the simple glass analyzed above. Typical errors using the standards that had been acquired from a different glass were < 5% for major elements and approximately 10% for minor elements. More accurate results should be obtained if more homogeneous glasses were available. Similarly, the alteration phases that formed during water-glass reactions were quantitatively analyzed by using unreacted glasses as standards. In this case, the unreacted glass interior of a reacted sample can advantageously serve as an internal standard, and, thus, further eliminate the statistical errors associated with sample preparation variation such as carbon coating thickness.[4]

References

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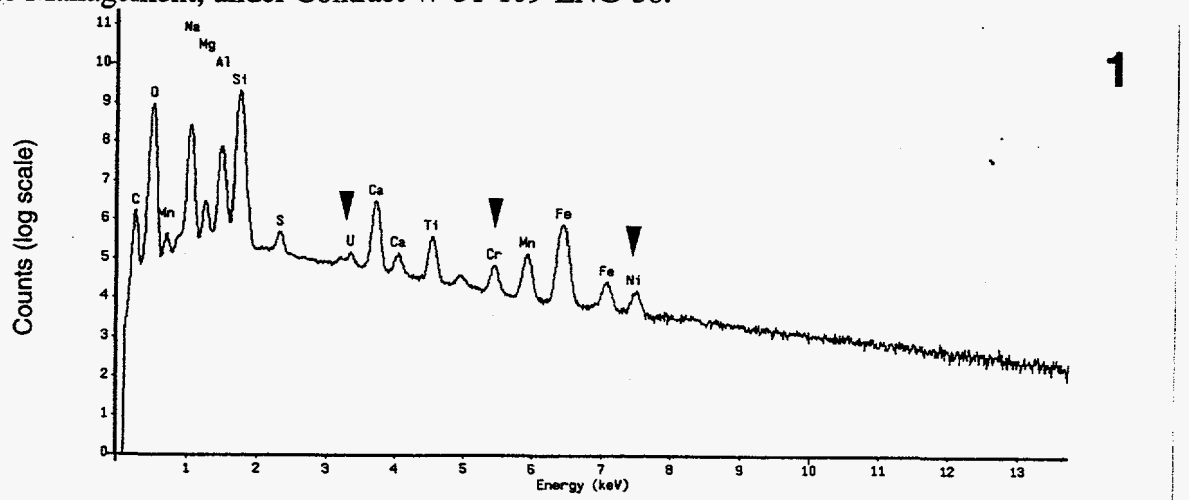
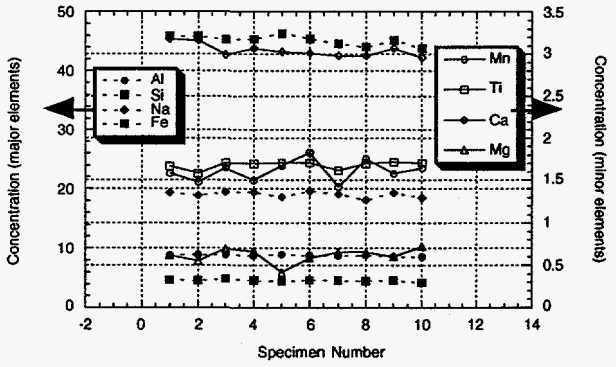
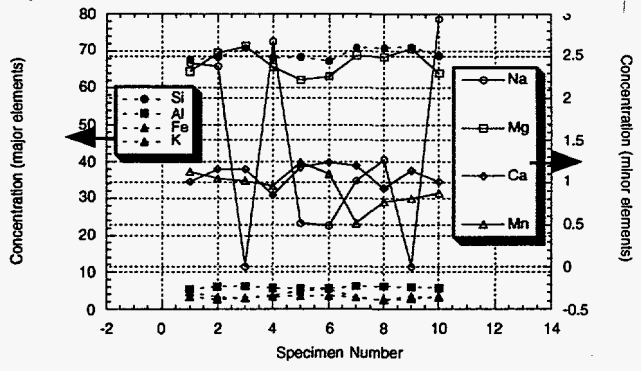
4. This research was sponsored by the U. S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-38.





2a: SRL 131 glass



2b: SRL 202 glass

Table 1. EDS analysis of a simple glass. A-analyzed by ICP/MS; B-analyzed using standardless routine; C-analyzed using the same glass as standard. The values shown represent the average of 5 spectra.

	A wt%	B wt%	C wt%
O-K	46.31	58.22	45.82
Na-K	14.81	16.23	17.39
Al-K	6.35	4.71	6.24
Si-K	26.13	17.47	25.37
Ca-K	2.86	1.17	2.65
K-K	1.22	0.45	1.21

Table 2. EDS analysis of complicated glasses. using the same glass itself or a different glass as reference. The values represent the average of 5 spectra.

	Glass I nominal[a]	(wt.%) stds.[b]	σ	Relative Error %	Glass II nominal[a]	(wt.%) stds.[b]	σ	Relative Error %
Al	3.2	3.2	0.02	0.0	1.9	1.9	0.08	0.0
Ca	0.3	0.5	0.02	15.0	0.9	1.08	0.06	20.0
Fe	8.4	8.4	0.12	0.0	5.3	6.6	0.1	25.0
K	4.2	4.2	0.03	0.0	-[c]	-[c]	-[c]	-[c]
Mg	0.5	0.5	0.04	0.0	1.1	0.72	0.1	35.0
Na	5.9	6.1	0.1	3.5	12.5	12.7	0.2	1.6
O	44.6	45.5	0.5	2.0	46.4	47.1	0.5	1.5
Si	19.2	19.2	0.1	0.0	22.8	23.3	0.2	2.2
U	0.5	0.55	0.1	10	-[c]	-[c]	-[c]	-[c]

[a] analyzed by ICP/MS, [b] glass I used as standard, [c] element not present.

Fig. 1. EDS spectrum of SRL131 waste glass showing clear peaks for trace elements U (0.25 wt%), Ni (0.44 wt%), and Cr (0.47%). The spectrum was acquired for 300 seconds using a takeoff angle of 45°.
Fig. 2. Concentration variation among particle specimens randomly selected from the same glass indicating the sample homogeneity or the repeatability of a measurement under stable conditions, which reflects the highest accuracy achievable by using these glasses as standard references.