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# X-RAY SPECTROMETRIC DETERMINATION OF GLASS CONTENT OF MELTS INCORPORATING RADIOACTIVE WASTE: A FEASIBILITY STUDY

R. V. SLATES

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AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

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**X-RAY SPECTROMETRIC DETERMINATION  
OF GLASS CONTENT OF MELTS INCORPORATING  
RADIOACTIVE WASTE: A FEASIBILITY STUDY**

by

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## **ABSTRACT**

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X-ray fluorescence spectrometry was evaluated for the determination of glass content and homogeneity of glass incorporating high-level radioactive waste. Accuracy and precision were determined for analyses of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{NiO}$  in specimens of known composition. These specimens were prepared by fusing powdered glass with nonradioactive synthetic waste. Matrix effects of sodium on these analyses were specifically evaluated. X-ray fluorescence spectrometry was shown to be applicable to the proposed determinations by comparing the known glass contents of 14 glass waste compositions with those calculated from experimentally determined concentrations of  $\text{SiO}$  or  $\text{TiO}_2$ .

## **CONTENTS**

---

Introduction	7
Experimental Description	7
Instrumentation	7
Glass Waste Buttons	8
Analytical Procedure	10
Matrix Correction Calculations	11
Accuracy and Precision Calculations	11
Results and Discussion	12
Matrix Calculations without Correction for Sodium	12
Matrix Calculations with Correction for Sodium	16
Applications	19
Conclusions	22
Acknowledgements	23
References	24

## LIST OF FIGURES

---

- 1 Calculated Concentration vs Known Concentration for  $\text{SiO}_2$ .  
No Matrix Correction for Sodium 16
- 2 Calculated Concentration vs known Concentration for  $\text{TiO}_2$ .  
No Matrix Correction for Sodium 17
- 3 Calculated Concentration vs Known Concentration for  $\text{SiO}_2$ .  
Matrix Corrected for Sodium 20
- 4 Calculated Concentration vs Known Concentration for  $\text{TiO}_2$ .  
Matrix Corrected for Sodium 21

## LIST OF TABLES

---

- 1 Glass Mix 21 Composition 8
- 2 Synthetic Waste Sludge Compositions 8
- 3 Glass Waste Button Compositions 9
- 4 X-ray Intensities from Glass Waste Spectra 13
- 5 Matrix Correction Coefficients, Excluding Sodium Correction 14
- 6 Concentrations Calculated Without Sodium Matrix Correction 15
- 7 Accuracy and Precision of Glass Waste Analysis 15
- 8 Matrix Correction Coefficients, Including Sodium Correction 18
- 9 Calculated Concentrations with Sodium Matrix Correction 19
- 10 Glass Content of Glass Waste Buttons Calculated from Experimentally Determined Concentrations of  $\text{SiO}_2$  and  $\text{TiO}_2$  22





## X-RAY SPECTROMETRIC DETERMINATION OF GLASS CONTENT OF MELTS INCORPORATING RADIOACTIVE WASTE: A FEASIBILITY STUDY

### INTRODUCTION

About 20 million gallons of high-level radioactive waste are stored in tanks at the Savannah River Plant.<sup>1</sup> A program is underway to demonstrate the technology required to convert SRP waste to a high integrity form for long-term management.

One conceptual method for converting high-level liquid waste to solid form is fusion of the concentrated waste with glass. The fusion would form massive glass rods which would be encased in steel canisters about 10 ft long and 2 ft in diameter.<sup>2</sup>

Safe transport and long-term storage will require that the glass content of the solid waste product be within predetermined limits. An analytical method which can accurately determine the glass content of the solid waste product is therefore required. This study evaluates spectrometric determination of SiO<sub>2</sub> and TiO<sub>2</sub> by X-ray fluorescence as a basis for determining the glass content and homogeneity of glass waste melts.

### EXPERIMENTAL DESCRIPTION

#### Instrumentation

An energy dispersive X-ray fluorescence spectrometer with secondary target excitation was used for all analyses. The instrument consisted of a KeveX 0810 X-ray tube excitation subsystem, a Siemens Kristalloflex 2H X-ray generator with smoothing attachment, and a Finnigan Model QM 77-90 spectrum analysis subsystem. The KeveX 0810 subsystem had a chromium anode X-ray tube and an 80-mm<sup>2</sup> lithium-drifted silicon detector with a 0.025-mm beryllium window. Detector resolution was 175 eV at 5.9 keV. The Finnigan spectrum analysis subsystem controlled the instrument during analysis and provided broad calculational capability through its dedicated 4K word computer with 32K word disk.

## Glass Waste Buttons

Glass waste buttons of different known compositions were prepared for this study by fusing nonradioactive synthetic waste with powdered Glass Mix 21. The composition of Glass Mix 21 is given in Table 1; the composition of each synthetic waste sludge is reported in Table 2; and the compositions of the glass waste buttons are shown in Table 3. Compositions of synthetic waste were chosen to simulate the different types of SRP high-level waste. The synthetic wastes were made by combining accurately weighed quantities of chemically pure metal oxides. The composition of each fused glass waste button was calculated from the accurate weights of its components.

TABLE 1

Glass Mix 21 Composition

<i>Constituent</i>	<i>wt %</i>
Li <sub>2</sub> O	4.0
B <sub>2</sub> O <sub>3</sub>	10.0
Na <sub>2</sub> O	18.5
SiO <sub>2</sub>	52.5
CaO	5.0
TiO <sub>2</sub>	10.0

TABLE 2

Synthetic Waste Sludge Compositions

<i>Button Number</i>	<i>Composition, mole %</i>				
	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>CaO</i>	<i>MnO<sub>2</sub></i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>NiO</i>
1	30.0	0.0	25.0	35.0	10.0
2	0.0	10.0	25.0	55.0	10.0
3	30.0	10.0	0.0	50.0	10.0
4	30.0	10.0	25.0	35.0	0.0
5	30.0	0.0	25.0	45.0	0.0
6	0.0	0.0	25.0	75.0	0.0
7	0.0	0.0	0.0	90.0	10.0
8	0.0	10.0	0.0	90.0	0.0
9	30.0	0.0	0.0	60.0	10.0
10	0.0	10.0	25.0	55.0	10.0
11	30.0	10.0	0.0	60.0	0.0
12	0.0	0.0	0.0	100.0	0.0
13	27.0	6.0	16.0	50.0	1.0
14	7.0	2.0	23.0	58.0	10.0

TABLE 3

## Glass Waste Button Compositions

Button Number	Glass Mix 21 in Button, wt %	Composition, wt %								
		NaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO	Li <sub>2</sub> O +B <sub>2</sub> O <sub>3</sub>
1	35.0	6.47	14.12	18.38	1.75	3.50	10.03	37.40	3.45	4.90
2	35.0	6.47	0.0	18.38	4.00	3.50	8.71	51.05	2.99	4.90
3	20.0	3.70	15.35	10.50	3.81	2.00	0.00	58.09	3.75	2.80
4	20.0	3.70	17.61	10.50	4.23	2.00	12.51	46.65	0.0	2.80
5	20.0	3.70	15.63	10.50	1.00	2.00	11.11	53.26	0.0	2.80
6	35.0	6.47	0.0	18.38	1.75	3.50	7.23	57.77	0.0	4.90
7	20.0	3.70	0.0	10.50	1.00	2.00	0.0	77.23	2.77	2.80
8	35.0	6.47	0.0	18.38	3.45	3.50	0.0	63.30	0.0	4.90
9	35.0	6.47	11.23	18.38	1.75	3.50	0.0	51.03	2.74	4.90
10	20.0	3.70	0.0	10.50	3.77	2.00	10.72	62.82	3.69	2.80
11	35.0	6.47	11.35	18.38	3.83	3.50	0.0	51.57	0.0	4.90
12	20.0	3.70	0.0	10.50	1.00	2.00	0.0	80.00	0.0	2.80
13	65.0	12.02	5.97	34.13	3.98	6.50	3.02	25.12	0.16	9.10
14	65.0	12.02	1.47	34.13	3.48	6.50	4.12	27.64	1.54	9.10

The glass waste melts were fused at 1150°C for 3 hours in kyanite or aluminum oxide crucibles. The melt was then poured into cylindrical graphite molds and solidified into buttons. Internal stresses were relieved by annealing the buttons at 500°C for one hour. The buttons are 20 mm in diameter and 10 to 15 mm thick.

Each glass waste button was potted in *Kold-Weld*<sup>a</sup> resin to provide the 1.25-inch-diameter size required by the sample changer. The surface of each specimen was ground flat and polished with successively finer grades of diamond dust polishing abrasive on silk cloth. The final polish was made with 1-micron diamond dust on *Microcloth*<sup>b</sup> by using a *Syntron*<sup>c</sup> automatic polisher.

### Analytical Procedure

All analyses were performed by the same procedure. The spectrometer was set to analyze X-rays from approximately 0.9 keV to 8.9 keV. Although this region includes  $K_{\alpha}$  X-rays of elements from sodium through copper, the thick beryllium window of the detector precluded detection of sodium X-rays. Each glass waste button was analyzed in vacuum for 500 seconds. Fluorescence was induced by unfiltered X-rays from a chlorine secondary target. The X-ray tube was operated at 10 mA, 25 kV. Net intensities were determined from the spectrum of each button for the  $K_{\alpha}$  X-rays of aluminum, silicon, calcium, titanium, manganese, iron, and nickel. The net intensities were corrected for instability of the X-ray generator by the method of Van Espen and Adams.<sup>3</sup> A small-diameter copper wire, positioned immediately below the glass waste button during analysis, served as an external standard and superimposed a copper  $K_{\alpha}$  peak in each spectrum. Normalizing all net intensities to a constant copper intensity eliminated the effect of generator instability.

---

a. *Kold-Weld* resin is manufactured by Precision Dental Manufacturing Co., 62 East Lake St., Chicago, Illinois 60601.

b. *Microcloth* is manufactured by A. B. Buehler Ltd., 2120 Greenwood St., Evanston, Illinois 60204.

c. *Syntron* automatic polishers are manufactured by Syntron Division, FMC Corporation, Homer City, Pennsylvania.

## Matrix Correction Calculations

X-ray interactions with other elements in the sample may diminish or enhance the observed intensities in X-ray fluorescence spectrometry. The effect of the elemental matrix must be included in the calculations to determine accurately the concentration of the element from the intensity of its fluorescent X-rays. The Lucas-Tooth and Price<sup>4</sup> matrix correction model used in this study is defined in Equation 1.

$$E_1 = B_1 + I_1 [B_2 + B_3I_1 + B_4I_2 + B_5I_3 \dots B_{n+2}I_n] \quad (1)$$

$E_1$  denotes the oxide concentration of element 1 in the glass waste solution. The experimentally determined  $K_\alpha$  X-ray intensities are denoted by  $I_1, I_2$ , etc. The subscript 1 applies only to the element being determined. Other subscripts denote the other metal elements. The subscripted B values are empirically determined matrix correction coefficients. These coefficients were evaluated for each metal oxide by a least squares fit of Equation 1 to the 14 sets of experimental data. A separate set of coefficients was obtained for each metal oxide determined in the glass waste buttons. After the matrix correction coefficients are evaluated, the composition of unknown glass waste buttons is determined by using Equation 1, the experimental X-ray intensities, and the correction coefficients.

## Accuracy and Precision Calculations

The accuracy and precision of the X-ray spectrometric determinations were evaluated for each metal oxide from the slope and standard error of the least squares regression line of a graph of the calculated concentration versus the known concentration. If an analytical method is reliable, the calculated concentrations of Equation 1 will reproduce, within experimental uncertainty, the known concentration for each metal oxide in the glass waste buttons. An analytical bias is indicated if the slope of the least squares regression line deviates significantly from unity. The precision of the analytical method is given by the scatter of the data points and is numerically equal to the standard error of the points around their regression line.

When the slope and intercept of the regression line are insignificantly different from unity and zero respectively, any potential bias errors must be small compared with precision errors. The bias errors can be included in the estimate of precision by calculating the standard error around the line of unit slope through the origin rather than around the regression

line. This technique eliminates the need to evaluate accuracy and precision separately because the analytical method is by definition completely accurate, and because all errors are assessed simultaneously in the standard error estimate of precision.

All standard error values were calculated around the line of unit slope through the origin by Equation 2. The relative standard error is defined in percent by Equation 3.

$$\text{Standard Error} = \sqrt{\frac{\sum(\text{Calc wt \%} - \text{Known wt \%})^2}{(\text{Number of Analyses} - 2)}} \quad (2)$$

$$\text{Relative Standard Error} = \frac{100 (\text{Std Error})}{\left[ \frac{\text{Highest wt \%} + \text{Lowest wt \%}}{2} \right]} \quad (3)$$

## RESULTS AND DISCUSSION

The results of this study are discussed in the following two sections. In both sections, the accuracy and precision of this X-ray spectrometric method are evaluated for determination of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO, TiO<sub>2</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and NiO in glass waste buttons. In the first section, the matrix effects of sodium are not considered. In the second section, the calculations include a matrix correction for sodium. The matrix correction for sodium improved the precision and accuracy for all metal oxides determined in the glass waste buttons.

### Matrix Calculations Without Correction for Sodium

X-ray fluorescence spectra were experimentally determined for each glass waste composition by the procedure outlined in the "Experimental Description" of this report. The resulting  $K_{\alpha}$  X-ray intensities are reported in Table 4 for aluminum, silicon, calcium, titanium, manganese, iron, and nickel. Matrix correction coefficients were evaluated by least squares fit of Equation 1 to the intensity - composition data. The matrix correction coefficients are given in Table 5. They do not include a correction for the matrix effect of sodium.

The accuracy and precision of this analytical method, including the matrix correction calculation, were evaluated for each metal oxide from the slope and standard error of the least squares regression line of a graph of the calculated concentration versus the known concentration as described in the "Experimental Description." The metal oxide concentrations

TABLE 4

## X-Ray Intensities from Glass Waste Spectra

Glass Waste Button	Net $K_{\alpha}$ X-Ray Intensities, counts during 500-sec period						
	Al	Si	Ca	Ti	Mn	Fe	Ni
1	1642	20501	8016	9951	11767	21292	2995
2	549	19829	11880	9515	10930	31048	3206
3	1173	22526	10532	10576	323	22211	5100
4	1284	22738	10344	10561	7674	15725	8
5	1023	22700	8255	11138	7745	19489	0
6	328	18925	7837	10236	10284	42226	0
7	432	21937	8436	11165	656	34450	3648
8	611	18493	10974	9182	463	49669	0
9	1503	18528	7819	10088	412	39224	2443
10	510	22448	10427	10900	7157	21657	4003
11	1387	18174	11827	9019	450	39263	0
12	307	22919	8569	11608	360	37223	0
13	1312	19164	9758	9900	6978	29122	620
14	724	19960	9044	9964	9947	29739	3289

were calculated by Equation 1 from the X-ray intensities of Table 4 and the matrix correction coefficients of Table 5. The calculated concentrations are reported in Table 6. Graphs of the calculated concentration versus the known concentration are given in Figures 1 and 2 for  $\text{SiO}_2$  and  $\text{TiO}_2$ . These metal oxides are of major interest in the glass waste analysis. The standard error and the relative standard error were calculated by Equations 2 and 3 for each metal oxide (upper portion of Table 7).

The standard error data of Table 7 show that the X-ray spectrometric method without matrix correction for sodium gives poor precision for the determinations of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$ , and  $\text{Fe}_2\text{O}_3$ . For example, the  $\text{SiO}_2$  determination from 10.50 to 34.13% is reliable only to  $\pm 5.67\%$  absolute; and the  $\text{TiO}_2$  determination from 2.00 to 6.50% is reliable only to  $\pm 1.05\%$  absolute. The  $\text{NiO}$  determination, in sharp contrast to the other determinations, is highly accurate in the concentration range 0.00 to 3.75% when calculated without a matrix correction for sodium.

TABLE 5

Matrix Correction Coefficients, Excluding Sodium Correction

Coefficient Identification	Coefficient Values <sup>a</sup>						
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO
B <sub>1</sub>	0.10462E 00	0.14231E-01	0.83485E-02	-0.46252E-03	0.16500E 00	-0.71251E 00	-0.22500E-02
B <sub>2</sub>	0.17044E 00	0.12910E-01	0.43108E-02	0.48053E-02	-0.24723E-01	-0.37654E-02	-0.40397E-01
B <sub>3</sub>	-0.41440E-05	-0.55228E-06	-0.90249E-08	-0.61079E-07	0.17109E-06	-0.42810E-08	0.44164E-06
B <sub>4</sub>	0.13764E-05	-0.56593E-06	-0.26447E-06	-0.22094E-06	0.10159E-05	0.99798E-08	0.27635E-05
B <sub>5</sub>	-0.35701E-05	-0.28885E-07	-0.70399E-07	-0.12836E-06	0.25473E-06	0.30369E-06	-0.37814E-07
B <sub>6</sub>	-0.11091E-04	0.24039E-06	-0.12894E-06	-0.31776E-07	0.33042E-06	0.24484E-07	0.55864E-06
B <sub>7</sub>	-0.16046E-05	-0.34943E-07	-0.21663E-07	-0.11686E-07	0.12586E-05	-0.68750E-07	0.24902E-05
B <sub>8</sub>	-0.99664E-06	-0.66228E-07	-0.25621E-07	-0.20044E-07	0.70770E-07	-0.13615E-07	0.27166E-06
B <sub>9</sub>	-0.12992E-05	-0.34861E-07	-0.99660E-08	-0.85872E-08	-0.95573E-08	0.32770E-08	0.18830E-06

a. 0.14231 E-01 means  $0.14231 \times 10^{-1}$ .



TABLE 6

## Concentrations Calculated Without Sodium Matrix Correction

Glass Waste Button	Calculated Concentration, wt %						
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO
1	14.678	18.328	1.993	3.567	9.952	36.496	3.448
2	-2.714	20.683	4.420	3.829	9.165	49.816	2.988
3	14.655	8.655	3.475	1.917	0.351	55.597	3.747
4	18.541	12.650	3.589	2.368	11.746	38.728	-0.007
5	12.985	15.268	2.191	2.692	12.161	45.790	-0.002
6	-1.523	25.579	1.549	4.737	6.863	47.956	-0.002
7	2.165	12.272	1.723	2.394	0.597	74.921	2.768
8	1.388	17.315	3.100	3.544	-0.120	62.631	-0.002
9	10.604	24.632	1.567	4.220	0.011	46.699	2.738
10	1.552	16.152	3.619	2.855	10.158	50.957	3.688
11	10.646	23.610	4.493	4.032	-0.091	48.877	-0.002
12	1.241	3.308	0.699	0.742	0.728	90.314	-0.002
13	7.604	28.520	3.391	4.654	3.129	40.299	0.160
14	1.727	23.546	3.061	4.451	4.153	46.511	1.538

TABLE 7

## Accuracy and Precision of Glass Waste Analysis

	NaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO
NOT CORRECTED FOR MATRIX EFFECT OF SODIUM								
Highest wt %		17.61	34.13	4.23	6.50	12.51	80.00	3.75
Lowest wt %		0.00	10.50	1.00	2.00	0.00	25.12	0.00
No of Analyses		14	14	14	14	14	14	14
Std Error, %		1.65	5.67	0.57	1.05	0.53	9.53	0.003
Rel Std Error, %		18.7	25.4	21.8	24.7	8.47	18.3	0.16
CORRECTED FOR MATRIX EFFECT OF SODIUM								
Highest wt %	12.02	17.61	34.13	4.23	6.50	12.51	80.00	3.75
Lowest wt %	3.70	0.00	10.50	1.00	2.00	0.00	25.12	0.00
No of Analyses	14	14	14	14	14	14	14	14
Std Error, %	0.00	1.39	0.09	0.50	0.03	0.36	2.21	0.001
Rel Std Error, %	0.00	15.8	0.40	19.2	0.66	5.72	4.21	0.053

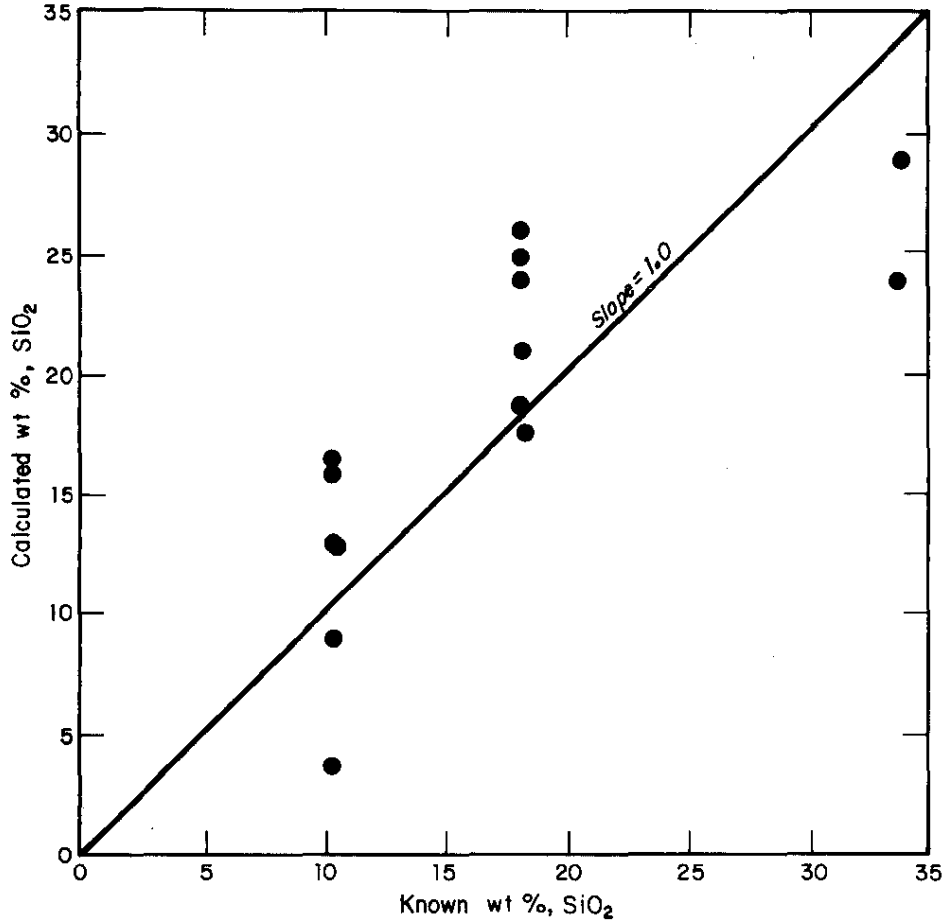


FIGURE 1. Calculated Concentration vs Known Concentration for SiO<sub>2</sub>.  
No Matrix Correction for Sodium

#### Matrix Calculations with Correction for Sodium

Sodium X-rays could not be detected with the X-ray spectrometer used in this study. The intensities of the sodium X-rays emitted during analysis of the glass waste buttons are therefore unknown. The matrix effects of sodium on the accuracy and precision of this X-ray spectrometric method, however, could still be evaluated for all determinations except that for NaO. This evaluation was accomplished by substituting for the unknown sodium X-ray intensity of each glass waste composition its sodium oxide content.

Matrix correction coefficients, evaluated by least squares fits of Equation 1 to the 14 sets of composition - intensity data, are given in Table 8. These coefficients include a correction for the matrix effects of sodium. The metal oxide content of each glass waste composition was calculated by Equation 1 from the

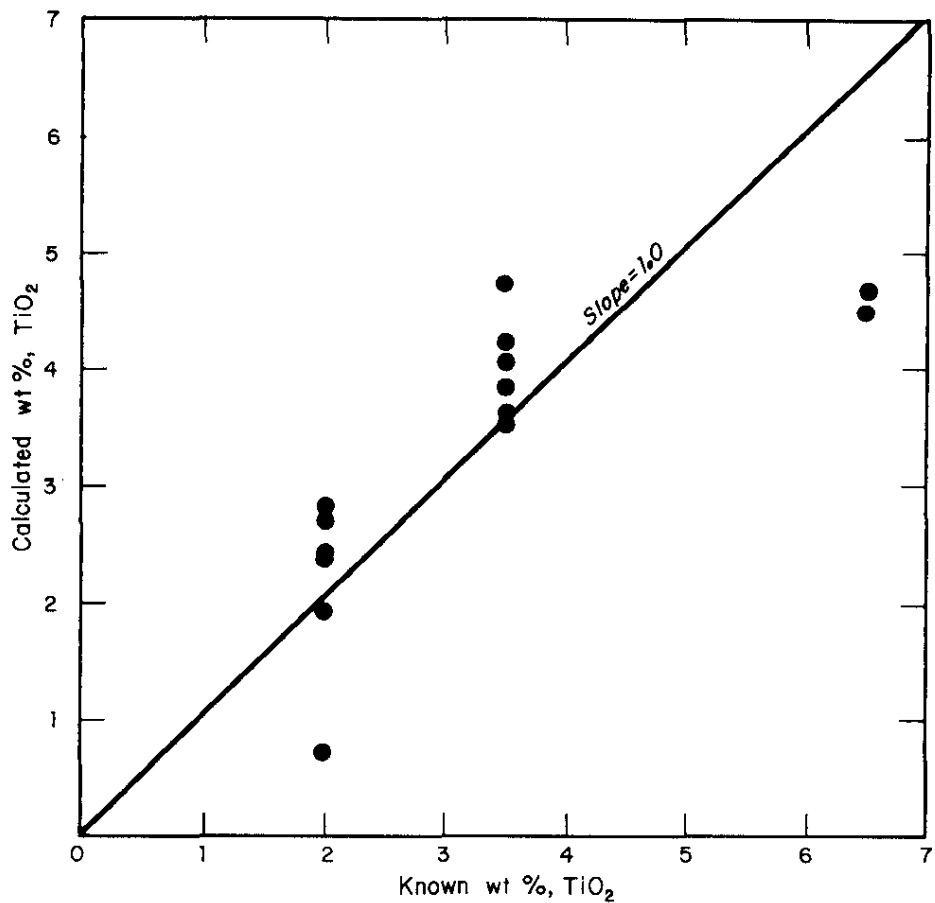


FIGURE 2. Calculated Concentration vs Known Concentration for TiO<sub>2</sub>.  
No Matrix Correction for Sodium

matrix correction coefficients of Table 8 and the experimentally determined X-ray intensities of Table 4 with sodium oxide contents substituted for the unknown intensities of the sodium X-rays. The calculated compositions are given in Table 9. The calculated concentrations for NaO are identical to the known values because the assumed intensities for the sodium X-rays involved neither experimental nor statistical uncertainty.

The accuracy and precision of the X-ray spectrometric method, including the matrix correction for sodium, were evaluated for each metal oxide from the slope and standard error of the least squares regression line of graphs of the calculated composition versus the known composition. These graphs for SiO<sub>2</sub> and TiO<sub>2</sub> are given in Figures 3 and 4. The standard error and relative standard error are reported in the lower section of Table 7. The X-ray spectrometric method was more accurate

TABLE 8

## Matrix Correction Coefficients, Including Sodium Correction

Coefficient Identification	Coefficient Values <sup>a</sup>							
	NaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO
B <sub>1</sub>	0.58208E-10	0.93083E-01	-0.22872E-05	0.42202E-02	-0.13336E-03	0.10399E 00	-0.17645E 00	-0.90162E-05
B <sub>2</sub>	0.10000E 01	0.31443E 00	0.77326E-03	0.23784E-02	0.18694E-03	0.53717E-01	0.12873E-01	-0.10144E-01
B <sub>3</sub>	0.13877E-08	-0.13005E-04	-0.49081E-07	0.99612E-08	-0.25621E-07	-0.21516E-06	-0.85080E-07	0.24553E-06
B <sub>4</sub>	0.46649E-10	-0.67819E-03	0.14272E-03	0.16523E-04	0.54308E-04	-0.20093E-03	-0.16201E-03	-0.76293E-04
B <sub>5</sub>	0.93397E-11	-0.22647E-05	-0.10949E-07	-0.16393E-06	0.82273E-09	-0.31614E-05	-0.86963E-06	0.98393E-06
B <sub>6</sub>	0.96737E-11	-0.46894E-05	0.56981E-08	-0.22620E-07	0.24468E-08	-0.10554E-05	-0.37121E-07	-0.24053E-06
B <sub>7</sub>	0.26333E-10	-0.12933E-04	0.27615E-07	-0.10370E-06	0.16283E-08	-0.45739E-06	-0.12789E-06	0.17181E-06
B <sub>8</sub>	0.40066E-11	-0.21243E-05	-0.31352E-08	-0.15569E-07	-0.23949E-09	-0.11404E-05	-0.40487E-06	0.10504E-05
B <sub>9</sub>	0.38234E-11	-0.17749E-05	-0.21991E-08	-0.16744E-07	0.30308E-09	-0.31408E-06	-0.69522E-07	0.11669E-06
B <sub>10</sub>	0.26548E-11	-0.14514E-05	-0.46646E-08	-0.63122E-08	-0.82074E-09	-0.17159E-06	-0.50281E-07	0.54784E-07

a. 0.58208 E-10 means  $0.58208 \times 10^{-10}$ .

TABLE 9

## Calculated Concentrations with Sodium Matrix Correction

Glass Waste Button	Calculated Concentration, wt %							
	NaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO
1	6.470	14.605	18.354	1.942	3.474	10.006	38.184	3.449
2	6.470	-1.966	18.448	4.378	3.492	9.020	51.890	2.989
3	3.700	14.136	10.391	3.551	2.037	0.328	58.013	3.748
4	3.700	18.596	10.531	3.519	2.046	12.000	44.520	0.000
5	3.700	13.807	10.520	1.974	1.965	11.851	53.994	0.000
6	6.470	-0.894	18.290	1.202	3.539	7.033	58.220	0.000
7	3.700	2.180	10.562	1.596	1.975	0.286	79.894	2.769
8	6.470	0.620	18.266	3.133	3.504	0.001	60.815	0.000
9	6.470	11.156	18.436	1.357	3.520	0.188	49.128	2.739
10	3.700	2.710	10.453	3.366	1.989	10.418	58.487	3.688
11	6.470	11.390	18.505	4.326	3.462	0.435	55.162	0.000
12	3.700	-0.250	10.531	1.083	1.996	-0.296	80.531	0.000
13	12.020	6.137	33.996	3.896	6.500	3.040	23.794	0.160
14	12.020	1.321	34.250	3.532	6.502	4.108	28.885	1.539

and precise for all determinations when matrix corrections were made for sodium. The accuracy and precision of the SiO<sub>2</sub> and TiO<sub>2</sub> determinations improved most significantly when the sodium matrix correction was applied. The improvement is readily apparent when Figures 1 and 2 are compared with Figures 3 and 4. The standard error for the SiO<sub>2</sub> determination decreased from 5.67% absolute without sodium correction to only 0.09% with sodium correction. The standard error for TiO<sub>2</sub> decreased similarly from 1.05% absolute to 0.03%.

The accuracy and precision of Fe<sub>2</sub>O<sub>3</sub> and NiO determinations showed moderate improvement when the sodium matrix correction was applied. The standard error for the Fe<sub>2</sub>O<sub>3</sub> determination decreased from 9.53% absolute to 2.21%, while that for the NiO determination decreased from 0.003% absolute to 0.001%. Accuracy and precision for the Al<sub>2</sub>O<sub>3</sub>, CaO, and MnO<sub>2</sub> determinations were only slightly improved.

## APPLICATIONS

Immobilization of highly radioactive waste by fusion with glass can be assured only if the glass content of the product is maintained within predetermined limits. X-ray fluorescence

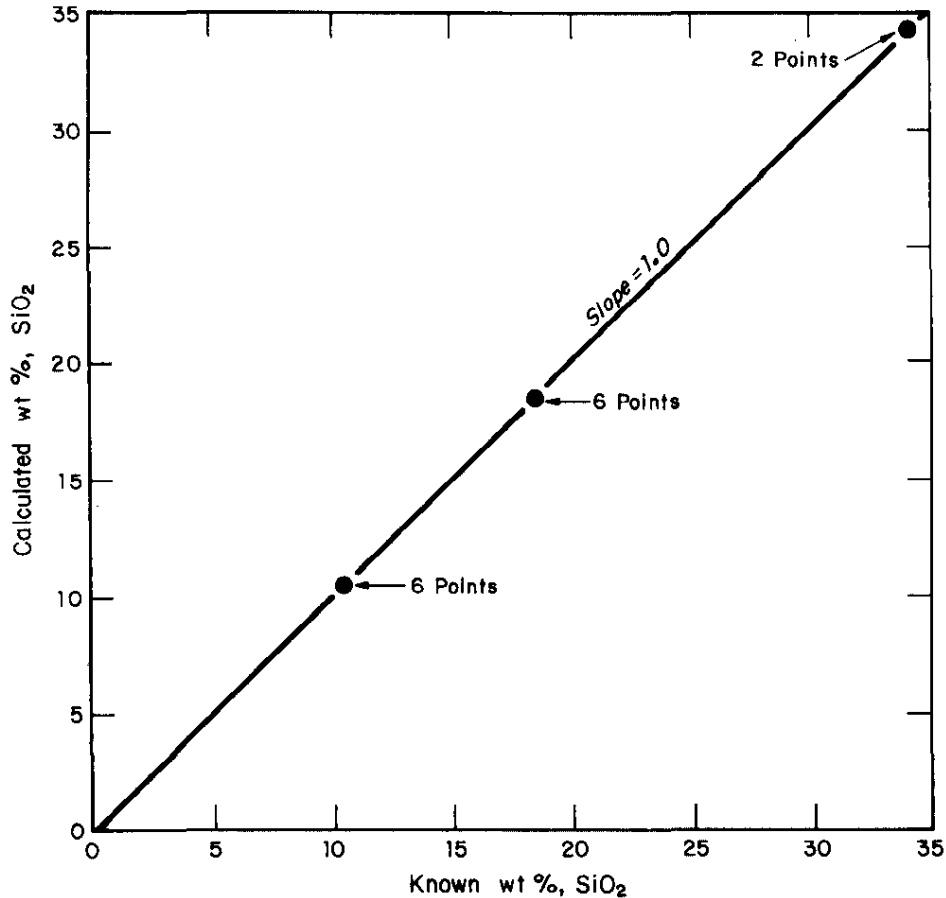


FIGURE 3. Calculated Concentration vs Known Concentration for SiO<sub>2</sub>. Matrix Corrected for Sodium

spectrometry can determine the glass content of glass waste product and simultaneously evaluate product homogeneity. Since SiO<sub>2</sub> and TiO<sub>2</sub> are absent in most high-level waste but present in Glass Mix 21, the SiO<sub>2</sub> and TiO<sub>2</sub> of the glass mix are diluted by fusion with waste. The glass content of the glass waste product can thus be determined from the known composition of the glass mix and the experimentally determined composition of the glass waste product by Equations 4 and 5.

$$\text{wt \% Glass in Product} = \frac{\text{wt \% SiO}_2 \text{ in Product}}{\text{wt \% SiO}_2 \text{ in Glass Mix}} \quad (4)$$

$$\text{wt \% Glass in Product} = \frac{\text{wt \% TiO}_2 \text{ in Product}}{\text{wt \% TiO}_2 \text{ in Glass Mix}} \quad (5)$$

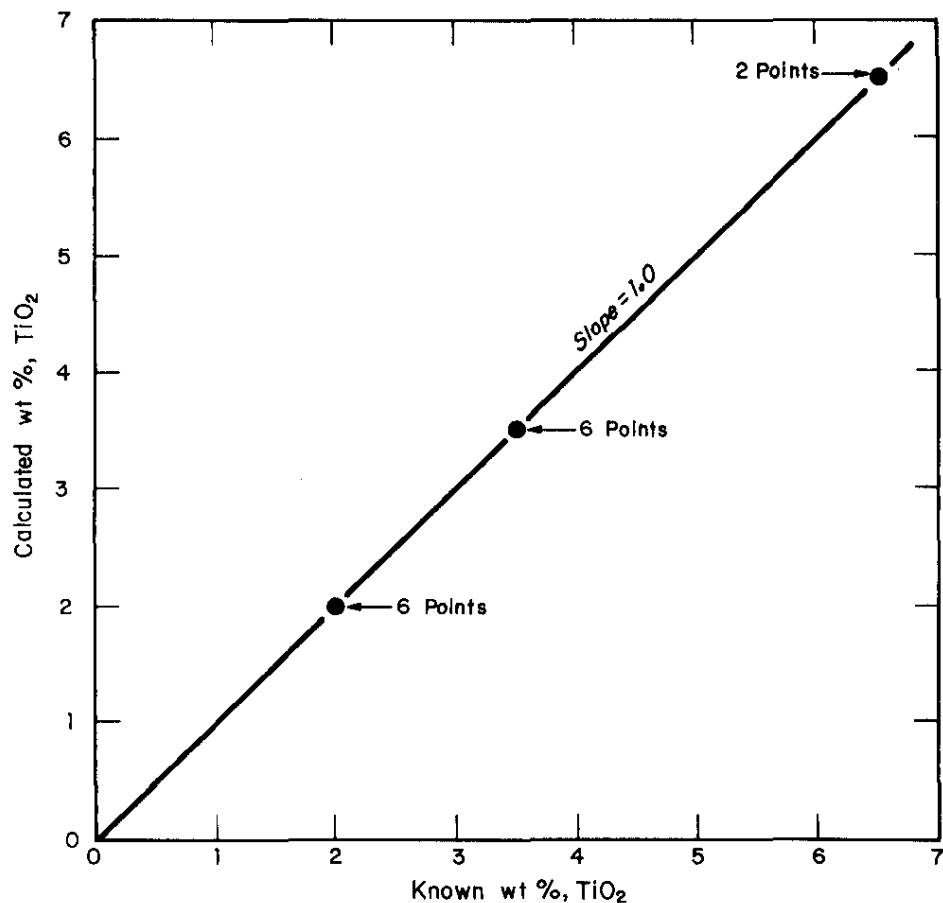


FIGURE 4. Calculated Concentration vs Known Concentration for TiO<sub>2</sub>. Matrix Corrected for Sodium

The accuracy of the X-ray spectrometric method for determining the glass content of glass waste product was demonstrated from the glass waste button analyses. The glass content was calculated by Equations 4 and 5 from the experimentally determined compositions of Table 9 and the glass mix composition of Table 1. The calculated and known glass contents are compared in Table 10. The glass content of the glass waste buttons was determined to an accuracy of  $\pm 0.5\%$  absolute from the SiO<sub>2</sub> analysis and to an accuracy of  $\pm 0.6\%$  absolute from the TiO<sub>2</sub> analysis.

TABLE 10

Glass Content of Glass Waste Buttons Calculated from Experimentally Determined Concentrations of  $\text{SiO}_2$  and  $\text{TiO}_2$

Glass Waste Button	Known wt % Glass in Button	<u>Experimentally Determined wt. % Glass</u>	
		Based on $\text{SiO}_2$	Based on $\text{TiO}_2$
1	35.0	34.96	34.74
2	35.0	35.14	34.92
3	20.0	19.79	20.37
4	20.0	20.06	20.46
5	20.0	20.04	19.65
6	35.0	34.84	35.39
7	20.0	20.12	19.75
8	35.0	34.79	35.04
9	35.0	35.12	35.20
10	20.0	19.91	19.89
11	35.0	35.25	34.62
12	20.0	20.06	19.96
13	65.0	64.75	65.00
14	65.0	65.24	65.02

## CONCLUSIONS

$\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{NiO}$  can be reliably determined in glass waste forms by X-ray fluorescence spectrometry with the matrix correction model of Lucas-Tooth and Price.<sup>4</sup>  $\text{SiO}_2$  can be determined for a 500-second count to an accuracy of  $\pm 0.3\%$  absolute at concentrations from 10.50 to 34.13%.  $\text{TiO}_2$  can be determined to  $\pm 0.1\%$  absolute at concentrations from 2.00 to 6.50%, and  $\text{NiO}$  can be determined to  $\pm 0.003\%$  absolute at concentrations below 3.75%. The  $\text{SiO}_2$  and  $\text{TiO}_2$  determinations are reliable, however, only if the matrix correction calculations include a correction for the matrix effects of sodium.

$\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  can also be determined by this direct X-ray spectrometric method, but the accuracy and precision are rather poor. For a 500-second count,  $\text{MnO}_2$  can be determined to an accuracy of  $\pm 1\%$  for concentrations below 12.5%.  $\text{Fe}_2\text{O}_3$  concentrations from 25.1% to 80.0% can be determined only to  $\pm 6\%$  accuracy.  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  could not be determined reliably by this X-ray method by using the Lucas-Tooth and Price<sup>4</sup> matrix correction.



The feasibility of accurately and precisely determining the glass content of glass waste compositions by direct X-ray spectrometric analysis of the fused solid has been demonstrated for synthetic waste fused in glass. The glass content of glass synthetic waste compositions can be determined to an accuracy of  $\pm 0.5\%$  absolute based on  $\text{SiO}_2$  analysis or to  $\pm 0.6\%$  absolute based on  $\text{TiO}_2$  analysis. The X-ray spectrometer which will determine the glass content of actual glass waste product must be capable of determining NaO because the silicon and titanium X-ray intensities must be corrected for the severe matrix effects of sodium.

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