WSRC-TR-90-528, Rev. 1

THE DETERMINATION OF THE Fe^{2+}/Fe^{3+} RATIO IN SIMULATED NUCLEAR WASTE GLASS BY ION CHROMATOGRAPHY (U)

CAROL M. JANTZEN

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Distribution Category:UC-701

Keywords: waste glass, redox,
oxidation/reduction equilibria,
DWPF, analytic chemistry

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Publication Date: October 1990

Authorized Derivative Classifier

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ABSTRACT

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass in the Defense Waste Processing Facility (DWPF). In this facility, control of the oxidation/reduction (redox) equilibrium in the glass melter is critical for processing of the nuclear waste. Therefore, the development of a rapid and reliable analytical method for the determination of the redox equilibrium is of considerable interest.

Redox has been determined by measuring the ratio of ferrous to ferric ions in the glass melt. Two analytical techniques for glass redox measurement have been investigated for the DWPF: Mossbauer Spectroscopy which may be subject to interferences from the radiation in actual waste, and a rapid and simple chemical dissolution/spectrophotometric technique. Comparisons of these techniques have been made at several laboratories including Clemson University.

In the study attached,[1] the determination of the redox ratio by Ion Chromatography (IC) was investigated as a potential new technology. Clemson University performed IC analyses on the same glasses as previously examined by wet chemical and Mossbauer techniques. Results from all three techniques were highly correlated and IC was reported to be a promising new technology for redox measurement.

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[1] Clemson University Subcontracts AX-0720822 AND AX-0824656

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THE DETERMINATION OF THE Fe^{2+}/Fe^{3+} RATIO IN SIMULATED NUCLEAR WASTE GLASS BY ION CHROMATOGRAPHY (U)

INTRODUCTION

The oxidation/reduction (redox) equilibrium in the Defense Waste Processing Facility (DWPF) melter is critical to the processing of high-level nuclear waste glass. The glass needs to be somewhat reducing to minimize glass foaming[1,2] and devitrification.[3] However, overly reducing conditions may cause metallic species to form in the melt. The metallic species can agglomerate, settle to the floor of the melter, and potentially short the joule-heated electrodes.[4-7] Reducing conditions in the DWPF melter can be caused by formic acid additions during waste sludge processing, aromatics from the tetraphenylborate (TPB) precipitate hydrolysis, and the presence of activated charcoal in some of the DWPF wastes. Oxidizing conditions can be caused by nitrate formed from the sodium nitrite corrosion inhibitors in the sludge, and from air inleakage into the melter.

The melter redox state can be measured from the Fe^{2+}/Fe^{3+} ratio of the final solidified glass. An Fe^{2+}/Fe^{3+} ratio between 0.1-0.5 has been recommended as an acceptable range for glasses produced in the DWPF.[8] This range appears optimal in terms of avoiding both (1) foaming, and (2) precipitation of metallic species during glass melting. This redox range agrees with the range determined at Pacific Northwest Laboratory in support of the West Valley project,[7,9] and redox determinations from Case Western University.[2] Redox ratios of 0.1-0.5 correspond to melter fugacities between 10^{-4} and 10^{-8} atmospheres based on calibration curves developed by Schreiber[10] for DWPF glasses.

A rapid and reliable method for predicting the melter redox conditions using the Fe^{2+}/Fe^{3+} ratio determined from a vitrified feed sample has been developed by Baumann.[11-13] In this procedure the feed sample is vitrified in a closed crucible at 1150°C and then cooled to room temperature. A sample of the cooled glass is dissolved in HF/H_2SO_4 in the presence of NH_4VO_3. The ammonium vanadate protects the Fe^{2+} so the procedure can routinely be performed in air.[11-13]

Mossbauer Spectroscopy has been extensively examined[14-16] for measurement of the Fe^{2+}/Fe^{3+} ratio of vitrified melter feed samples. Mossbauer Spectroscopy has the advantage that the glass does not need to be dissolved. A comparison of the ferrous iron to total iron ratio, expressed as $Fe^{2+}/\Sigma Fe$ by wet chemical techniques and Mossbauer Spectroscopy has been conducted at Pacific Northwest

Laboratory.[9,17] These results indicated that the ratios from the Mossbauer spectra overestimated the proportion of $Fe^{2+}/\Sigma Fe$ by a factor of 1.2 and the Fe^{2+}/Fe^{3+} ratio by 1.5. The authors attributed the bias to the Mossbauer curve fitting technique and not to errors in the wet chemical methodology. However, the wet chemical technique used in the PNL study was performed in air and did not use the NH_4VO_3 to protect the Fe^{2+}. This could, indeed, cause the lower Fe^{2+} ratios for the wet chemical methodology[11,12] and the observed bias. Comparisons of the redox ratios determined by Mossbauer and wet chemical techniques was also investigated at The Carnegie Institute of Washington Geophysical Laboratory,[18] at Clemson University,[14,16] and at SRL.[15] No systematic bias was found in any of these studies.

The Clemson study[14,16] also compared Baumann's colorimetric procedure to other wet chemical procedures. That study concluded that the colorimetric procedure was more reliable and reproducible than the other wet chemical methods. However, it was noted that neither Baumann's procedure nor the other analytical techniques gave reliable results for highly oxidized or highly reduced glasses.

This study was initiated to compare a new technology, analysis of aqueous Fe^{2+} and Fe^{3+} by ion chromatography, to the wet chemical and Mossbauer technologies previously examined by Clemson University.[14,16]

CONCLUSIONS AND RECOMMENDATIONS

The ion chromatography (IC) technique developed at Clemson University for analyzing Fe^{2+} and Fe^{3+} in DWPF glasses requires that the glasses be dissolved before the aqueous species can be determined. A dissolution step in H_2SO_4 and HF similar to that used by Wilson[19] and Baumann[11-12] was used but NH_4VO_3 was not used to stabilize the Fe^{2+}. However dissolution was achieved in acid digestion bombs in 15-60 seconds in a microwave oven. The samples were stabilized in H_3BO_3 solution to complex the fluoride. This step is also similar to the dissolution methodology developed by Baumann.[11-12] At this point the Clemson procedure calls for injecting the aqueous solution directly into the IC and measuring the Fe^{2+} and Fe^{3+} spectrally. For comparison, the Baumann[11-12] procedure uses an Fe^{2+}-specific chromogen and measures the Fe^{2+} spectrophotometrically. Subsequently all the iron must be reduced to Fe^{2+} so that total Fe can be measured spectrophotometrically and Fe^{3+} determined.

The Clemson study measured the redox ratios of the same glasses by IC that had previously been analyzed spectrophotometrically and by

Mossbauer Spectroscopy. The correlation coefficient between the IC and the spectrophotometric method was 0.932 while the coefficient relating the IC results to those of Mossbauer Spectroscopy was 0.928. Clemson also determined that Mn^{2+} could be determined by IC but cautioned that other transition metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} ions present in the dissolved glass might interfere with spectral analysis of Fe^{2+}, Fe^{3+}, and Mn^{2+}.

The Clemson study concluded that IC is a promising method for determining the Fe^{2+}/Fe^{3+} ratio in DWPF glasses. They maintained that the IC can be automated for routine analysis. It is recommended that the Analytic Development Division investigate coupling Baumann's dissolution technique[11-12] with IC analysis for DWPF redox determinations.

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ATTACHMENT A

THE DETERMINATION OF THE Fe^{2+}/Fe^{3+} RATIO IN SIMULATED NUCLEAR WASTE GLASS BY ION CHROMATOGRAPHY

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemistry

---

by
Nancy Ann Brock
August 1990

August 3, 1990

To the Graduate School:

This thesis entitled "The Determination of the Fe^{2+}/Fe^{3+} Ratio in Simulated Nuclear Waste Glass by Ion Chromatography" and written by Nancy Ann Brock is presented to the Graduate School of Clemson University. I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Chemistry.

Thesis Advisor

We have reviewed this thesis
and recommend its acceptance:

Ronald R Willin

Accepted for the Graduate School:

Larrell J. Brown

ABSTRACT

The value of the Fe^{2+}/Fe^{3+} ratio of iron-containing rocks, minerals, and glasses is a useful number and has been determined by Mössbauer spectral and wet chemical methods. The ratio is important in the immobilization of high-level nuclear waste in borosilicate glass. Measuring the redox conditions is important in this nuclear waste process because problems occur in the glass formation if the ratio is not within a given range. In this study, the ratio in simulated nuclear waste glass samples have been determined by ion chromatography. The ratio values for these sampls have also been measured by Mössbauer spectral and spectrophotometric techniques.

The Fe^{2+}/Fe^{3+} ratios of fifteen simulated nuclear waste glass samples, containing 3 to 10% iron, ranged from 0.10 to 1.60. The samples were dissolved by acid digestion and then buffered with KH_2PO_4 and aliquots of the solution injected into the ion chromatograph. Upon separation on the column, the ions combined with a chelate complexing reagent and the intensity measured using a visible detector. Through peak area measurements and standard solutions the Fe^{2+}/Fe^{3+} ratios were determined. The chromatograms of many of these samples showed, not only Fe^{2+} and Fe^{3+} peaks, but also at least one other, due to manganese(II).

Manganese was known to be present in several of the fifteen simulated nuclear waste glass samples. The total amount of manganese(II) determined and ranged from 1.30 to 3.4%.

The Fe^{2+}/Fe^{3+} ratio values obtained by ion chromatography were compared to the values determined by the spectrophotometric method and Mössbauer spectral method and the values were similar for all three methods. The correlation coefficient between ion chromatography and spectrophotometric methods was 0.932 and the coefficient was 0.928 between the ion chromatography and Mössbauer methods. Ion chromatography appears to be a good method for the analysis of the glass samples.

ACKNOWLEDGMENTS

I would like to express thanks to Dr. James C. Fanning for his encouragement during my years at Clemson University. I would like to thank members of my research group and friends for their patience and help while I was completing my research and thesis. The U.S. Department of Energy and Savannah River Site are gratefully acknowledged for the providing the funding for this project. Finally, I express sincere thanks to my family for their encouragement, support, and love throughout my life.

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CHAPTER I

INTRODUCTION

A serious problem for many years has been the high level radioactive nuclear waste generated by nuclear power and nuclear weapons plants. The problem is serious because nuclear waste can remain hazardous for millions of years. Two key terms in dealing with nuclear waste are disposal and storage. **Disposal** is defined as "the isolation of nuclear waste, by natural and man-made barriers, that does not require continued human maintenance or control" (1). **Storage** is "the isolation that permits easy access to radioactive waste; requires continuous surveillance" (1). Because research is still underway on the disposal of the nuclear waste, spent-fuel rods and defense wastes are being temporarily stored in surface containers or stainless steel tanks (2). One method which is to be used for the disposal of nuclear waste is to immobilize the waste in a glass matrix, which is water impervious, and bury the package in a remote location (3).

The Savannah River Site (SRS), near Aiken, South Carolina, has been the nation's primary maker of plutonium and tritium for nuclear warheads for many years. The main isotope used for the warheads is ^{239}Pu. Over 300,000 m^3 of high level nuclear waste was produced at SRS in thirty-two years of operation. Waste generation is expected to continue at the rate of 10,000 m^3 per year (4). In order to reduce the volume, the waste has been evaporated to 120,000 m^3 which contains about a billion curies of radioactivity. It is now stored on site in fifty-one carbon steel tanks. Construction began in 1983 on what will be the world's largest solidification facility for this high-level nuclear waste. Beginning in September 1990, the waste will be solidified into a durable borosilicate glass at the Defense Waste Process Facility (DWPF). The DWPF is located near the tank farm and separation areas at SRS to minimize the transfer of the liquid waste through pipelines (4). Transferring the waste is minimized because of the radionuclides, such as ^{137}Cs and ^{239}Pu, contained in the waste.

The nuclear waste must go through several steps or washing procedures before it can be converted into the borosilicate glass. Figure 1 illustrates steps of the DWPF process. The insoluble portion, sludge, has settled to the bottom of these carbon steel tanks while the excess liquid and soluble substances are contained in the top layer. The excess liquid must be removed to reduce the volume of waste actually being converted. This liquid layer is pumped out and the water evaporated. However, prior to this, sodium titanate is added to the soluble portion to remove trace quantities of the radionuclide ^{90}Sr. Sodium tetraphenylborate is added to precipitate the ^{137}Cs. The ^{90}Sr and ^{137}Cs precipitates are then added to the sludge. Water is evaporated and the soluble

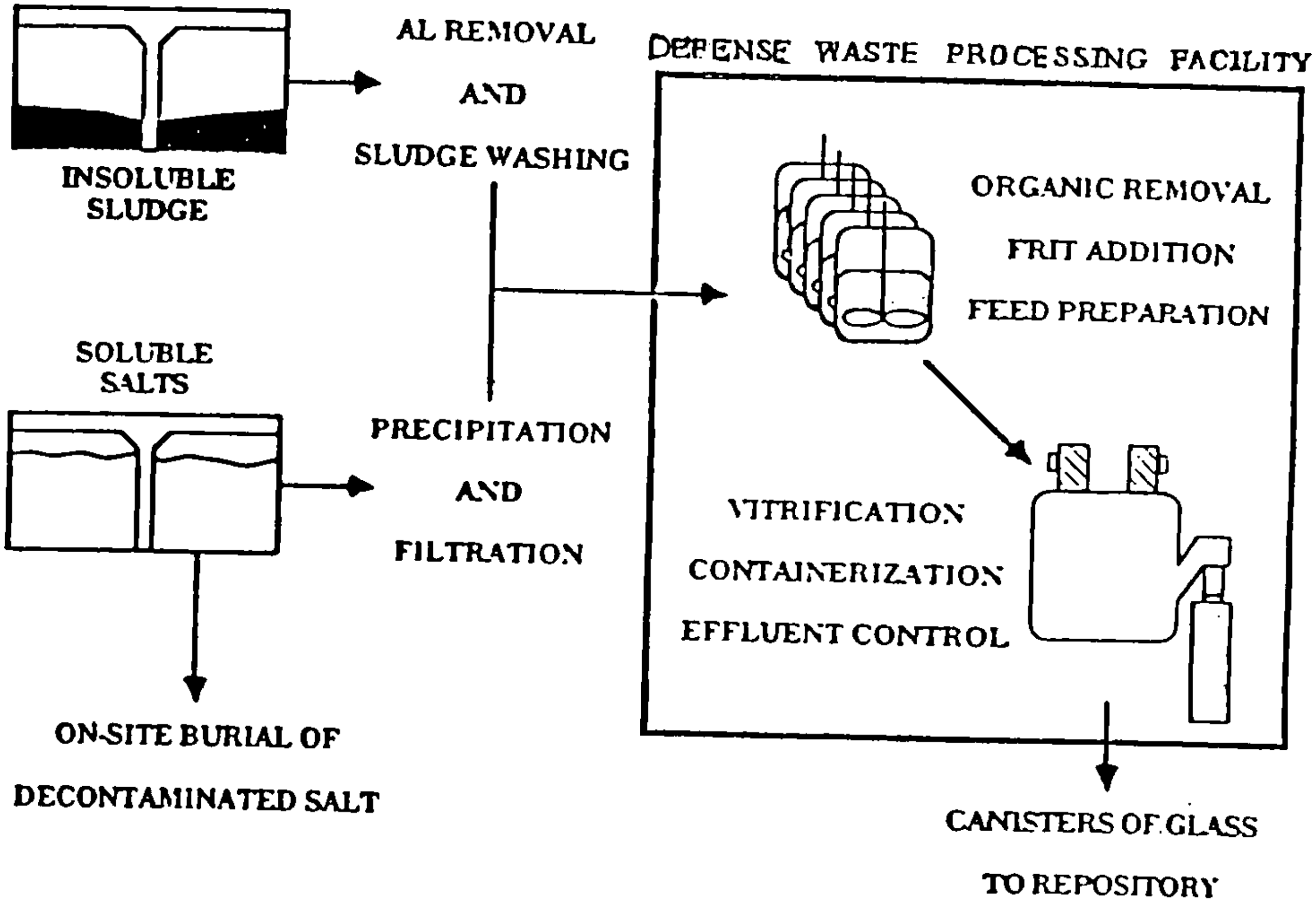

Figure 1. Description of the immobilization of SRP high-level nuclear waste.

salts are made into low-level radioactive sodium salt cakes and buried on-site (3).

After the soluble portion is treated, the insoluble portion, is then washed. The aluminum is removed first since its presence in high concentrations will promote crystal formation in the glass. These crystals will promote the devitrification of the glass. The sludge is washed again to reduce the salt content and these washings are added to the liquid layer before it is made into salt cakes. At the DWPF organic compounds are removed from the sludge which is then treated with formic acid to improve feed rheology and to form metallic mercury which is removed. Glass frit (sodium borosilicate) is added to the waste stream. The resulting slurry (feed) is passed into a joule-heated glass melter and converted to borosilicate glass at 1150°C. The molten glass is then poured into stainless steel canisters. This glass is to be kept on site until a federal repository site is named (3).

For the production of good quality nuclear waste glass the Fe^{2+}/Fe^{3+} ratio is a very important since it gives a measure of the redox operating conditions (5) of the melter where the glass is formed. It is an indicator of the glass' potential to devitrify which would cause fracturing of the glass. The ratio should fall in the range of 0.1 to 0.6 (6, 7, 8). Problems will occur in the melter if the ratio does not fall within this range. When the nuclear waste feed containing the glass frit is fed into the joule-heated melter, and oxidizing conditions are present ($Fe^{2+}/Fe^{3+} < 0.1$), oxygen forms causing excess foam to be produced. The foam blocks the flow of the feed into the melter. If the ratio is greater than 0.6, the conditions are too reducing. Precipitates such as metal sulfides form and can produce conductive layers between the electrodes which can produce an electrical short in the melter (9).

Methods of Determination

Suitable routine procedures do not exist for determining the Fe^{2+}/Fe^{3+} ratio for the simulated nuclear waste glass. Since standards with precisely known amounts of Fe^{2+} and Fe^{3+} do not exist, several methods of analyzing the glass are needed in order to obtain the most accurate ratio for a particular glass. Most of these methods are wet chemical analyses, wherein a sample is dissolved prior to analysis; however,in the Mössbauer spectral method the glass sample is analyzed as a finely ground solid.

Mössbauer spectroscopy involves transitions between certain nuclear energy states that result from the resonance absorption of gamma radiation by a sample. The ^{57}Fe isotope exhibits a Mössbauer effect, thus iron-containing solids give Mössbauer spectra. The solid sample is placed in an suitable holder and positioned between a ^{57}Co gamma radioactive source and detector and analyzed by passing the gamma rays through the sample. The ^{57}Co isotope decays to ^{57}Fe emitting a 14.4 keV gamma ray in the process, this radiation is absorbed by the iron containing species of the sample. In the case of the glasses, this would be the Fe^{2+} and Fe^{3+} ions, both in different environments. Spectra are collected over time and analyzed using a computer. The peak areas for the Fe^{2+} and Fe^{3+} peaks would be determined by a curve fitting program. From the calculated areas, which are proportional to the amount of each ion, the Fe^{2+}/Fe^{3+} ratio for each glass is calculated (10).

There are three wet chemical methods for determining the Fe^{2+} and Fe^{3+} in silicate materials: redox titrations, spectrophotometric methods, and ion chromatography (IC). The general procedure for one redox titration begins by dissolving the glass with HF/H_2SO_4. An inert atmosphere is needed to prevent the Fe^{2+} from oxidizing. Boric acid is then added to bind the F^-, and an indicator is added. Standard solutions are used to titrate the sample. The Fe^{3+} is reduced and the titration repeated. Knowing the Fe^{2+} and total iron concentrations, the ratio is calculated (10). This method does not work well with the simulated nuclear waste glasses because of the interfering ions in the nuclear waste samples. The spectrophotometric method dissolution process is similar to the titration method. Ammonium vanadate is added to prevent any oxidation of the Fe^{2+}. The Fe^{2+} is complexed with a chelating reagent forming an intensely colored species and the absorbance measured. Again the iron is reduced to Fe^{2+}, the absorbance is remeasured and the ratio calculated (11).

Redox titration and spectrophotometric methods have been well studied and are relatively routine methods for determining the Fe^{2+} and Fe^{3+} content in silicates. Ion chromatography, on the other hand, had not been used for silicate analysis when this project was begun. The Dionex Corporation has shown that both Fe^{2+} and Fe^{3+} can be determined by ion chromatographic analysis. Research is now complete on using this method to determine the Fe^{2+}/Fe^{3+} ratio of nuclear waste glass samples and is discussed in the following chapters. However, it is important to understand the basic concepts of the ion chromatograph.

Ion Chromatography

Chromatography is a separation method of two or more components in a mixture or sample. Separation is obtained by two immiscible phases coming into contact. The two phases in chromatography are the stationary phase and the mobile phase (12). The components are gradually separated in the mobile phase when the appropriate phases are in contact. Interactions occur between the components and the stationary phase, which is usually a column. The separated components elute in the order of increasing interaction with the stationary phase. For example, the component with the lowest interaction with the column resin elutes first (12). Ion chromatography is the exchange process that occurs between ions in the mobile phase or eluant and the exchange groups covalently bonded to the beads in the stationary phase. The stationary phase is a polystyrene based resin crosslinked with divinyl benzene. Figure 2 is a schematic of this resin. The exchange process between the cation (M_1^+) and the resin can be represented by the equation

$$-SO_3^-H^+ + M_1^+A^- \rightleftharpoons -SO_3^-M_1^+ + H^+A^-. \tag{1}$$

The H^+ represents protons, M^+ represents any transition metals, and A^- represents any counterion. The H^+ is replaced by the M_1^+ when the components travel through the column in the mobile phase. When a cation with a higher affinity for the column flows through the column, the M_1^+ elutes off the column first (13).

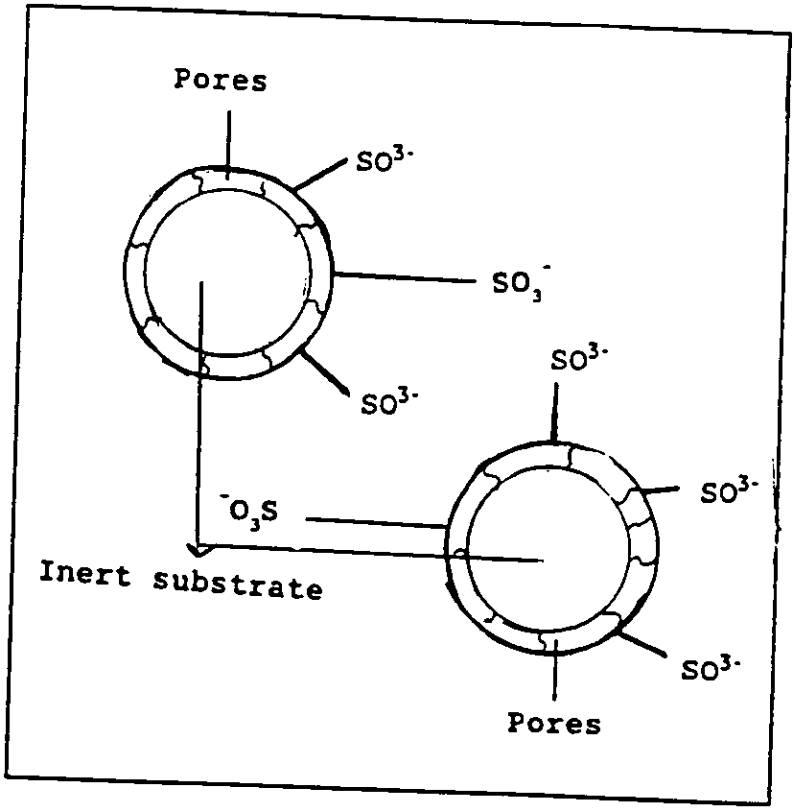

Figure 2. Cation Exchange Resin

Components of the Ion Chromatographic System

Figure 3 illustrates the different components of a chromatographic system. The mobile phase or eluant, at the beginning of the system, is pumped through the system and the flow rate regulated. The sample is injected onto the guard column and is transported through the columns. Contaminants are collected in the guard column which extends the life of the separator column. After the sample is transported through the guard column, metal ion separation occurs in the separator column. After this separation the metal ions combine with the complexing reagent and form an intensely colored species. The visible detector detects the colored species and the results are recorded by an integrator. Quantitative results are determined by calculations of peak areas which are proportional to the species' concentrations (13).

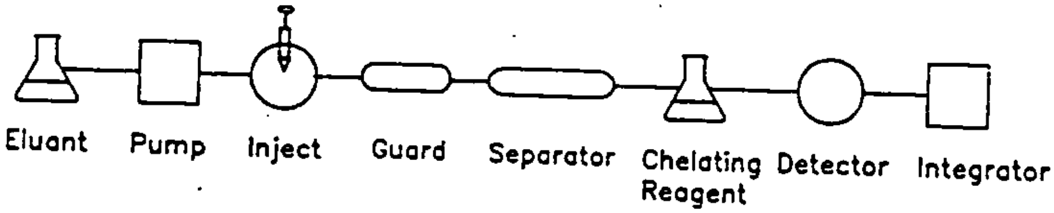

Figure 3. Components of the Ion Chromatographic System

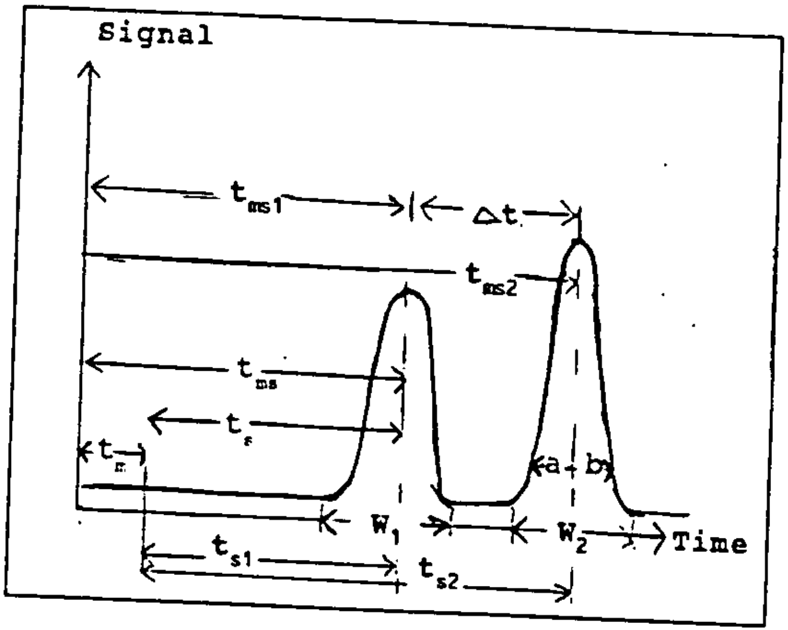

Figure 4. Typical Chromatogram that Illustrates concepts of IC

Terminology of Ion Chromatography

In order to effectively use ion chromatography, it is important to understand some of the terms and principles behind it. A few terms that should be understood are tailing, resolution, selectivity, capacity ratio, and column efficiency. Resolution, selectivity, and capacity ratio are the terms used to assess the quality of separation in a chromatogram. Figure 4 is a typical chromatogram that illustrates the concepts.

The peak shape in a chromatogram is approximated by a Gaussian curve. The gross retention time of the peak (t_{ms}) and dead time (t_m) are used to determine the net retention time (t_s) by the equation $t_s = t_{ms} - t_m$. The dead time is the ime it takes the sample to migrate from the injector to the detector. The gross retention time is the time the component takes to elute or the time at the peak maximum. The net retention time identifies a particular component. Tailing is the rapid increase of the detector signal and comparatively slow decrease of the signal, producing a distorted asymmetric peak. The tailing factor (T) is calculated from

$$T=\left|\frac{b}{a}\right| \tag{2}$$

where a and b are defined in Figure 4.

Resolution (R) is one of the parameters used to assess the quality of separation of the peaks. Resolution is calculated by the equation

$$R=\frac{2\left(t_{ms2}-t_{ms1}\right)}{W_1+W_2} \tag{3}$$

where t_{ms1}, t_{ms2}, W_1, and W_2 are shown in Figure 4. An $R=0.5$ is necessary to recognize two components as separate peaks while an $R>1.5$ indicates complete separation of the two peaks.

Selectivity (α) is the measure of the relative separation of the two signals. It is determined by the ratio of the net retention times of the signals. The equation

$$\alpha=\frac{t_{ms2}-t_m}{t_{ms1}-t_m} \tag{4}$$

shows how the selectivity is calculated.

Capacity ratio, k', is the ratio of the moles of solute in the stationary phase to the moles of solute in the mobile phase. Low k' values indicate that the capacity of the column is inefficient and poor separation occurs. If the k' values are too high separation is better but, longer analysis time and peak broadening is a problem. The capacity ratio is calculated from the equation

$$k' = \left(\frac{C_s}{C_m}\frac{V_s}{V_m}\right) = K\left(\frac{V_s}{V_m}\right) = \left(\frac{t_s}{t_m}\right) \tag{5}$$

where K is the distribution coefficient, C_s and C_m are the concentration of solute in the stationary and mobile phases, respectively. V_s is the volume of the solute in the stationary phase, and V_m is the volume of the solute in the mobile phase.

Column efficiency can be determined by the number of theoretical plates, N, the column has. A thermodynamic equilibrium of the sample molecules occurs in the theoretical plates between the mobile and stationary phases. This equation

$$H = \frac{L}{N} \tag{6}$$

shows the relationship between the plate height (H) and the number of theoretical plates (N) in the column. H is the distance a solute moves while undergoing one partition. L is the column length, and N is the number of theoretical plates and is a measure of the peak broadening (14).

Advantages of Ion Chromatography

Ion chromatography has several advantages over other methods such as photometry, gravimetry, and colorimetry. Speed, sensitivity, selectivity, and simultaneous analysis are some of the advantages of IC over the wet chemical methods. Speed is important because it reduces the analysis time which saves money and reagents. Sensitivity is important because it allows low concentrations (ppb) of ions to be detected. Preconcentration of the sample is not needed. Selectivity in IC simplifies the identification of unknown ions in a sample. Transition metals and polyvalent ions are determined at a higher degree of selectivity than in the past. Simultaneous analysis, the last advantage allows several components in a sample to be analyzed at one time. A cation or anion profile is normally obtained in less time than other methods take for a single analysis (15).

Purpose of Research

Monitoring the redox conditions of the glass formation in the melter at the DWPF is very important. These conditions can be monitored by determining the Fe^{2+}/Fe^{3+} ratio. The Mössbauer spectral and spectrophotometric methods are being used to determine the ratio. Prexamination of another potential method which might give even more reliable results is the goal of this research. Ion chromatography is a new method that might be used to analyze the simulated nuclear waste glasses. This method is to be examined and the results from this method are to be compared with those of the other methods to determine if there is a "best" method for analyzing the ratio in the glass samples.

CHAPTER II

EXPERIMENTAL

Ion Chromatography

Sample Preparation

The glass samples, supplied by SRS, contained about ten percent iron and were generally brown or black in color. In order to analyze the samples by ion chromatography they were first ground to a fine powder using an agate mortar and pestle then weighed (20-30 mg) into a Teflon® Sample Cup, and 0.50 mL of concentrated H_2SO_4 and 1.5 mL of concentrated HF carefully added. The mixture was allowed to stand for a few minutes. If the glass was not entirely dissolved, the container was capped and placed in a Parr Microwave Acid Digestion Bomb and heated for 15 to 60 seconds in a General Electric standard household microwave oven. (CARE SHOULD BE TAKEN IN USING MICROWAVE EQUIPMENT! READ INSTRUCTIONS WITH THE ACID DIGESTION BOMB BEFORE USING IT.) Early in the project, a steel bomb and a standard lab oven heated to 110°C was used to dissolve the samples. The microwave oven gave much better results since the shorter heating times required for dissolution had the advantage of producing less oxidation of Fe^{2+}.

After the samples were dissolved and/or heated, 25 mL of 4% boric acid (H_3BO_3) solution were added to the hot solution to remove the fluoride ion as BF_4^-. Once the solution cooled, it was transferred to a 100 mL volumetric flask and 10 mL of 0.5 M potassium phosphate monobasic (KH_2PO_4) were added. The solution was then diluted to volume with deionized water. Sample was then injected into the chromatograph's 50 µL sample loop. (See below.) If the solution contained any undissolved particles, even after heating, a 0.20/0.25 mm filter wheel (Nalgene Syringe Filter CA) was attached to the syringe before injecting the sample into the ion chromatograph.

Solution Preparation

All solutions were prepared with reagent grade chemicals and deionized water. Some solutions require special preparations and are described below.

Pyridine 2,6 - dicarboxylic acid (PDCA). A 3 mM PDCA solution (buffered to pH 4.7) was used for the majority of the experiments and was prepared as follows: PDCA (0.501 g) was weighed out, placed in a 250 mL Erlenmeyer flask, and then 100 mL of 0.0086 M LiOH added. The solution was stirred with some heating to dissolve the PDCA, then transferred to a 1.0 L volumetric flask. Glacial acetic acid (11.4 mL) and anhydrous sodium acetate (16.406 g) were added. The solution was diluted to volume with deionized water and mixed thoroughly.

4-(2-Pyridylazo) resorcinol monosodium salt monohydrate (PAR). The 0.30 mM PAR solution used for the experiments was prepared as follows: 0.0766 g (0.3 mM) was weighed out into a 1.0 L volumetric flask and 400 mL of ammonium hydroxide added. The solution was stirred until the PAR was dissolved. Finally, 600 ml of 1.7 M acetic acid were added and the solution mixed thoroughly.

The following solutions were also prepared: 0.100 M Na_2SO_3, 0.0086 M LiOH, 1.7 M acetic acid, 0.5 M KH_2PO_4, and 4% boric acid solution.

Instrumentation

The Dionex Series 2003i ion chromatography (IC) system consisted of an eluant degassing module (EDM), basic chromatography module (CMB), eluant delivery module, analytical pump (APM), reagent delivery module (RDM), Opti/Ion^{TM} Visible Detector (VSM), and Spectra-Physics 4270 Integrator. The EDM with its six ports allowed high purity (HP) helium to be connected to each eluant bottle, thus enabling the solutions to be degassed at a pressure of 5 psi.

Fifty microliters of sample were injected onto the column through one of the CMB sample ports. Sample passed through the HPIC-CG-5 guard column and HPIC-CS-5 separator column. The solutions were fed onto the column by the dual-piston analytical pump which controlled the flow rate at 1.0 mL/min. The high pressure limit of the pump was set at 1400 psi.

The RDM pumped the PAR reagent at 40 psi producing a PAR flow rate of approximately 0.7 mL/min. HP helium was used to degas the PAR reagent and to pump the reagent through the membrane reactor, wherein the PAR combined with the ions from the sample solution. The solution flowed through the visible detector cell which was set at 520 nm for these experiments. The sensitivity range was set at 0.5 AUFS.

Operation of the Ion Chromatograph

Under normal operating conditions, helium was passed through the solutions for about 25 minutes prior to obtaining chromatographs. Two tanks of helium were required for this instrument. The HP helium was connected to the EDM and the ultra high pure (UHP) helium was connected to the CMB, RDM, and APM. After the helium tanks were connected to the proper tubing, the UHP helium tank regulator was set at 100 psi and the HP helium tank pressure set at 30 psi. Both tanks were opened and the IC turned on. The solutions were degassed for approximately 10 minutes. Next, the PDCA was selected on the APM and the column equilibrated. When the pump pressure stabilized to around 1200 psi, the LED light came on indicating that the pump was ready. If the column pressure did not stabilize within five minutes the pump had to be primed.

After the pressure stabilized, the PAR reagent was turned on. The system was allowed to run for 15 minutes before injecting the sample. The auto zero button was pressed and the chart recorder/integrator was checked to insure that it was functioning properly. The run time was checked and adjusted if necessary. A syringe was filled with 3 mL of the sample, all air removed, and a 0.20/0.25 mm filter wheel was attached if required. The syringe was inserted into the sample port with care being taken not to trap any air. Then, the injection unit was turned to load, and 3 mL of sample was injected onto the column. The injection switch was turned to 'Inject' at the same time as the 'Inject A' button on the integrator was pressed. The integrator monitored the experiment by giving retention times and peak areas of the species detected as they eluted off of the column.

Standard Curves

Standard curves were used to determine the concentration of each analyte with the curves being established prior to analyzing the glass samples. A 1000 ppm Fe^{2+} solution, using reagent grade ferrous ammonium sulfate, was prepared. A few milliliters of 0.1 M sulfuric acid were added to the iron solution to prevent the oxidation of Fe^{2+}. An appropriate aliquot (100 μL, 250 μL, etc.) was then pipetted into a volumetric flask and diluted to volume with the same background matrix solution as was used in analyzing the glasses. This solution had the same amount of concentrated sulfuric and hydrofluoric acids, boric acid and monobasic potassium phosphate (KH_2PO_4) as the glass sample solutions. The Fe^{3+} standard was 1000 ppm certified atomic absorption grade $FeCl_3$ solution (Fisher Scientific). The concentrations of the Fe^{3+} standard solutions ranged from 1.0 ppm to 10.0 ppm. The solutions were diluted in the same manner as the Fe^{2+} standard solutions. Each solution was injected into the IC three times and the peak areas averaged. Figure 5 and 6 show typical standard curves for Fe^{3+} and Fe^{2+} where the concentration (ppm) was plotted versus peak area, and a linear regression analysis was carried out. The correlation coefficient for both curves was 0.995. The iron concentration of the sample solution of Fe^{2+} and Fe^{3+} was then determined by comparing the sample's peak area to the standard curve. Standard curves were prepared prior to determining the Fe^{2+}/Fe^{3+} ratio in the samples. Standard solutions were measured often during the course of the research.

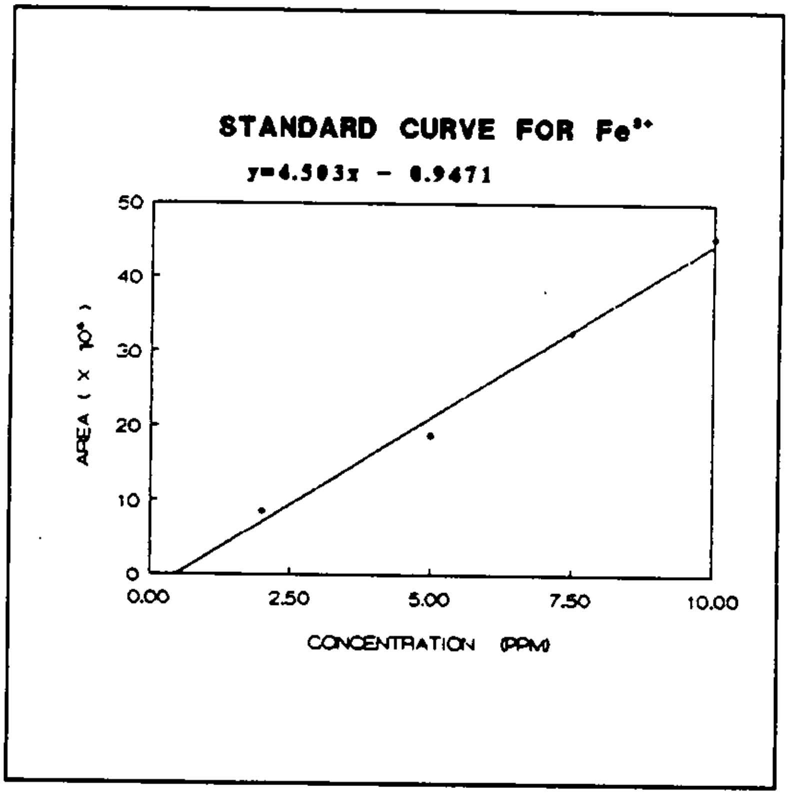

Figure 5. Standard Curve for Fe^{3+}

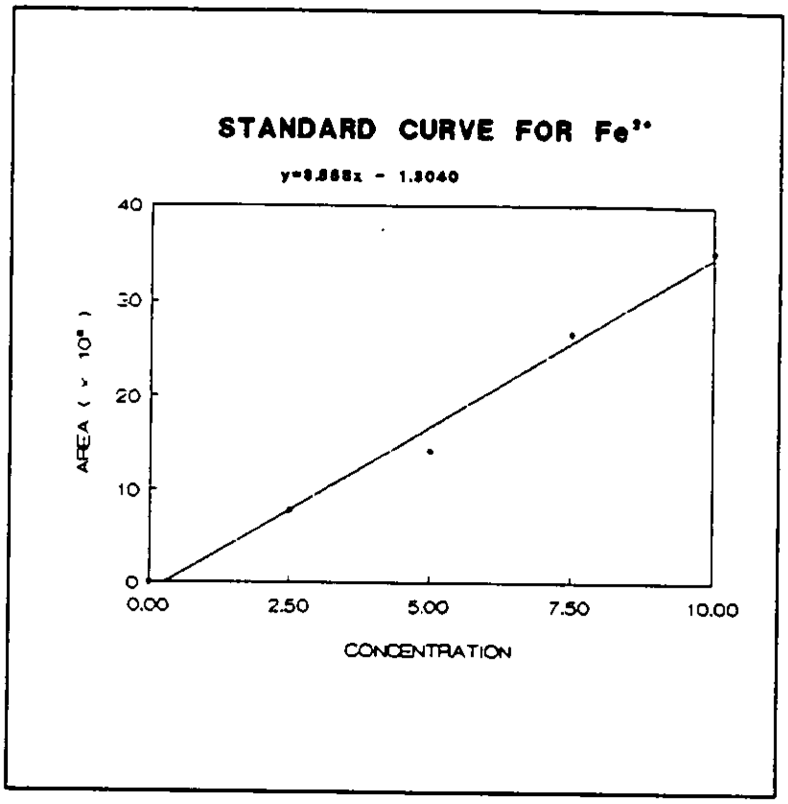

Figure 6. Standard Curve for Fe^{2+}

Spectrophotometric Determination of Fe^{2+}/Fe^{3+} Ratio

A second procedure used to analyze the glass for the Fe^{2+}/Fe^{3+} ratio was the spectrophotometric method. The glass was dissolved according to the procedure given by Bauman et al. (10). This method involved acid digestion in an HF/H_2SO_4 mixture, with 10 mg of NH_4VO_3 added to the 30 mg (approximately) of the glass. The glass was then heated for 45-60 seconds in a microwave oven using a microwave digestion bomb. Next, a pH 5 buffered ferrozine solution was added to the solution, developing the Fe^{2+} color. The absorbance (A_1) of the Fe^{2+}/ferrozine solution was measured at 560 nm. Ascorbic acid, reducing agent, was added to convert all of the iron to

Fe^{2+}. The absorbance (A_2) was measured again. The ratio was calculated by the equation

$$R = \frac{A_1}{(A_2 - A_1)} . \qquad (7)$$

The spectra were obtained using a Guided Wave Model 200 Spectrum Analyzer with a 70 mm Wand Assembly interfaced to an IBM-XT computer. The fiber optic chemical sensing probe was placed in the solution and ten spectra were taken of each sample over the range of 530 to 590 nm using wavelength increment of 1 nm. The computer averaged the spectra and saved them on disk. Ten spectra of water were used as the references, averaged, and saved on a disk. The software for this analysis was provided by Guided Wave. The majority of the Fe^{2+}/Fe^{3+} values obtained by the spectrophotometric method were measured by an undergraduate research assistant, Mark Edge, and the values are given in R. T. Hunter's M.S. thesis (9).

Mössbauer Spectral Determination of Fe^{2+}/Fe^{3+} Ratio

The third method for analyzing simulated nuclear waste samples is Mössbauer spectroscopy. It involved grinding the glass to a fine powder with an agate mortar and pestle. The powder was placed in the middle of 1 mm hole in an aluminum holder and supported by collodion. Mylar® tape was placed on each side to keep the solid in place. The sample was positioned between the ^{57}Co gamma radioactive source and detector. The spectra, showing peaks due to each of the two ions, were collected over several hours and the data stored on a computer. The peak areas for the Fe^{2+} and Fe^{3+} peaks were then determined. Iron foil was used as the standard.

The spectrometer was an Austin Sciences Associates (ASA) Mössbauer Spectrometer Controller with a wave form generator, pulse amplifier, and servoamplifier. The detector was an ASA proportional counter with a gas-filled chamber with two electrodes. The analyzer was a Nuclear Data ND65 Multichannel Analyzer (MCA). The data were transferred serially to an Apple IIe computer. The data were saved to a floppy disk and then transferred to the IBM Mainframe Computer by modem. A computer program (Shawfit) supplied by the Mössbauer Data Center-UNC-A was used to analyze the spectra and determine the ratios. The majority of the Fe^{2+}/Fe^{3+} values determined by the Mössbauer spectral method were obtained by R. Todd Hunter (9).

CHAPTER III

RESULTS

Composition of Simulated Nuclear Waste Glass

Research on immobilizing the radioactive waste in glass has been in progress for several years at SRS and nonradioactive simulated waste has been used for the majority of the experiments. Many glasses have been produced from these experiments at DWPF. Fifteen of these glasses were analyzed in this research. The Fe^{2+}/Fe^{3+} ratio of these glasses had been measured by other methods and the glasses used had a range of ratio values extending from 0.0 to about 1.60.

Nuclear waste glass is composed of over sixty elements including several metal ions. Table 1 shows the composition of two typical research-generated glasses, 165/AL/Q and 165/TDS-Cl. This table shows the elemental weight percent of each metal ion is given. Generally these glasses contain about 5 to 10% iron. Note that other metals such as Cr, Mn, Ni, and Al are also present in the simulated nuclear waste glass samples. Figures 7 and 8 are the radio frequency (rf) glow discharge mass spectra of the vitrified simulated DWPF glass and high iron glass, respectively (16). These spectra confirm that other metal ions, Cr^{2+}, Mn^{2+}, and Ni^{2+}, are present in the glasses or sludge. The peak height does not represent the relative amounts of each metal.

Table 1. Elemental Weight Percent of Glasses

	165/AL/Q	165/TDS-Cl
Al	5.41	3.2
Ca	1.02	1.3
Fe	5.31	9.27
Mg	0.526	0.584
Mn	1.13	1.76
Na	6.34	6.69
Li	1.87	2.01
Ni	0.77	0.99
Si	24.74	26.61
Cr	0.13	0.14
B	2.67	2.79
U	0.78	1.05
Sr	0.04	0.05
Zr	0.78	0.88
Ti	0.04	0.0
K	0.0	0.0

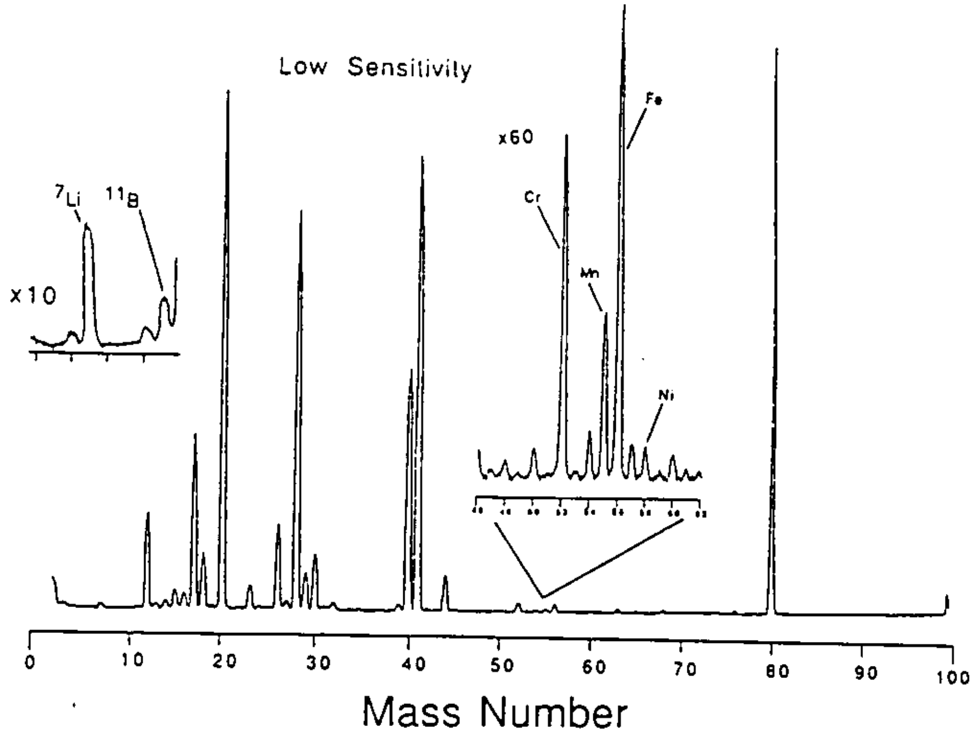

Figure 7. Radio Frequency Glow Discharge Mass Spectrum of Vitrified Simulated DWPF Glass

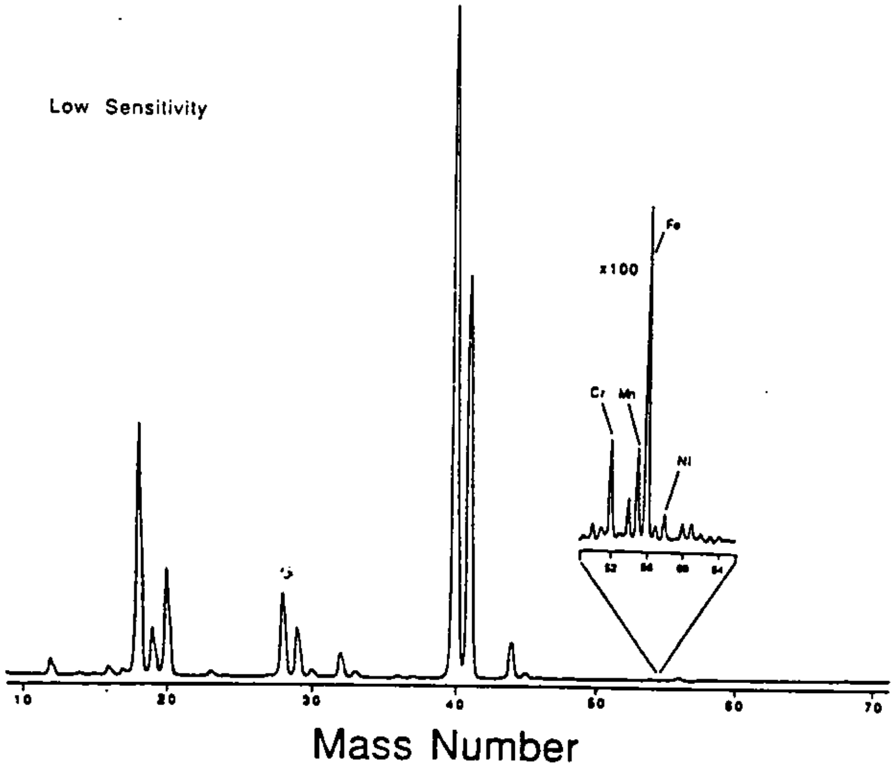

Figure 8. Radio Frequency Glow Discharge Mass Spectrum of High Iron Glass

Procedure Development

A large number of methods are given in the literature for the analysis of iron. Recently, new instrumental methods have been reported for analyzing iron under a variety of different conditions. An example of these is the analysis of iron in solution by ion chromatography. The Dionex Corporation reports two methods of such analysis. However, only one of their methods differentiates between Fe^{2+} and Fe^{3+} ions with the other method analyzing only for Fe^{2+}. The method used in this study was basically patterned after the first of the two Dionex methods with the initial procedure following that given by Dionex (17) and as modified by K. M. Brewer as part of a senior research project. The method established by Dionex could not be used since iron was analyzed in a simple aqueous solution. Since the matrix of the iron in the solution of dissolved glass was more complex, the procedure and parameters had to be modified considerably. The optimum flow rate for the eluant, PDCA, was determined to be 1.0 mL/min. and flow rate for the PAR reagent was determined to be 0.7 mL/min. The combined flow rate of the waste solution had to be 1.7 mL/min. These two parameters were altered over a wide range to insure that they were optimum.

Other instrumental parameters that had to be adjusted were wavelength and detector sensitivity. The iron/PAR complex had its strongest absorption band at 520 nm. Other wavelengths (440 nm and 570 nm) on the Opti/Ion Vis filter wheel were tried. However, the best results occurred at 520 nm. The sensitivity factor was set 0.5 AUFS for all of the analyses.

The initial buffering capacity of the PDCA (pH 4.7) was too low. The initial preparation added 5.7 mL of glacial acetic acid and 8.203 g of anhydrous sodium acetate to 1.0 L of the PDCA solution. The buffering capacity had to be increased to 11.4 mL of glacial acetic acid and 16.406 g of anhydrous sodium acetate to 1.0 L of PDCA solution in order to eliminate the doubling of the Fe^{3+} peak. K. M. Brewer discovered that this was a result of the large difference in the pH of the sample solution and the eluant. Once the buffer components were doubled, the double peaks disappeared, producing a single Fe^{3+} peak. However, for glasses 9 and 10, some Fe^{3+} peak broadening was observed with the new buffer solution.

In determining the Fe^{2+}/Fe^{3+} ratio in the glass samples, Fe^{2+} oxidation was a major problem. Many procedures, dissolution processes, and reagents were tried in attempts to overcome this oxidation. A procedure was tried which was patterned after the Bauman spectrophotometric method and required using different concentrations of the chemicals to dissolve the glass. This modified Bauman procedure involved adding 100 μL of NH_4VO_3 solution to about 30 mg of glass, then adding 500 μL of concentrated sulfuric acid and 500 μL concentrated HF to dissolve the glass. Next, the glass was heated for two hours at 120°C in a laboratory oven, 0.5 g of solid boric acid added, and the solution allowed to cool (10).

Once cool, an aliquot was transferred to a volumetric flask and diluted to volume. A syringe was filled with 2 mL of the solution and injected into the ion chromatograph in order to rinse the injection loop. Next, 3 mL was drawn into the syringe and injected into the instrument. This process resulted in a chromatogram with Fe^{2+} and Fe^{3+} peaks, however, the Fe^{2+} peak was too small. Figure 9 illustrates this point with glass 165U/TDS/800/96. The Fe^{3+} peak has a retention time of 4.25 minutes and the Fe^{2+} has a retention time of 13.04 minutes. Other methods had shown this sample to contain a significant amount of Fe^{2+}. Evidently oxygen was entering the system at some point in the procedure. In an acidic dissolution mixture, the vanadate ion prevents Fe^{2+} oxidation by the following equilibrium reaction:

$$VO_3^- + Fe^{2+} + 4H^+ \rightleftharpoons VO^{2+} + Fe^{3+} + 2H_2O. \tag{8}$$

The low pH of the solution shifted the equilibrium to the right producing the vanadyl ion, the water, and Fe^{3+}. The equilibrium shifted back to form Fe^{2+} when the boric acid was added and when the sample solution comes into contact with the IC eluant. Apparently under the conditions of the IC analysis, vanadate could not prevent Fe^{2+} oxidation. There was also some indication that the ammonium vanadate interfered with the Fe^{3+} peak, giving a larger area under the peak.

Another approach was to use various reagents in solutions at different concentrations and states in order to minimize oxidation. It was thought that adding the solid form would minimize oxygen addition, by air, to the solution. Both a solution of boric acid and solid boric acid gave the same results. Twice the amount of solid boric acid (1.0 g) produced the same amount of oxidation. A similar experiment was tried with ammonium vanadate. The concentration of ammonium vanadate was doubled and solid was used, however, neither produced satisfactory results. Figure 10 is a chromatogram of the same glass sample in Figure 9 except for the dissolution procedure used twice the ammonium vanadate.

The glass dissolution and the solution preparation were done in a nitrogen filled glove bag. All the materials were placed in the glove bag and the system was purged three times with nitrogen. After the purging the ammonium vanadate was added to the pre-weighed glass sample and then the sulfuric and hydrofluoric acids added. After about fifteen minutes, the solution was capped and placed in the acid digestion bomb and heated for two hours. The bomb was removed from the oven, cooled, and placed in the glove bag with the other necessary materials. Then the boric acid was added, the sample was transferred to a 100 mL volumetric flask, diluted to volume with deionized water, and injected into the instrument. Again this was unsatisfactory. The Fe^{2+} was still smaller than expected as shown in Figure 11.

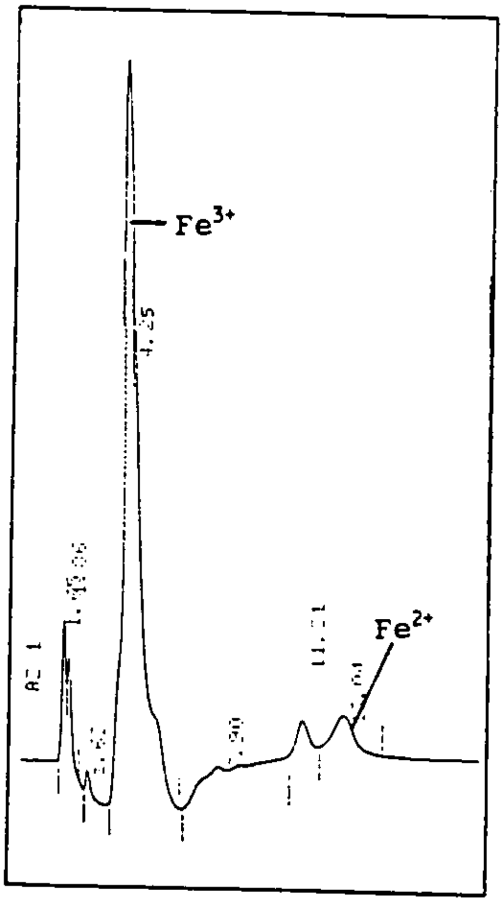

Figure 9. Chromatogram of 165U/TDS/800/96 Analyzed 7/24/87

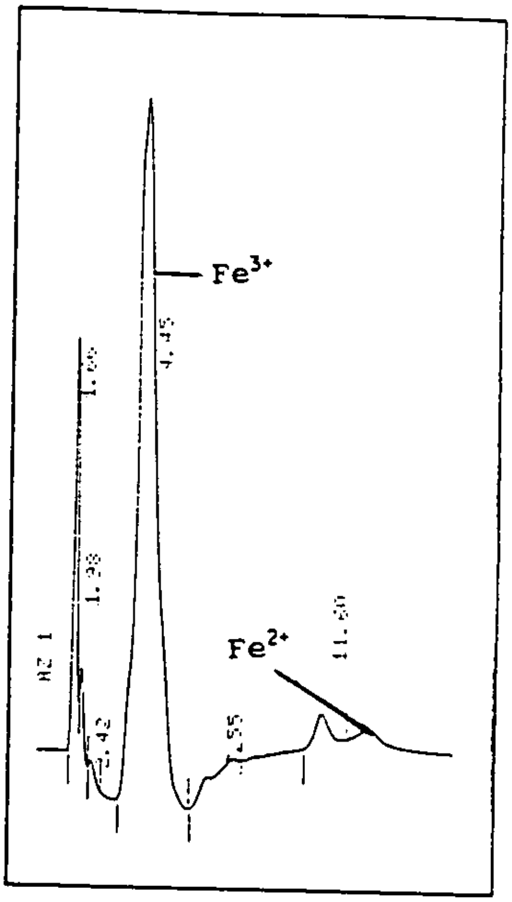

Figure 10. Chromatogram of 165U/TDS/800/96 Analyzed 7/23/87

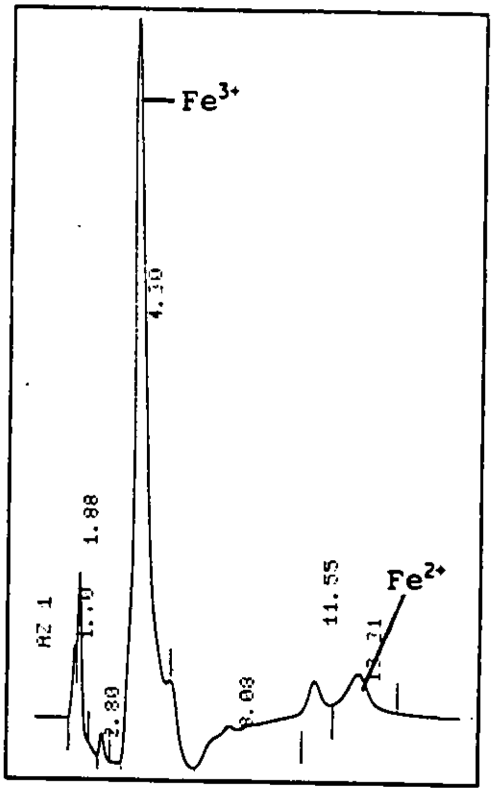

Figure 11. Chromatogram of 165U/TDS/800/96 analyzed 7/28/87.

Another procedure was tried where argon and helium were used instead of nitrogen to purge the solutions needed for IC analysis and also pressurize the IC system. Nitrogen is normally used for these operations. The results with argon were basically the same as with nitrogen, while helium seemed to be better than argon or nitrogen. Helium has been found to purge the oxygen from the solutions better than the other two gases (18). The sample solution, deionized water, and reagent solutions were degassed with helium. Before being used for degassing, helium was bubbled through a large container of water. These solutions after preparation were degassed again with helium. Only the concentrated acids were not degassed because of the small amount used. This procedure resulted in a Fe^{2+} peak that was resolved more, but some oxidation still occurred.

The chromatograms obtained from early experiments showed Fe^{2+} peaks which were not sharp and distinct. This problem was solved by modifying a procedure which appeared in the most recent literature.

While this research was underway, a procedure to determine the Fe^{2+}/Fe^{3+} ratio in nuclear waste glasses by IC was reported by Bunnell et al. at the Pacific Northwest Laboratory (PNL) (19). The reported procedure was somewhat sketchy in detail, but involved the acid digestion of the glasses with the addition of boric acid, potassium hydrogen phosphate and ammonium hydroxide. This procedure did not give the specific concentration of potassium hydrogen phosphate.

After some experimentation, the best concentration of KH_2PO_4 to use was determined to be 0.5 M. The NH_3 (aq) that was required in the new procedure was inadvertently omitted in one experiment. The results were better, but the Fe^{2+} peak was still not fully resolved. Therefore, some experimentation was carried out to modify the procedure with regard to the amount of NH_3 (aq) to use. NH_3 (aq) was present in some glass sample solutions and omitted in others. The results were better when the NH_3 (aq) was left out. The Fe^{2+} peak was sharper and larger in the chromatograms of the glass sample solutions without the NH_3 (aq) added.

Another modification of the reported procedure was to determine the effect upon Fe^{2+} oxidation of heating the glass during dissolution. Several of the glasses were dissolved using the acid mixture, with and without the heating step. It was discovered that heating the glass during dissolution appeared to cause some oxidation to occur. Using the PNL procedure and no heating seemed to give good results. The ratio determined when no heating was used was actually closer to that found by the spectrophotometric and Mössbauer spectral methods. If several glass specks were still present after the acids were added to the glass sample, the glass was heated using a microwave oven instead of a laboratory oven to dissolve the specks. The total heating times in the microwave oven ranged from 15 to 60 seconds. The considerable reduction of the heating time lessened the potential for oxidation and a better chromatogram was obtained as shown in Figure 12.

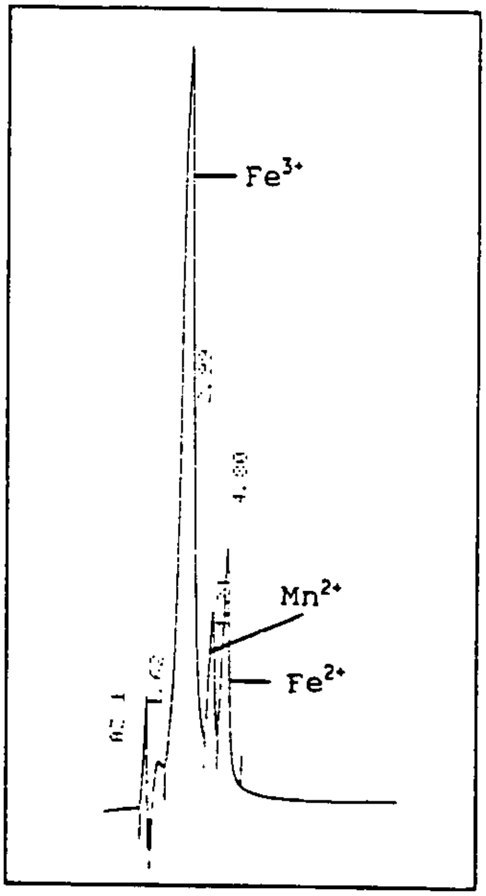

Figure 12. Chromatogram of 165U/TDS/700/3 Analyzed 2/23/89

This modified version of this IC procedure was used throughout the remainder of the glass analysis. After all the experimentation and modifications were finished, the procedure for determining the Fe^{2+}/Fe^{3+} ratio by IC was completed and is given in Chapter II of this report.

Ion Chromatography Analysis Results

A total of fifteen glasses with Fe^{2+}/Fe^{3+} ratios ranging from 0.0 to 1.60 were analyzed several times over the past two years. Table 2 shows the list of the glasses and the ratios as analyzed by IC. The first column of Table 2 is the code name of the glasses as given by SRS to identify the glasses produced from various experiments and the second column is the ratio and standard deviation in that glass. The third column shows the date the glass was analyzed with the number in parenthesis representing the different times the glass was analyzed. All were done by the modified PNL method. Glass 1 was analyzed five times. In the first analysis the ratio was determined to be 0.36 ± 0.00 after being analyzed using two different samples. In the analysis a year later, the ratio was calculated to be 0.37 ± 0.01 using three different samples. Glass 2 was analyzed three different times and gave values of 0.29, 0.33 ± 0.00, and 0.29 ± 0.00 on the dates (month/year) 6/88, 7/88, and 2/89, respectively. Some deviation does occur and reasons for this are discussed below.

Table 2. Fe^{2+}/Fe^{3+} Ratios of Simulated Nuclear Waste Glass Samples

Glass	Ion Chromatography	Analyzed Month/Year (# of times)
1. 165/HI FE/O/QUENCHED*	0.36 ± 0.00	6/88 (2)
	0.37 ± 0.01	6/89 (3)
2. 165U/TDS/700/3*	0.29	6/88
	0.33 ± 0.001	7/88 (2)
	0.29 ± 0.002	2/89 (2)
3. 165U/TDS/800/96*	0.23 ± 0.01	6/88 (2)
	0.29 ± 0.004	7/88 (2)
	0.32 ± 0.03	6/89 (2)
4. 165U/TDS/900/96*	0.27 ± 0.06	6/88 (3)a
	0.54	6/88 b
	0.26	7/88
	0.38 ± 0.05	3/89 (2)
5. 165U/TDS/700/1.5*	0.27 ± 0.02	5/89 (3)
	0.30 ± 0.01	6/89 (3)
6. 165/TDS*	0.53 ± 0.05	6/88 (5)
	0.45 ± 0.02	2/89 (2)
	0.56	10/88
7. 165U/AL/800/3*	0.16 ± 0.03	6/88 (6)
8. 165U/AL/700/24*	0.18	6/88
	0.15 ± 0.05	7/88 (4)
	0.23 ± 0.01	6/89 (3)
9. 165/AL/700/12*	0.19 ± 0.02	7/88 (4)
	0.17	5/89
10. Fe_3O_4 + 1% PBA	0.76 ± 0.02	7/88 (2)
	0.62 ± 0.07	6/89 (2)
11. Fe_2O_3 + 5% NaCOOH	1.01 ± 0.07	3/89 (3)
	0.96 ± 0.11	6/89 (2)
12. 5% Fe_2O_3 + 5% $Fe(COOH)_3$	0.27 ± 0.03	7/88 (3)
	0.25 ± 0.08	3/89 (4)
	0.28 ± 0.01	6/89 (3)
13. 2.0 U_2O_3*	0.18	3/89 (2)
14. 165/FRIT/IRON/Cr_2O_3/ GROUND	0.0	5/89
15. 165/FRIT/IRON/MnO/ GROUND*	0.0	5/89

a= No Heating b= Heating *=Mn^{2+} peak in chromatograms

The ion chromatograms of all of the glass samples showed peaks due to Fe^{3+}. Two glasses (Glasses 14 and 15) had no Fe^{2+} peaks since the glasses had been prepared under oxidizing conditions, in air. These two glasses were analyzed to insure that the Fe^{3+} was not being reduced to Fe^{2+} or that Fe^{2+} was not introduced into the dissolution process by any reagent. Table 3 lists the retention times and date analyzed for selected iron and manganese peaks. The chromatograms all showed one or two peaks that elute before 1.5 minutes. These peaks were due to the background matrix in which the glasses were dissolved.

A majority of the glasses have at least one peak between the iron peaks. These glasses are marked with an asterisk in Table 2. Glass 4 was the only glass sample that had two peaks between the iron peaks in the chromatogram and is shown in Figure 13. One was due to manganese while the other was probably due to copper. Glass 15, prepared with 1.69 % of Mn, was analyzed to determine the retention times of the Mn^{2+}, and it was found to be 3.77 minutes on a column which had been used over a year. This corresponds to the retention times of the extra peak that was present in the chromatograms of the other glasses. For example, glass 13 has an extra peak with a retention time of 3.70 minutes, and glass 8 has a retention time of 3.73 minutes. Both were analyzed between March and June of 1990. This indicated that the unknown peak was manganese. To confirm this, standards of nickel, chromium, uranium, copper, and manganese, all possibly present in the waste glass, were prepared. Chromatograms of the standards were obtained at several wavelengths to determine if the metal ion/PAR species absorbed at 520 nm. Then, if they could be analyzed at that wavelength, the retention times of the metal ions were determined.

Table 3. IC Peak Retention Times Found on Selected Chromatograms of Simulated Nuclear Waste Glass Samples (all times in minutes)

Glass	Date	Fe^{3+}	Mn^{2+}		Fe^{2+}
1.	6/22/89	2.86	3.72		4.16
2.	2/23/89	2.99	4.24		4.80
3.	6/27/89	2.93	3.95		4.44
4.	3/01/89	3.28	4.50	(5.83)	6.92
5.	6/22/89	2.72	3.76		4.21
	5/23/89	2.69	3.90		4.43
6.	2/23/89	2.61	3.73		4.19
7.	6/22/89	3.32	7.39		8.54
8.	6/22/89	2.67	3.64		4.12
	6/22/89	2.74	3.73		4.22
	6/23/89	2.91	3.80		5.53
9.	7/28/88	3.04	6.96		8.00
10.	7/19/88	3.54	---		9.01
	7/19/88	3.53	---		8.96
11.	3/29/89	2.52	---		4.02
12.	6/05/89	2.76	---		4.66
13.	3/29/89	2.61	3.70		4.23
14.	5/18/89	2.66	----		---
15.	5/23/89	2.58	3.77		---

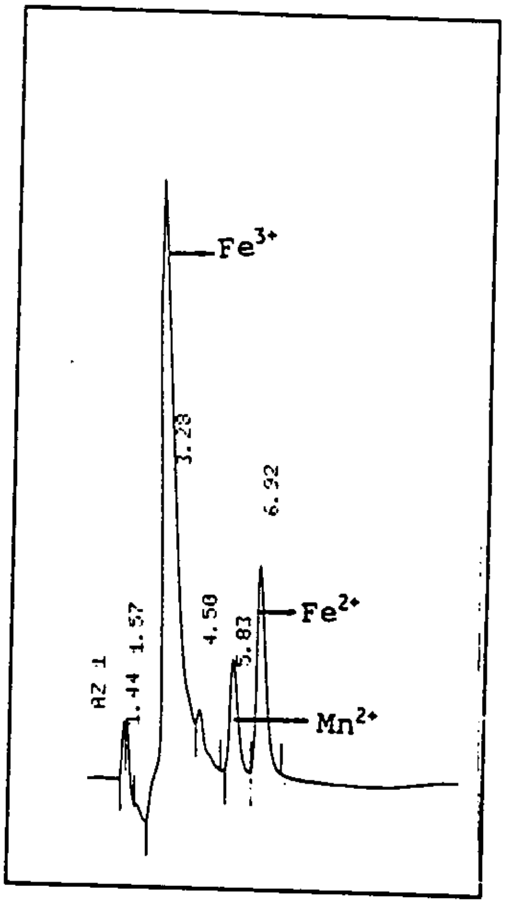

Figure 13. Chromatogram of 165U/TDS/900/96 Analyzed 3/1/89

Finally, several solutions of dissolved glass were doped with the metal ions. Copper, nickel, and manganese all eluted between the iron peaks, (3.3, 3.5, 3.7 minutes). These retention times corresponded to those established by Dionex. The manganese ion eluted at the same time as the extra peak, causing the peak area to increase. Standard solutions of Mn^{2+} were prepared, injected into the chromatograph three times, and an average taken. The standard curve, correlation coefficient of 0.996, is shown in Figure 14. Four of the other glasses had no extra peaks between the iron peaks. These glasses were 10, 11, 12, and 14.

The Fe^{3+} retention times ranged from 3.54 to 2.52 minutes over a period of one year using the same column, while the Fe^{2+} peak varied from 9.01 to 4.12 minutes over the same period. The Mn^{2+} elution time fluctuated from 6.96 to 3.70 minutes. The decrease in retention times was due to column deterioration. Tailing of the peaks was not a problem in the majority of the glasses.

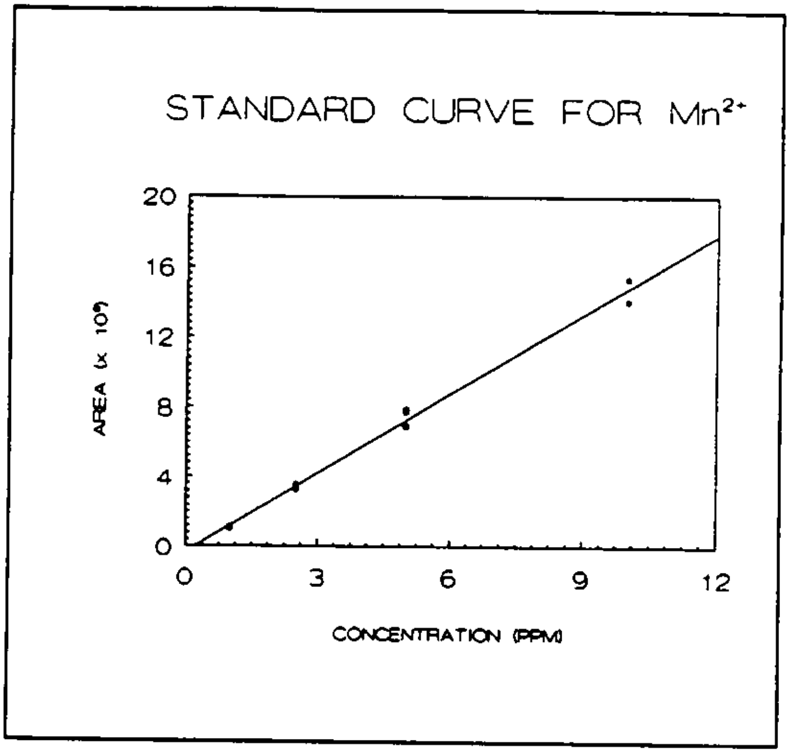

Figure 14. Standard Curve for Mn^{2+}

CHAPTER IV

DISCUSSION AND CONCLUSION

Ion chromatography is not only a good method for analyzing glasses for Fe^{2+} and Fe^{3+}, but also for other ions such as Mn^{2+}. If proper separation and peak resolution of the ions are able to be obtained by this method, then the ion concentrations can be determined. For the glass solutions examined in this study, the Fe^{3+} eluted first, Mn^{2+} next and finally Fe^{2+}. Cu^{2+}, if present in the glass sample, appears to elute at a retention time slightly less than that of Fe^{2+}. Therefore, if a substantial amount of Cu^{2+} is present and no separation of the Fe^{2+} and Cu^{2+} occurs, the Fe^{2+} determination will be in error. It is possible for other ions to be analyzed also.

The ratios obtained by the IC method compare reasonably well with those obtained by other methods. Table 4 shows the average ratio determined by IC, spectrophotometric, and Mössbauer spectral methods. Glass 4 had ratios of 0.41, 0.39, and 0.31 respectively. Glass 6 has an IC ratio (0.50) closer to that of the spectrophotometric method (0.48) than the Mössbauer method (0.23). Most of the other ratios tend to agree more with those determined by the spectrophotometric method. The spectrophotometric method is the method being used at this time for nuclear waste glass analysis (20).

Table 4. Average Fe^{2+}/Fe^{3+} Ratios of Simulated Nuclear Waste Glass Samples by Three Methods

Glass	IC	Mössbauer	Spectropho.
1. 165/HI FE/0/QUENCHED	0.36	0.20	0.28
2. 165U/TDS/700/3	0.35	0.41	0.52
3. 165U/TDS/800/96	0.32	0.35	0.46
4. 165U/TDS/900/96	0.41	0.31	0.39
5. 165U/TDS/700/1.5	0.30	0.35	0.37
6. 165/TDS	0.50	0.23	0.48
7. 165U/AL/800/3	0.21	0.26	0.26
8. 165U/AL/700/24	0.17	0.14	0.21
9. 165U/AL/700/12	0.24	0.13	0.53
10. Fe_3O_4 + 1% PBA	1.2	1.4	1.3
11. Fe_2O_3 + 5% NaCOOH	1.0	1.6	1.7
12. 5% Fe_2O_3 + 5% $FE(COOH)_3$	0.34	0.66	0.53
13. 2.0 U_2O_3	0.18	0.11	0.15
14. 165/FRIT/IRON/Cr_2O_3/ GROUND	0.0	0.0	0.0
15. 165/FRIT/IRON/MnO/ GROUND	0.0	0.0	0.0

Figure 15 shows the relationship between the Fe^{2+}/Fe^{3+} ratio values obtained by IC and Mössbauer spectral methods. There is a correlation coefficient of 0.928. The relationship between the IC and spectrophotometric method values is shown by Figure 16 with a correlation coefficient 0.932. The spectrophotometric method and the Mössbauer spectral method values correlate with a coefficient of 0.922 (9). There is a slightly better correlation between the IC and spectrophotometric values.

In analyzing glasses over a three year period, problems other than Fe^{2+} oxidation have occurred. One minor problem was the deterioration of the column over time. The column was cleaned using the methods described in the Dionex manual; however certain organic and metal contaminants are probably not removed. In the beginning of the analysis the retention times of the Fe^{2+} was 9 minutes and Fe^{3+} was 4 minutes. After about three years the retention times decreased to 4.5 and 3.0 minutes, respectively as shown in Figures 17 and 18. This might lead eventually to peak interferences giving false areas. For this study, this was not a major problem since the Mn^{2+} peak was properly resolved from the two iron peaks even in a column that was three years old.

Table 5 shows the concentration and percent of iron and manganese in the glass sample solutions. Glass 1 solution analyzed on 6/22/89 contains 7.09 ppm of Fe^{2+}, 18.7 ppm of Fe^{3+}, and 10.6 ppm of Mn^{2+}. In this glass sample solution the total percent iron ranged from 8.17 to 9.66 % which is expected for the glass samples. The percent manganese in the glass sample solutions ranged from 3.0 to 3.5 %. For the glass samples analyzed, the percent iron ranged from 1.0 to 3.5 %. Since a Mn^{2+} standard curve was determined late in the research, the percent manganese was calculated for only glass samples which were analyzed in 1989.

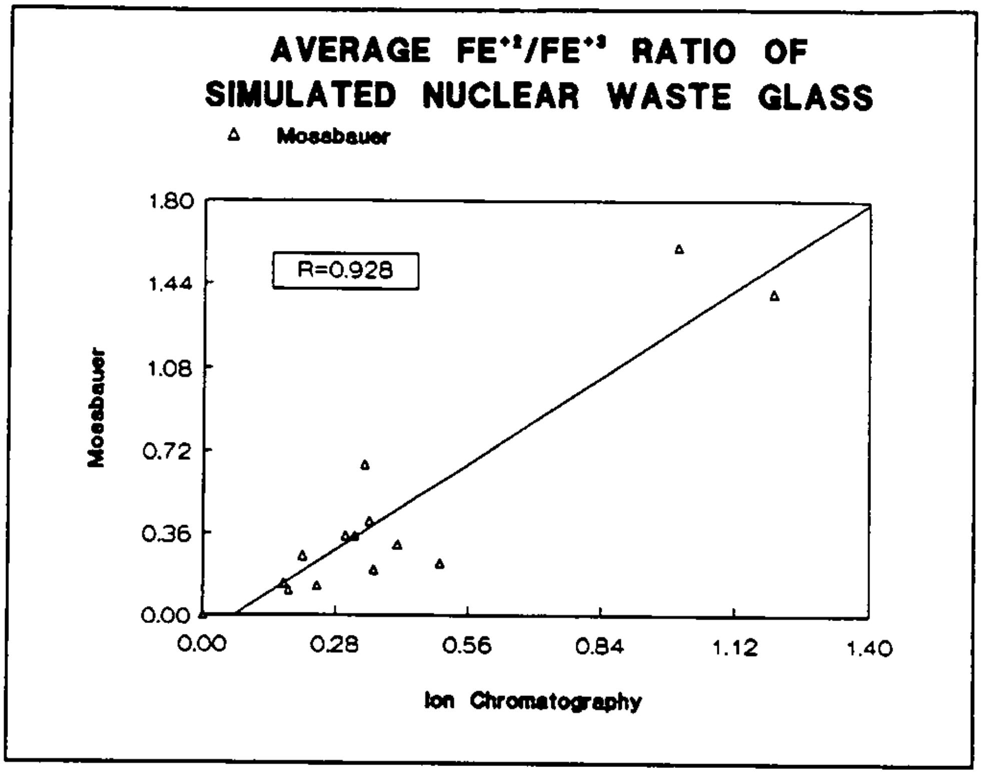

Figure 15. Scatter Plot of IC versus Mössbauer Ratio Values

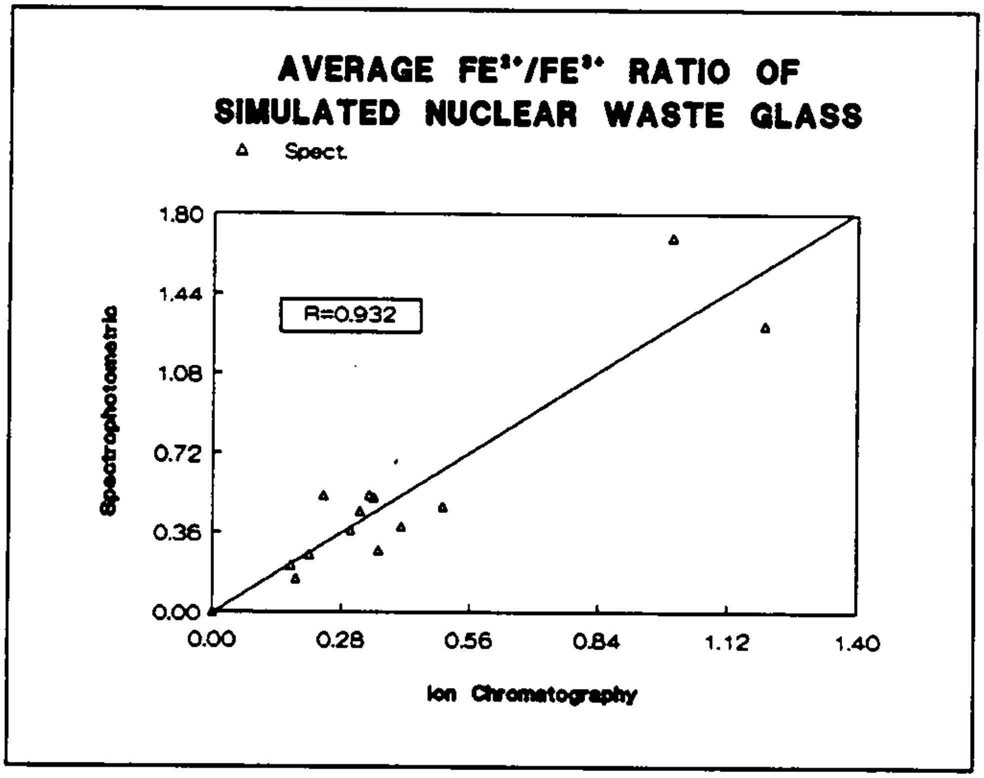

Figure 16. Scatter Plot of IC versus Spectrophotometric Ratio Values

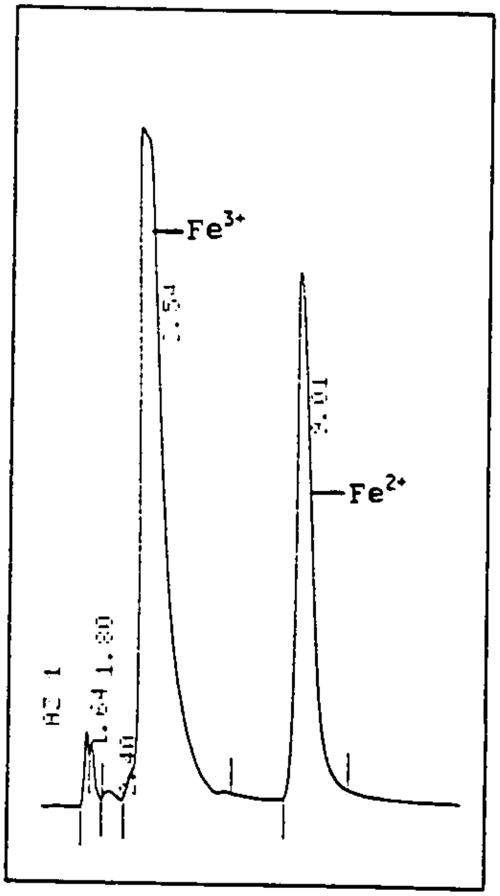

Figure 17. Chromatogram of Fe_3O_4 + 1% PBA Analyzed 2/23/89

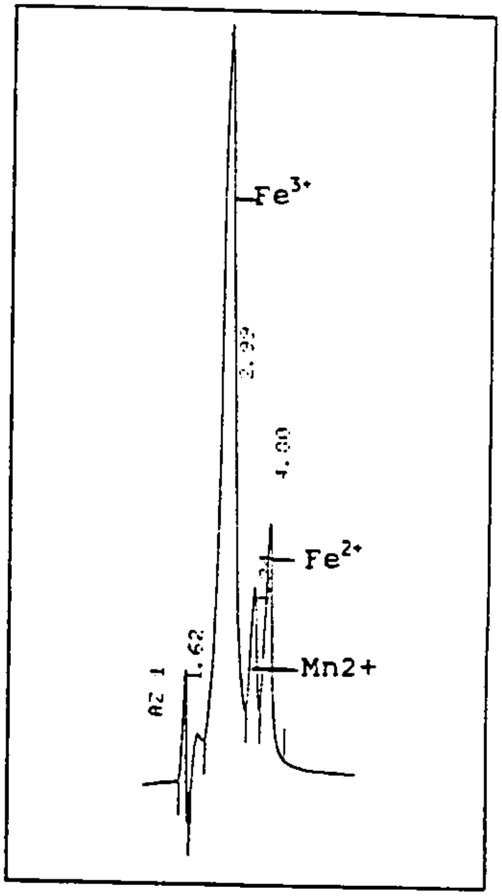

Figure 18. Chromatogram of 165U/TDS/700/3 Analyzed 2/23/89

Table 5. Iron and Manganese Solution Concentrations and Percents in Simulated Nuclear Waste Glass Samples as Determined by IC

GLASS	DATE	Fe^{2+} PPM/%	Fe^{3+} PPM/%	Mn^{2+} PPM/%	TOTAL IRON
1.	6/20/88	5.63/2.48	15.8/6.96		9.44
	6/20/88	5.76/2.54	16.2/7.12		9.66
	6/22/89	6.53/2.14	18.4/6.03	10.5/3.45	8.17
	6/22/89	6.95/2.28	18.3/6.00	9.16/3.00	8.28
	6/22/89	7.09/2.33	18.7/6.12	10.6/3.49	8.45
2.	6/20/88	5.33/1.67	18.4/5.76		7.43
	7/27/88	3.05/1.22	9.34/3.74		4.96
	7/27/88	3.11/1.24	9.45/3.78		5.02
	2/23/89	2.67/1.17	9.34/4.10	3.21/1.41	5.27
	2/23/89	3.46/1.78	12.0/6.15	4.77/2.09	7.93
3.	6/14/88	3.40/1.29	15.3/5.79		7.08
	6/17/88	2.96/1.12	12.3/4.64		5.76
	7/14/88	3.28/1.36	11.6/4.80		6.16
	7/14/88	3.33/1.38	11.5/4.78		6.16
	6/27/89	2.22/0.92	6.52/3.15	3.61/1.74	4.07
4.	6/29/88	2.41/1.01	9.67/4.07		5.08
	6/29/88	2.51/1.06	11.1/4.67		5.73
	6/30/88	2.87/1.21	8.44/3.54		4.75
	6/30/88	5.19/1.81	9.68/3.39		5.20
	7/08/88	3.44/1.15	13.5/4.52		5.67
5.	5/18/89	3.19/1.36	12.4/5.29	5.54/2.37	6.65
	5/18/89	3.25/1.39	12.6/5.37	5.36/2.29	6.76
	5/19/89	2.72/1.16	9.07/3.88	5.21/2.23	5.04
	6/22/89	4.06/1.77	13.7/5.99		7.76
	6/22/89	4.56/1.81	13.5/5.91	6.08/2.66	7.72
	6/22/89	4.01/1.75	14.3/6.23	5.93/2.59	7.98
6.	6/12/88	6.98/2.23	10.9/3.99		6.22
	10/14/88	3.64/1.71	8.26/3.88		5.59
	2/23/89	4.46/2.09	9.60/4.51	2.08/0.98	6.60
7.	7/08/88	1.76/0.66	14.4/5.14		6.07
	7/10/88	1.70/0.64	9.90/3.71		4.35
	7/10/88	1.70/0.64	9.51/3.56		4.20
	7/11/88	1.63/0.61	8.68/3.25		3.85
	7/26/88	1.22/0.58	8.56/3.91		4.47
	7/26/88	1.28/0.58	8.96/4.09		4.67

Table 5. (Continued)

8.	6/22/88	1.88/0.71	10.7/4.06		4.72
	7/12/88	1.32/0.48	10.1/3.66		4.14
	7/13/88	1.32/0.48	12.0/4.33		4.81
	7/26/88	2.23/0.82	10.4/3.76		4.58
	7/27/88	1.38/0.50	10.2/3.74		4.24
	6/22/89	1.29/0.62	5.66/2.71	3.37/1.61	3.33
	6/22/89	1.29/0.62	5.77/2.76	3.52/1.68	3.38
	6/23/89	1.35/0.65	5.76/2.75	3.66/1.75	3.40
9.	7/11/88	1.98/0.82	9.77/4.07		4.89
	7/12/88	1.70/0.71	9.82/4.09		4.80
	5/18/89	1.35/0.58	7.80/3.32	3.07/1.31	3.90
	7/28/89	1.61/0.62	8.80/3.40		4.02
	7/28/89	1.61/0.62	7.76/3.00		3.62
10.	7/19/88	7.54/2.83	10.1/3.81		6.64
	7/19/88	7.70/2.89	9.95/3.74		6.63
	6/26/89	7.24/2.60	12.7/4.57		7.17
	6/26/89	8.76/3.14	13.1/4.71		7.85
11.	3/15/89	7.12/3.41	6.55/3.14		6.55
	3/29/89	7.34/3.51	7.77/3.72		7.23
	3/29/89	6.95/3.33	6.86/3.28		6.61
	6/22/89	7.69/3.33	8.73/3.78		7.11
	6/23/89	9.91/4.29	9.58/4.14		8.43
12.	7/12/88	2.23/1.05	8.50/3.99		5.04
	7/12/88	2.13/1.00	8.72/4.09		5.09
	7/12/88	2.11/0.99	6.85/3.22		4.21
	3/15/89	2.45/1.11	7.41/3.35		4.46
	3/29/89	2.31/1.18	7.82/4.01		5.19
	3/29/89	1.19/0.61	5.94/3.05		3.66
	3/29/89	1.15/0.59	6.68/3.43		4.02
	6/05/89	1.49/0.72	6.36/3.07		3.79
13.	3/29/89	1.98/0.92	11.6/5.41	4.75/2.21	6.33
	3/31/89	2.16/1.00	12.0/5.59	6.33/2.94	6.59
14.	5/18/89		10.3/4.59		4.59
15.	5/18/89		9.90/3.90	3.87/1.52	3.90
	5/23/89			4.05/1.60	
	6/26/89		16.9/5.54		5.54

Another problem which might be potentially important is the elution of metal ions other than Fe^{3+}, Fe^{2+}, and Mn^{2+}. There was a distinct possibility that Cu^{2+} or Ni^{2+} was the cause of one of the extra peaks found in the chromatogram of glass 4. (See Figure 13.) Two peaks with retention times of 4.50 and 5.83 minutes were found between the two iron peaks. The peak at 4.50 minutes is the Mn^{2+} peak, while the other may be due to Cu^{2+} or Ni^{2+} since standard solutions of Cu^{2+} and Ni^{2+} when added to the glass samples produced peaks around that time. Glass 5 was doped with Cu^{2+} and Ni^{2+} and had retention times of 4.12 and 4.17 minutes, respectively, which are approximately the same as that of the Fe^{2+} peak. Fortunately the percentage of Cu^{2+} in the glasses is very low (< 0.1 %). Chromatograms of transition metals solutions from the literature show Cu^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} eluting between the iron peaks using the PDCA/PAR system. Since nuclear waste might have a wide range of elements there is always the possibility that some of the transition metals might interfere with this method.

In conclusion, ion chromatography is a promising method for determining the Fe^{2+}/Fe^{3+} ratio in the simulated nuclear waste glasses and other related materials. The values determined by IC compare well with the spectrophotometric and the Mössbauer spectral methods. It is possible for the IC to be automated so that human exposure to radioactive samples can be reduced. Because of the above reasons, IC should be considered as a routine analysis of glasses.

APPENDIX

This appendix contains the chromatograms of the simulated nuclear waste glass samples analyzed over a three year period by ion chromatography.

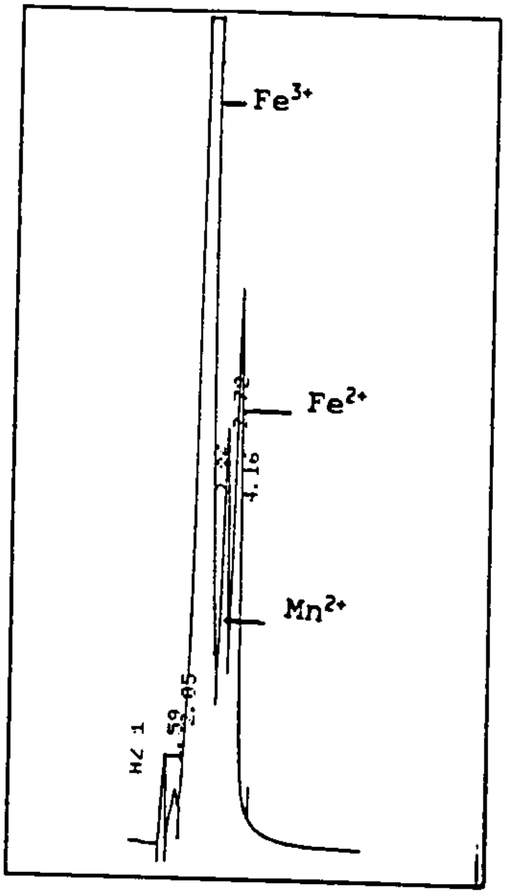

Figure A-1. Chromatogram of 165/HI FE/0/Quenched Analyzed 6/24/89

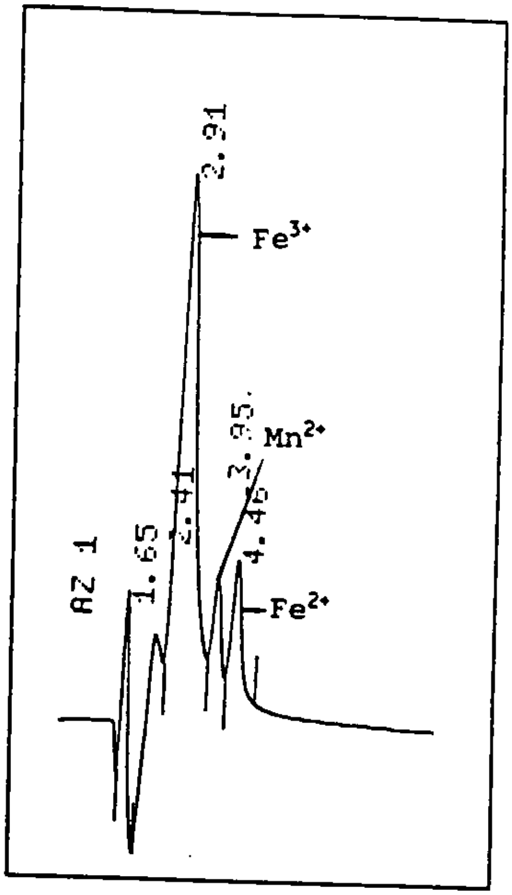

Figure A-2. Chromatogram of 165U/TDS/800/96 Analyzed 6/26/89

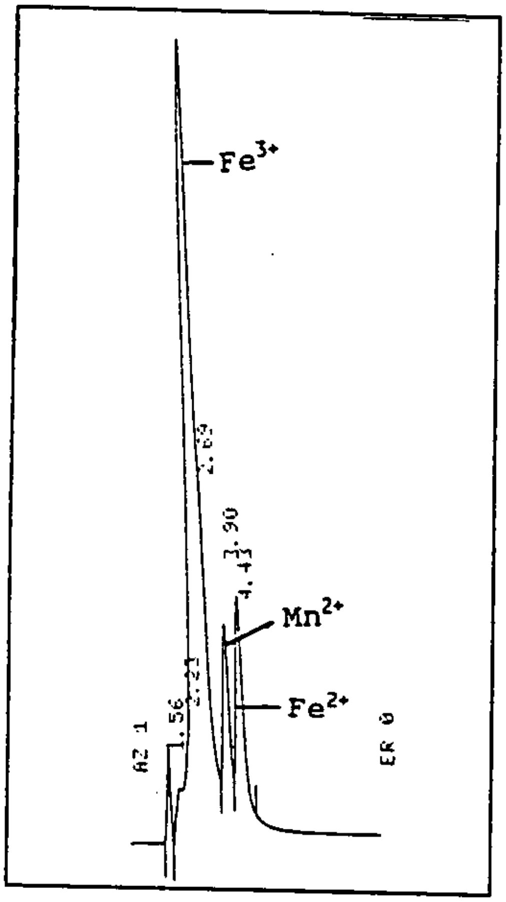

Figure A-3. Chromatogram of 165U/TDS/700/1.5 Analyzed 5/18/89

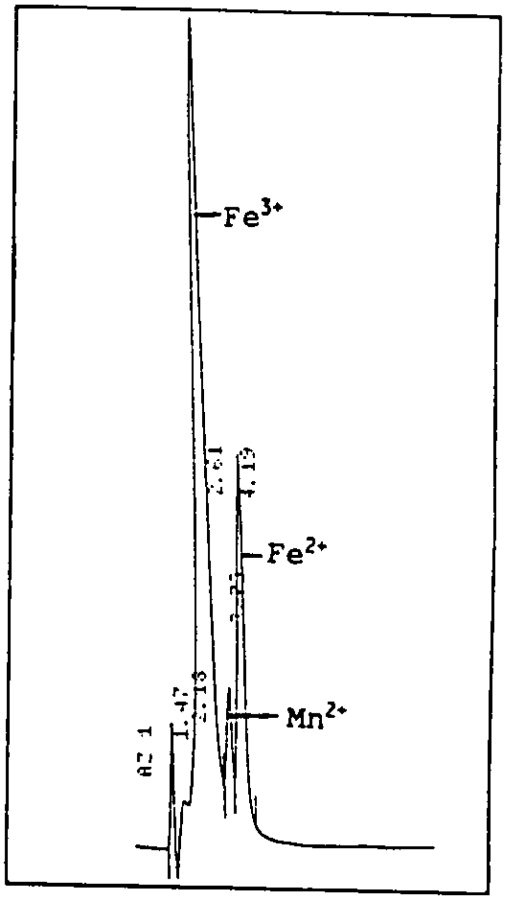

Figure A-4. Chromatogram of 165/TDS Analyzed 2/23/89

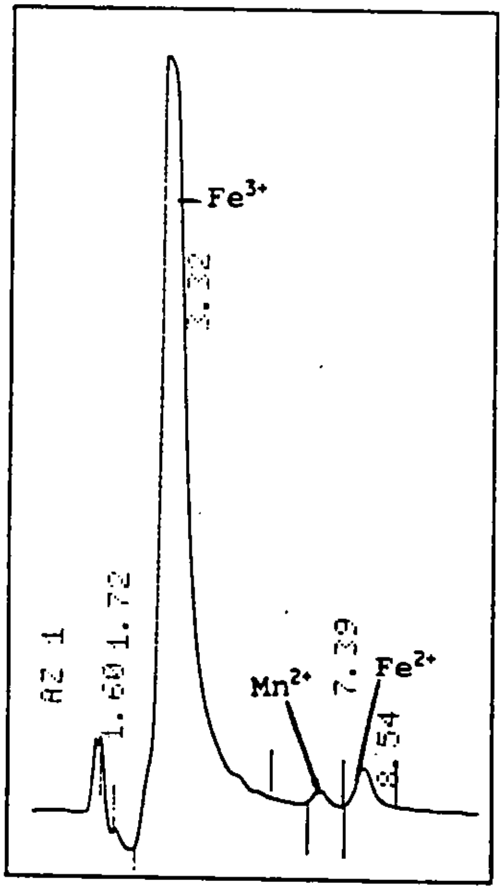

Figure A-5. Chromatogram of 165U/AL/800/3 Analyzed 7/26/88

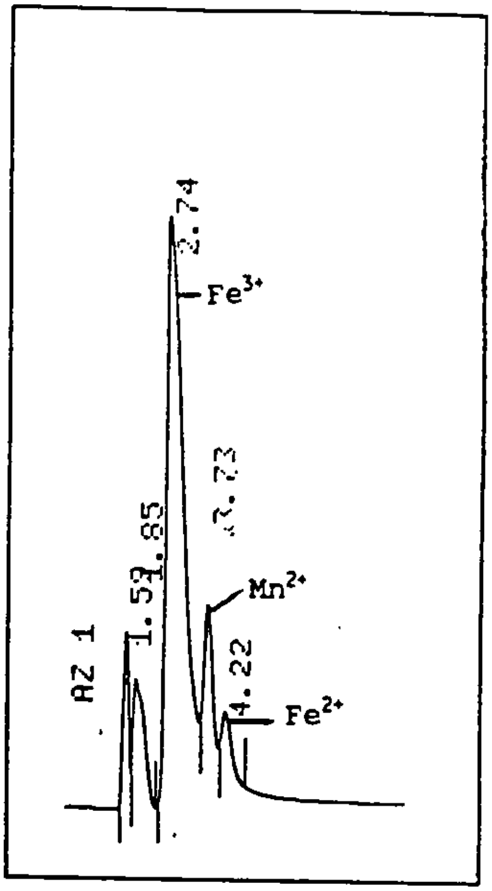

Figure A-6. Chromatogram of 165U/AL/700/24 Analyzed 6/22/89

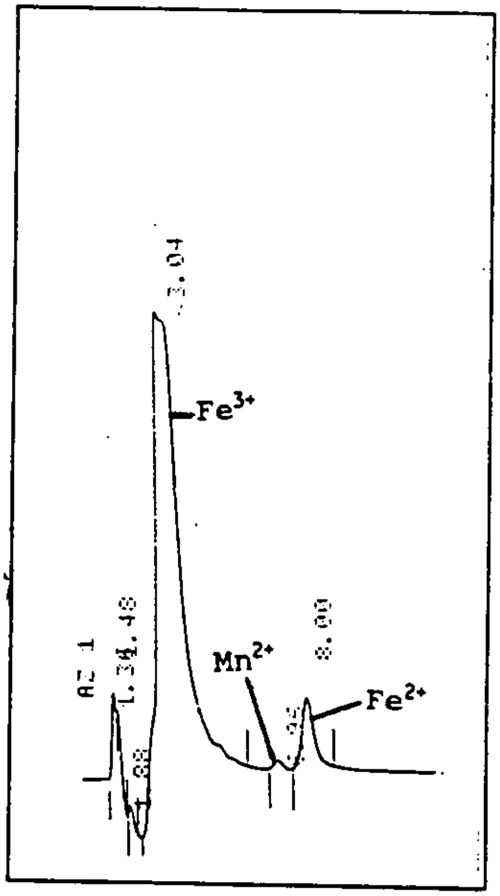

Figure A-7. Chromatogram of 165U/AL/700/12 Analyzed 7/28/88

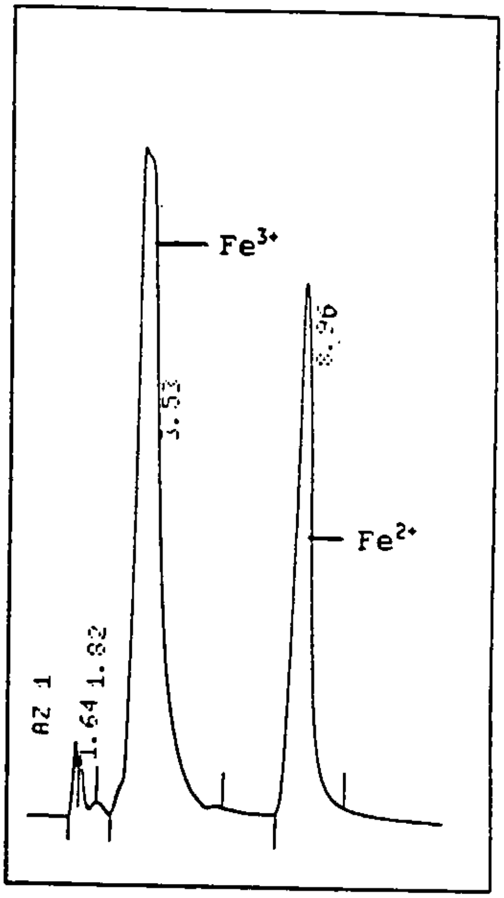

Figure A-8. Chromatogram of Fe_3O_4 + 1% PBA Analyzed 7/19/88

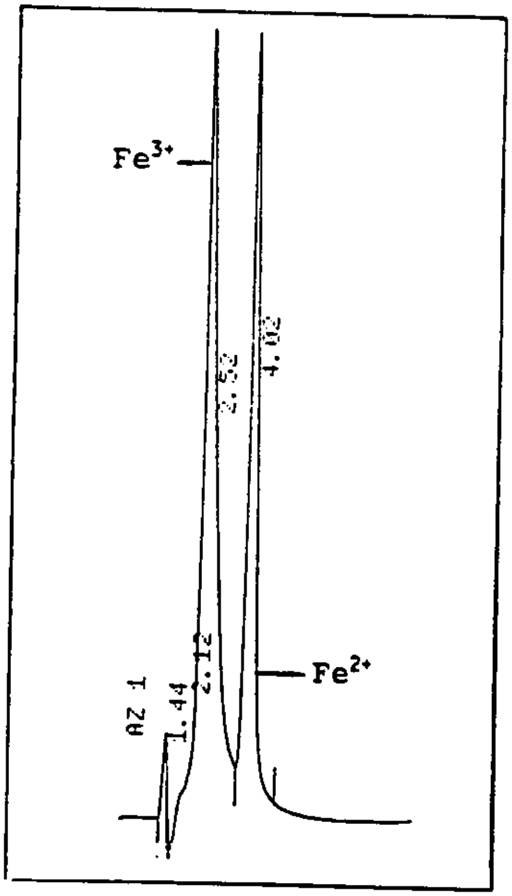

Figure A-9. Chromatogram of Fe_2O_3 + 5% NaCOOH Analyzed 3/29/89

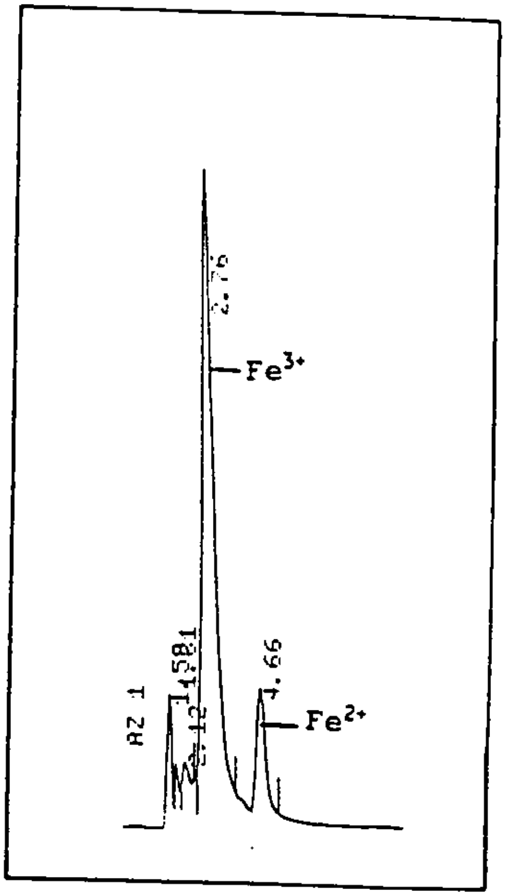

Figure A-10. Chromatogram of 5% Fe_2O_3 + 5% $Fe(COOH)_3$ Analyzed 6/05/89

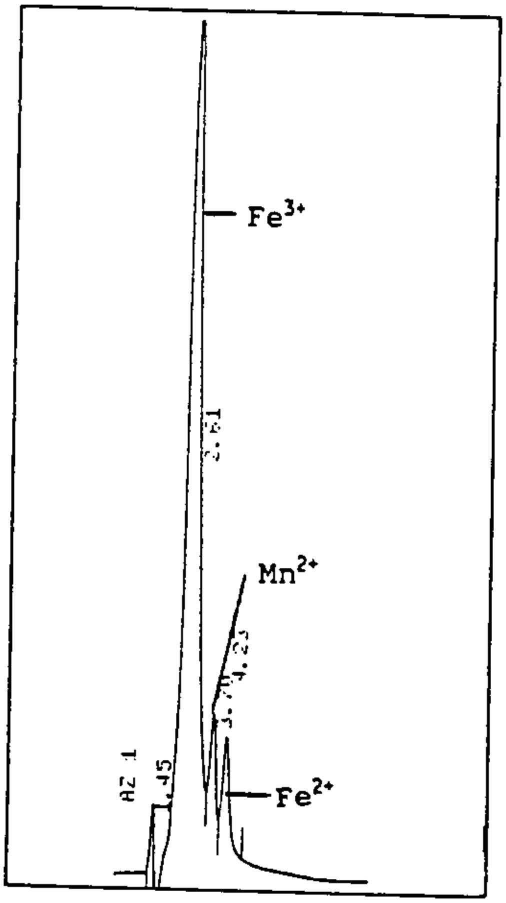

Figure A-11. Chromatogram of 2.0 U_2O_3 Analyzed 3/29/89

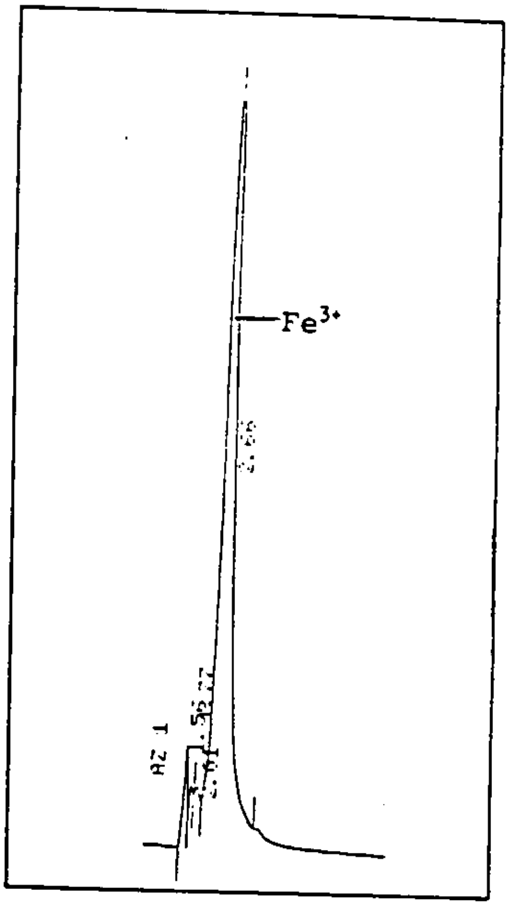

Figure A-12. Chromatogram of 165/FRIT/IRON/Cr_2O_3/GROUND Analyzed 5/18/89

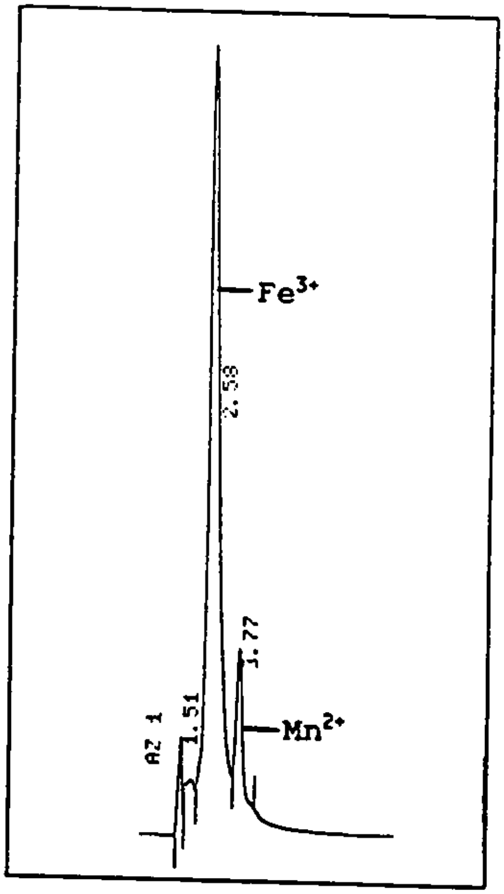

Figure A-13. Chromatogram of 165/FRIT/IRON/MnO/GROUND Analyzed 5/18/89

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23.	D. C. Beam, SRS, 773-A
24.	D. F. Bickford, SRS, 773-A
25.	S. L. Marra, SRS, 704-S
26.	J. R. Harbour, SRS, 773-43A
27.	J. F. Sproull, SRS, 704-S
28.	L. O. Westphal, HWVP at SRS, 704-S
29.	C. M. Jantzen, SRS, 773-A
30-50.	SRL Records, 773-A