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**MULTIMODAL SEPARATION OF ALKALI, ALKALINE EARTH,  
TRANSITION, POST-TRANSITION, LANTHANIDE, AND ACTINIDE  
METAL CATIONS IN WASTE SLUDGE (U)**

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A. C. Almon, W. F. Kinard, R. A. Dewberry, and N. E. Bibler

Westinghouse Savannah River Company  
Savannah River Site  
Aiken, South Carolina 29808

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# MULTIMODAL SEPARATION OF ALKALI, ALKALINE EARTH, TRANSITION, POST-TRANSITION, LANTHANIDE, AND ACTINIDE METAL CATIONS IN WASTE SLUDGE (U)

Amy C. Almon  
W. Frank Kinard  
Ray A. Dewberry  
Ned E. Bibler

Westinghouse Savannah River Company  
Savannah River Laboratory  
Aiken, South Carolina

## SUMMARY

An ion chromatographic method, which separates 36 different cations in a single chromatographic run, was developed to separate and analyze trace radionuclides present on high level radioactive waste samples. The method employs linear and step gradients and isocratic elution using four different eluents in six different eluent phases. The separation takes 45 minutes and has detection limits ranging from 0.1 ppm to 5.0 ppm, when using spectrophotometric detection for nonradioactive cations, depending on the sample matrix. The detection limits and relative standard deviation of the data are dependent upon the element and sample matrix. This method can be reliably performed in the laboratory if properly prepared samples are used. This study describes the applications, limitations, interferences, precision, and accuracy of this method.

Using this method, trace radionuclides, which are present in concentrations of only a few hundred disintegrations per minute per milliliter, can be separated and then analyzed by using liquid scintillation counting analysis and inductively coupled plasma mass spectrometry (ICP-MS). This paper will first describe the chromatographic separation as it was developed and applied to the analysis of aqueous samples with low ppm levels of nonradioactive cations. Next, the application of this method to the separation and analysis of high level waste tank samples will be discussed.

## INTRODUCTION

The Savannah River Laboratory is developing a method for the analysis of trace radionuclides in the high level radioactive wastes that will be immobilized and shipped to a federal repository. This method involves ion chromatographic separation of 36 elements including alkali, alkaline earth, transition, rare earth, noble metal, lanthanide, and actinide elements. The radionuclides of the separated species are then analyzed using liquid scintillation counting (LSC) and ICP-MS. The method is currently being tested and refined using sludge samples that are representative of the first feed going to the Defense Waste Processing Facility (DWPF) for vitrification.

Radionuclides that account for at least 0.01% of the total activity of the waste within the next 1100 years and have a half-life greater than 10 years must be reported.<sup>1</sup> These radionuclides and their half-lives are listed in Table 1.<sup>2</sup> Additionally, there are a number of other elements that interfere with detection either by ICP-MS or LSC. These nuclides are listed in tables 2 and 3 respectively. In total there are 39 elements in SRS waste samples, many of which must be separated from each other for analysis. The radionuclide inventory of all vitrified waste must be determined and reported before the glass canisters can be shipped offsite to a federal repository.

Current methods for determining reportable radionuclides involve the chemical separation of individual element and the subsequent radioisotope analysis using nuclear counting techniques.<sup>3</sup>

Coleman, et al. performed extensive work on the analysis of radioactive waste sludge using standard radiochemical methods.<sup>4</sup> Ion chromatographic methods exist to separate separate groups of elements from each other (alkali and alkaline earth cations,<sup>5,6</sup> transition metals,<sup>7</sup> lanthanide metals<sup>8,9</sup>), but no single method is currently available to effect a separation of elements, such as those listed in tables 1-3, that come from all regions of the periodic table. There is no ion chromatographic method available to effect a class separation of the actinides, although high performance liquid chromatography methods are available to separate some of the actinides from each other and selected transition metals.<sup>10</sup> The ion chromatographic method being developed simultaneously separates all of the elements, including those that cannot be determined by the existing wet chemical methods. This decreases the length of time required for analysis, personnel radiation and chemical exposure, and the amount of waste generated.

## EXPERIMENTAL SECTION

### Instrumentation

All chromatographic separations were performed using a Dionex Series 4500 Ion Chromatograph (Dionex Corporation, Sunnyvale, CA), which included the basic chromatography module, gradient pump, conductivity and spectrophotometric detectors, reagent delivery module, regenerant pump, post column reactor, and eluent degas module. The chromatograph was interfaced with a Spectra Physics Integrator for data acquisition, manipulation, and storage. The sample was injected using a Dionex 4000 psi injection valve which was plumed for a 500  $\mu$ L sample size. The large sample size (10 times larger than the standard injection size of 50  $\mu$ L) was necessary to recover enough of the separated sample for subsequent analysis by ICP-MS and LSC.

The columns used were a CG3 cation guard column and CS3 cation exchange column—both from Dionex. They were conditioned for at least 30 minutes at the start of each day's experiments and at least 10 minutes between each run by flowing fresh eluent through them.

For colorimetric detection of nonradioactive standards, a Dionex reagent delivery module and post-column membrane reactor were used to introduce the colorimetric complexing agent—0.15 mM Arsenazo III [2,2'-(1,8-dihydroxy-3,6-disulphonaphthalene-2,7-bisazo)bisbenzenearsonic acid, Aldrich]—into the column effluent. Nitrogen was used to pressurize the delivery module at 40 psi to deliver the Arsenazo at a flow rate of 1 mL/minute. A Dionex variable wavelength detector, set at 620 nm, was used as the detector.

For conductivity detection of nonradioactive standards, a Dionex basic conductivity module and conductivity cell were used. The column effluent was passed through a suppressor membrane, which converts the eluent to water by ion exchange with a regenerant solution running counter current to the eluent stream. This regenerant solution was 200 mM tetrabutylammonium hydroxide at a flow rate of 3mL/minute.

Radioactive samples were separated chromatographically into elemental fractions. These fractions were collected and analyzed using ICP-MS, LSC, and gamma spectroscopic analysis. ICP-MS measurements were done on a VG ICP-MS (VG/Fisons, Chicago, IL). Liquid scintillation measurements (alpha and beta emission data) were done using a Packard 2250CA Tricarb Liquid Scintillation Analyzer (Packard Instrument Co., Downers Grove, IL). Gamma spectroscopy was done using a germanium gamma detector (EG&G Ortec).

### Reagents

All chemicals and reagents met the applicable specifications of the Committee on Analytical Reagents of the American Chemical Society. Eluents and regenerant solutions were prepared from

18 MW deionized water that had been passed through a Millipore system for purification. The eluent reservoirs were degassed and kept under a reservoir of 20 psi nitrogen. Unless noted all reagents were used as received from the manufacturer. The liquid scintillation cocktail used was Optifluor (Packard, #6013425).

Nonradioactive ion chromatography cation standards were prepared by dilution of 1000 ppm stock standard solutions, which were procured from Spex Industries and traceable to the National Institute of Standards Technology. These diluted standard solutions were prepared fresh for each experiment.

### **Procedure**

The separation was achieved by elution off of a low capacity ion exchange resin using the separation program listed in table 4. The sample was injected at 0.5 minutes and the program was allowed to run for 50 minutes at a flow rate of 1 mL/minute.

During the chromatographic separation of nonradioactive standards, the alkali and alkaline earth cations were detected using conductivity detection; all other species were detected by spectrophotometric detection. The radionuclides separated from the waste solutions were collected by hand in 1 mL (1 minute) fractions and subsequently analyzed using ICP-MS and LSC. For LSC the fractions were collected into vials containing 14 mL of Optifluor; samples for ICP-MS analyses were collected and diluted to 5 mL, the volume required for analysis.

## **DISCUSSION**

### **Principle of the Method and Experimental Details**

The chromatogram for a standard solution containing 10 ppm of the nonradioactive elements from Table 5 using spectrophotometric detection is shown in Figure 1 (cesium and strontium do not complex with Arsenazo so no peak is seen; these elements must be detected by conductivity detection). The location and intensity of the peak are dependent upon the identity and concentration of the eluent solution.

The first elution step involves gradient elution of +1 cations. Negative and neutral species are unretained by the column stationary phase and elute in the column void volume. The next step is the isocratic elution of +2 cations, including the alkaline earths, some transition metals, and uranium in the form of the uranyl complex. The column is then conditioned for 5 minutes with  $\alpha$ -HIBA which effects linear gradient elution of transition metals and metal complexes;  $\alpha$ -HIBA is an organic ligand which complexes with the remaining transition, lanthanide, and actinide species.

Complexation with  $\alpha$ -HIBA by lanthanide and actinide species is dependent on atomic number; the strength of complexation is inversely proportional to atomic number. This differentiates the interaction of the lanthanide and actinide species with the column stationary phase and allows them to be separated from each other. Without the  $\alpha$ -HIBA, all the lanthanides would elute together in a single fraction as would the actinides.

The lanthanides are eluted first under mildly acidic conditions while the actinides are more strongly retained and require much stronger eluent conditions to come off the column. The ion chromatogram of a nonradioactive standard containing 10 ppm of all lanthanides (excluding promethium) is shown in Figure 2. The actinides are so strongly retained on the column that they require an acid concentration of greater than 1.0M to elute. All actinides, except thorium and uranium, remain trapped on the column under weaker eluent conditions.

Silver and palladium are precipitated by the chloride in the eluent and cannot be determined using this method.

### **Preparation of a Standard Curve**

For nonradioactive elemental analyses, standard curves are prepared by plotting the concentration of a known standard versus the peak height in either conductivity or absorbance units. The standard curves for each of the elements were made by the ion chromatograph using one standard and one blank and are stored in the instrument's memory. These calibration curves are verified by running a check standard each time the analysis is run.

### **Length of Time Required for Analysis**

The length of time for analysis depends on the elution times for the individual cation. After a sample has been properly prepared, the chromatographic run to elute all 36 cations takes 45 minutes.

### **Accuracy and Precision of Elemental Chromatographic Measurements**

Table 5 contains the data from replicate measurements of 1, 5, and 10 ppm nonradioactive elemental standards.<sup>4</sup> The accuracy and precision of the measurements decrease slightly with increasing retention time but remain sufficient for routine analyses (within +/-5% RSD).

The quality of the measurements depends on preparing an accurate standard curve. The validity of this curve should be verified before each analysis by running an NIST standard.

### **ANALYSIS OF WASTE TANK SAMPLES**

As stated earlier, this chromatographic method was developed to be used in the analysis of trace radionuclides in high level waste tank samples. These samples are particularly difficult to analyze because of the many different species present in the widely differing concentrations and the high level of radioactivity present. The samples are in the form of caustic sludges that must be dissolved by peroxide fusion or aqua regia prior to analysis. In these dissolution processes, 0.25 grams are dissolved in a shielded cell and diluted to 250 mL; only 20 mL of this dilution is removed from the cell. This yields a sample which has approximately  $10^6$  disintegrations per minute per mL in beta/gamma activity and can be directly handled in a radioactive hood.

Analysis of the trace radionuclides present in these samples require separate identification of different isotopes of the same species (for example, differentiation between Sr-90 and Sr-89), which is not possible with chromatographic analysis alone. Therefore the separated elemental fractions were collected and analyzed by ICP-MS or radioactive counting.

Qualitative identification of the separated isotopes was primarily done through ICP-MS by mass peak analysis. Thirty-six elements were separated from the waste samples and qualitatively identified; these are listed in Table 6. Of the 36 there were 6 isobaric pairs that required separation for identification by ICP-MS. These are denoted by an asterisk in Table 6. The ICP-MS data for the separated sample are displayed graphically in Figure 3. After the separation was complete, the column was flushed with 2 M HCl to remove any remaining species that may have been retained by the column. This wash was counted by LSC and no radionuclides were found.

Liquid scintillation counting or gamma counting was used to verify ICP-MS results and to determine radioisotopes with a high specific activity that were present at atomic concentrations too low to be detected by ICP-MS. Quantitative analysis of the samples that use the counting results in terms of Ci/gram of sludge or glass must take into account the sample dilutions, counting efficiency of the detector, and emission energy of the radioisotope. This work is in progress.

### **Problems and Interferences with Waste Samples**

The major difficulty with this analysis is the nature of the waste samples. High level nuclear waste contains many cationic and anionic species at widely differing concentrations, including chemicals from plant separation processes, laboratory waste, fission products, neutron activation products, uranium, plutonium, and other actinides. The sludge samples analyzed in this experiment contained approximately 85% of the elements in the periodic table. In many cases it was difficult to resolve all the peaks from each other. The multiple methods of data analysis permitted quantification of overlapping peaks (for example, the uranium elutes on the tail of the strontium peak). Strontium is quantified by LSC and uranium by ICP-MS so the data can be resolved.

The samples contained concentrations of iron and aluminum which were  $10^2$  to  $10^3$  times higher than the other constituents present.<sup>4</sup> The high concentrations of these two elements prevented the trace constituents from completely interacting with the column stationary phase and carried minor amounts of several elements with it; this effect can be seen in Figure 4. The iron elemental fraction contains traces of Ba, Zr, Ni, Mo, Pb, and Th. To counteract this effect, nonradioactive carriers (10  $\mu$ L of the 1000 ppm standards of stable elemental isotopes per 1 mL of sample) were added to the sample. This enabled the trace constituents to more effectively compete with the column surface, and the carry through effect of the iron and aluminum was diminished.

For radionuclide analysis, ion chromatography was used only to separate the cations into discreet fractions for subsequent analysis by liquid scintillation counting and ICP-MS. The cations were collected in 1 mL fractions. Since only a 50  $\mu$ L sample volume had been injected onto the column, this represented a 20-fold dilution which prevented detection of most of the trace constituents. To compensate for this, the injection valve was replumbed with a 500  $\mu$ L injection loop, this increasing the amount of sample injected onto the column and then recovered by 10-fold. Comparison of chromatographic runs using 1-ppm nonradioactive standard solutions showed no effect in precision or accuracy of the data or the effectiveness of the separation.

### **CONCLUSION**

In one chromatographic run, the ion chromatographic method can separate many cations from all areas of the periodic table on the same column. The method can be used for both radioactive and nonradioactive samples and can be used to analyze some waste samples that are very difficult to analyze because of the wide variety of species in varying concentrations found in them. As with any chromatographic separation, high concentrations of elements in the sample will saturate the column stationary phase and must be removed from the sample prior to analysis. This method appears applicable to the analysis of trace radionuclides which can be separated and analyzed using ICP-MS, liquid scintillation counting, and gamma counting. The direct interface of an ion

chromatograph with an ICP-MS using a thermospray coupling device is now being investigated. This would enable analyses to be performed more rapidly and accurately with less radiation exposure to workers.

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**Table 1. Radionuclides Required for Waste Compliance**

Nuclide	Half Life (Years)
Ni-59	$8 \times 10^4$
Ni-63	92
Se-79*	$7 \times 10^4$
Sr-90	28
Nb-93m	12
Zr-93*	$1 \times 10^6$
Tc-99	$2.1 \times 10^5$
Pd-107*	$7 \times 10^6$
Sn-126	$1 \times 10^5$
Cs-135*	$2 \times 10^6$
Cs-137	30
Sm-151*	93
Th-230*	80
U-234	$2 \times 10^5$
U-238	$5 \times 10^9$
Np-237	$2 \times 10^6$
Pu-238	89
Pu-239	$2 \times 10^4$
Pu-240	$7 \times 10^3$
Pu-241	13
Pu-242	$4 \times 10^5$
Am-241	$5 \times 10^2$
Am-243	$8 \times 10^3$
Cm-244	18

\*Cannot be determined in this sample matrix using standard radiochemical method.

**Table 2. Interfering Radioisotopes - These emit levels of activity which interfere with detection of reportable radionuclides (listed in Table 1).**

Nuclide	Half Life (Years)
Y-90	2.7 days
Ru-106	1.02
Sb-125	2.73
Cs-134	2.06
Ce-144	0.8
Pm-147	2.6
Er-154	8.8
Eu-155	5
Co-60	5
Am-241	433



**Table 3.** Isobaric Interferences - These have the same mass as a reportable nuclide so interfere with ICP-MS detection.

Element	Interference
Pd-107	Ag-107
Sn-126	Te-126
Cs-135	Ba-135
Sm-151	Eu-151
U-238	Pu-238
Ni-59	Co-59
Ni-63	Cu-63
Se-79	Br-79
Sr-90	Zr-90
Zr-93	Nb-93
Tc-99	Ru-99

**Table 4.** Separation Program for Cation Elution. E1 (Eluant 1) is 18 MΩ deionized water, E2 is 2 M HCl, E3 is 0.6 M HCl, 0.1 M diaminopropionic acid (DAP.HCl), and E4 is 0.4 M α-hydroxyisobutyric acid (α-HIBA). Flow rate: 1 mL/min.; columns: CS3, CG3; sample injection at 0.5 min.

Time (min)	E1	E2	E3	E4
0.0	98	1	1	0
0.5	98	1	1	0
5.0	93	0	7	0
12.0	93	0	7	0
12.1	0	0	0	100
16.0	0	0	0	100
16.1	70	0	25	5
30.0	70	0	25	5
40.0	0	80	15	5

**Table 5.** Replicate Chromatographic Measurements of 10 ppm NIST Standards Using Spectrophotometric Detection<sup>a</sup> at 620 nm with Arsenazo. Elution program is listed in Table 4.

Element	#1	#2	#3	#4	#5	Mean	St. Dev	RSD (%)
Cs	10.15	10.17	10.10	9.99	9.90	10.06	0.114	1.1
Sr	10.00	9.91	9.97	10.15	10.10	10.03	0.098	1.0
Ba	9.91	9.85	9.99	10.04	10.10	9.96	0.105	1.1
Y	10.43	9.93	9.90	10.00	9.78	10.01	0.249	2.5
Zr	9.45	9.75	9.79	10.10	10.00	9.82	0.252	2.6
Nb	10.00	10.17	10.00	10.10	9.94	10.04	0.092	0.9
Fe	10.10	10.07	10.11	10.13	10.13	10.11	0.025	0.2
Ru	9.98	9.91	9.87	10.12	10.01	9.98	0.097	0.1
Co	10.03	10.00	10.15	10.17	10.20	10.11	0.089	0.9
Rh	9.98	9.91	10.07	10.53	10.12	10.12	0.240	2.3
Ni	10.12	10.10	10.10	10.00	10.03	10.07	0.053	0.5
Pd	*							
Cu	9.84	10.21	10.00	10.05	9.99	10.02	0.133	1.3
Ag	*							
Al	9.43	10.11	9.38	9.97	9.94	9.77	0.336	3.5
Sn	8.91	10.25	9.47	8.49	8.93	9.21	0.677	7.4
Se	*							
La	10.31	9.92	9.94	10.66	10.74	10.31	0.386	3.7
Ce	10.00	10.00	10.23	10.05	9.73	10.00	0.179	1.8
Nd	9.70	9.79	10.73	10.14	9.54	9.94	0.525	5.5
Pm	9.88	10.12	10.00	9.73	9.55	9.86	0.224	2.3
Sm	10.15	10.05	9.84	10.27	10.01	10.06	0.161	1.6
Eu	9.98	10.10	9.23	10.11	10.43	9.97	0.446	4.5
Dy	10.00	9.38	10.19	10.15	9.73	9.89	0.337	3.4
Th	10.77	9.77	9.99	10.00	10.12	10.13	0.379	3.7
U	10.05	10.10	10.34	9.28	10.00	9.95	0.399	4.0

\* Unable to be determined using this method

<sup>a</sup> Cs and Sr determined by conductivity detection

**Table 6. Radionuclides Identified in SRS Sludge by IC Separation with ICP-MS and Radiochemical Counting Techniques**

Radionuclide	Major IC Fraction	ICP-MS	Detection Method(s)		
			alpha	beta	gamma
Tc-99	1	x		x	
Se-79	1			x	
Ru-106	2	x			x
Cs-134 <sup>a</sup>	5			x	
Cs-135	5	x			
Cs-137	5	x		x	
Ni-59	9	x			
Ni-63	9			x	
Co-60a	10	x			x
Sr-90	15	x		x	
U-234	16	x			
U-238	16	x			
Zr-93	22			x	
Th-230	24	x			
Sn-126	26			x	
Ba-137 <sup>a</sup>	27	x			x
Y-90 <sup>a</sup>	29			x	
Eu-154	33	x			x
Eu-155	33	x			x
Sm-151	34			x	
Pm-147 <sup>a</sup>	35			x	
Ce-144 <sup>a</sup>	38	x			x
Cm-244	42	x	x		
Am-241	43		x		x
Am-243	43		x		
Pu-238	44		x		
Pu-239	44	x	x		
Pu-240	44	x			
Pu-241	44			x	
Pu-242	44	x			
Np-237	45	x	x		

a Elements not necessary for Waste Compliance Reporting but which must be separated because of isobaric or radioactive interferences.

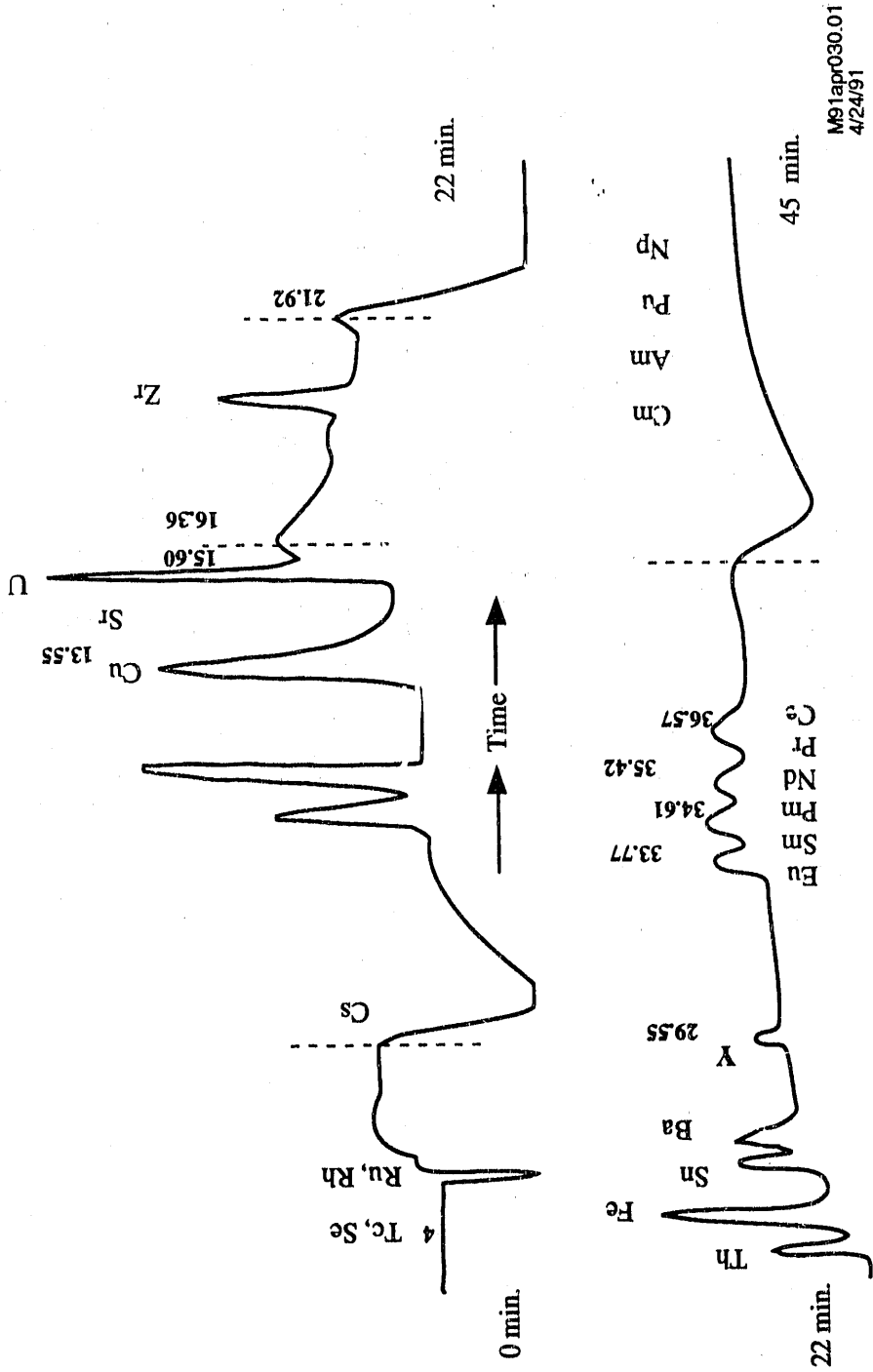
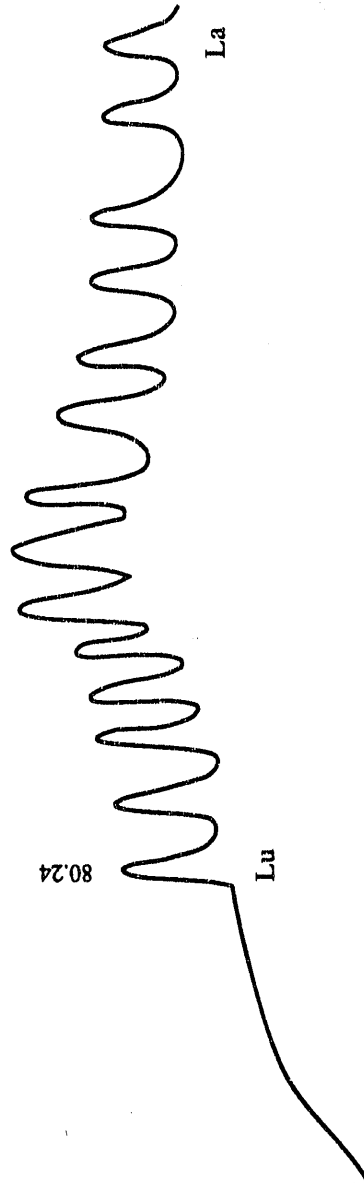
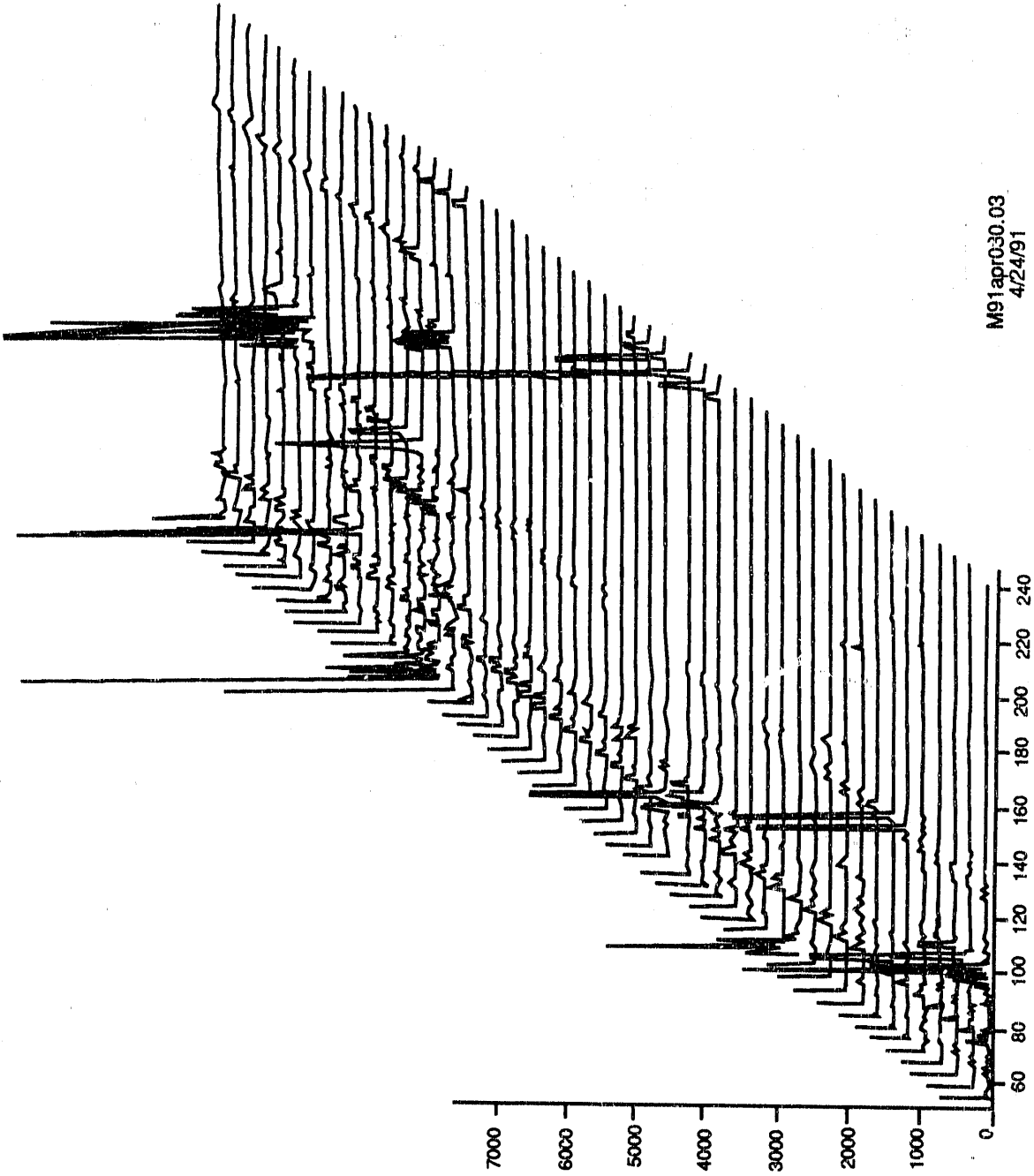


Figure 1: Chromatogram of Non-Radioactive Standard Using Spectrophotometric Detection.



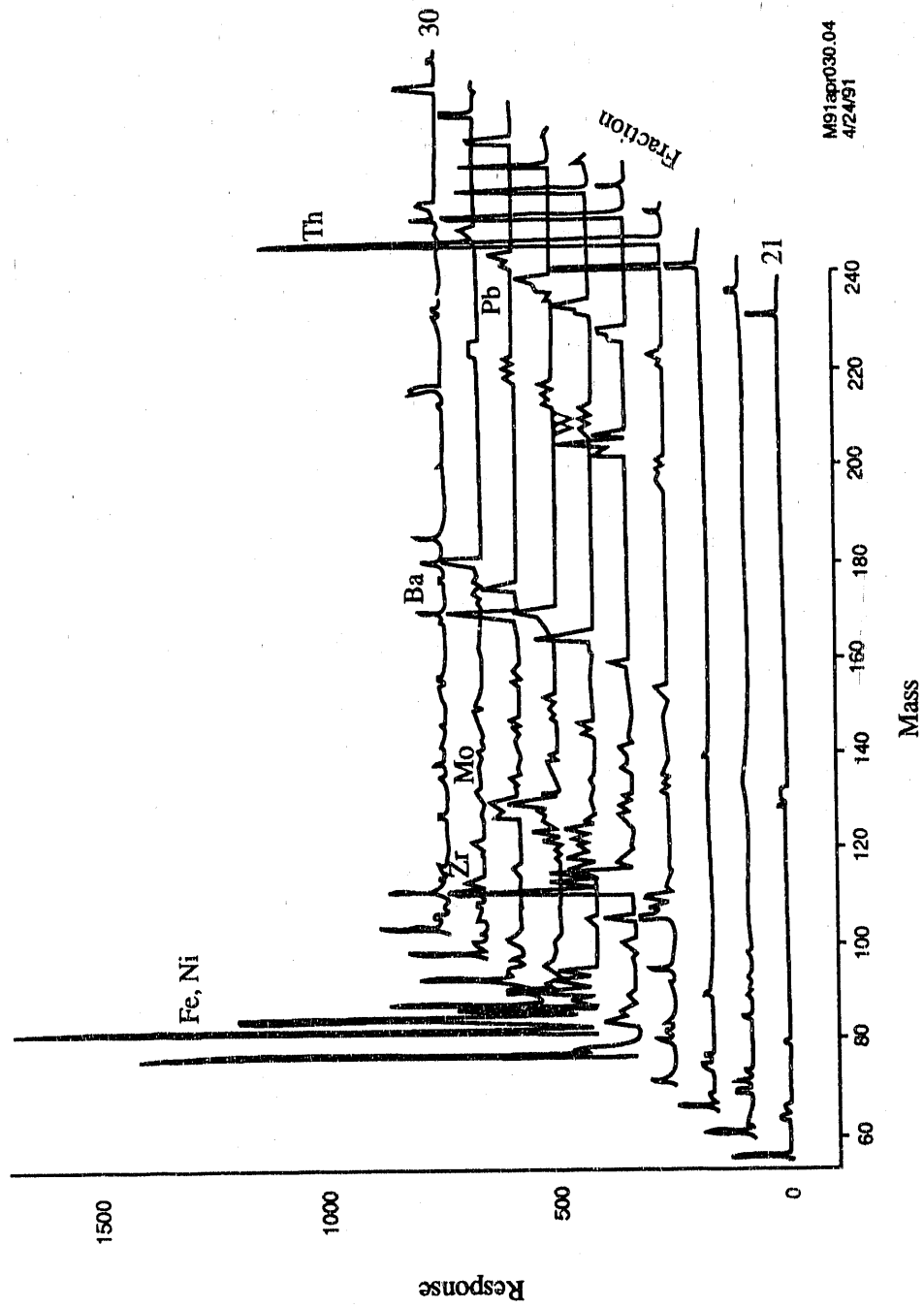
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Figure 2: Ion Chromatogram of 10ppm Lanthanide Standard.



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Figure 3: ICP/MS Scans of IC Fractions



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Figure 4: Effect of High Iron Concentration in Waste Samples.

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