

MEASUREMENT OF RADIONUCLIDES USING ION CHROMATOGRAPHY AND  
FLOW-CELL SCINTILLATION COUNTING WITH PULSE SHAPE DISCRIMINATION

FINAL REPORT for TASK 4

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Period of Performance

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## PROJECT SUMMARY

Radiological characterization and monitoring is an important component of environmental management activities throughout the Department of Energy complex. Gamma-ray spectroscopy is the technology most often used for the detection of radionuclides. However, radionuclides which cannot easily be detected by gamma-ray spectroscopy, such as pure beta emitters and transuranics, pose special problems because their quantification generally requires labor intensive radiochemical separations procedures that are time consuming and impractical for field applications. This project focused on a technology for measuring transuranics and pure beta emitters relatively quickly and has the potential of being field deployable. The technology combines ion exchange liquid chromatography and on-line alpha/beta pulse shape discriminating scintillation counting to produce simultaneous alpha and beta chromatograms.

The basic instrumentation upon which the project was based was purchased in the early 1990's. In its original commercial form, the instrumentation was capable of separating select activation/fission products in ionic forms from relatively pure aqueous samples. We subsequently developed the capability of separating and detecting actinides (thorium, uranium, neptunium, plutonium, americium, and curium) in less than 30 minutes (Reboul, 1993) and realized that the potential time savings over traditional radiochemical methods for isolating some of these radionuclides was significant. However, at that time, the technique had only been used for radionuclide concentrations that were considerably above environmental levels and for aqueous samples of relatively high chemical purity. For the technique to be useful in environmental applications, development work was needed in lowering detection limits; to be useful in applications involving non-aqueous matrices such as soils and sludges or complex aqueous matrices such as those encountered in waste samples, development work was needed in sample preparation and processing.

The general goal of this project was to address the issues mentioned above, and in so doing transform an interesting laboratory technique of limited applicability into a robust field instrument suitable for environmental restoration and waste management applications. The project consisted of the following tasks: (1) development of a low background, flow-cell detector, (2) identification of sample chemical and radiological interferences, (3) development of protocols for processing waste and/or environmental samples, and (4) integration and testing of the prototype system. The scope of work

associated with these tasks has been completed and the report for Tasks 1-3 was submitted previously. Presented here are the results for Task 4.

Based on the successes achieved in Tasks 1, 2, and 3, FETC exercised the contract option for Task 4, the goal of which was to integrate the sample processing and flow-cell detection components and develop a bench scale laboratory prototype (Task 4). This goal was achieved through three sub-tasks: (4.1) integration of the sample processing, chromatographic separation, and radiation detection components into a prototype bench-scale system, (4.2) perform analyses on the environmental water and waste tank surrogates which contain targeted radionuclides and (4.3) perform analyses on actual environmental water and waste tank samples. Specific accomplishments of Task 4 under these sub-tasks were: (1) completion of a digital pulse shape discrimination system which not only significantly reduces the hardware requirements but also is more user friendly than the analog system developed under Task 1; (2) characterization of the granular Parylene C coated CsI:TI scintillator, which is the key component of the pulse shape discriminating flow-cell detector, (3) identification and quantification of additional chemical interferences that may be important in certain applications; (4) integration of the sample processing, chromatography, and detection components of the system into a single unit; and (5) testing of the integrated system for a group of surrogate and real samples that are representative of the spectrum of matrices encountered at DOE sites.

Based on the results of Task 4, it is concluded that the system, with some limitations, is capable of analyzing alpha and beta emitters in samples that are representative of many of those encountered in the DOE complex. Based on analyses of both surrogate samples and actual samples from DOE sites, radionuclide concentrations obtained using this technology were generally within 20% of those obtained using standard laboratory protocols. In addition, analysis times were much less (by a factor of 3-5 for liquid wastes). Estimates of the capabilities of the system, in terms of analysis time and minimum detectable concentration, are presented in Table 10.

The principal advantages of the technology are (1) its ability to analyze a mixture of alpha and beta emitters in a relatively short period of time, much less than that required by traditional techniques, and (2) its relatively small size makes it amenable to field deployment. This translates into both a cost advantage and an operational advantage, especially in field applications. The limitation is that modifications of the sample processing protocol may be required for complex matrices such as soils. For

example, we found that our sample processing protocol worked well for a specific soil at SRS (Blanton series) but would need to be modified to reduce interferences in basalt from INEEL.

The original goal of this project was to develop a technology for the rapid analysis of waste samples and environmental media containing multiple non-gamma emitting radionuclides. This goal was clearly achieved for liquid waste samples in which radionuclide concentrations on the order of 100's of kBq/m<sup>3</sup> (1000's of pCi/L) can be analyzed in a few hours. For complex matrices such as soil or for typical environmental concentrations, the analysis time can extend to a couple of days. Although this is not rapid compared to the few hours required for liquid waste samples, it is considerably quicker than typical analysis times using current techniques. The next step in the path toward commercialization could be a site demonstration involving liquid waste samples such as those from the laboratory drain tank at SRTC or supernatant from high level waste tanks at SRS, ORNL or Hanford.

## ACKNOWLEDGEMENTS

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## INTRODUCTION

Radiological characterization and monitoring needs in support of environmental restoration and waste management activities at Department of Energy (DOE) facilities are extensive and diverse. Radionuclides which cannot easily be detected by gamma-ray spectroscopy such as pure beta emitters (e.g.  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , and  $^{63}\text{Ni}$ ) and actinides (e.g.  $^{232}\text{Th}$ ,  $^{235,238}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238,239,240,241}\text{Pu}$ ,  $^{241}\text{Am}$ ) pose special problems because their quantification generally requires labor intensive radiochemical separations procedures that are time consuming and generally not practical for field based measurements. This project addressed a generic need expressed in a DOE solicitation for “field-deployable instrumentation for the determination of isotopes and isobars” (DOE, 1993). Site specific needs have been identified at the Savannah River Site, Hanford Site, Los Alamos National Laboratory, and Idaho National Engineering and Environmental Laboratory (<http://em-Needs.em.doe.gov/1999/EMNeeds/SnDt.asp?NeedID=598&NeedCode=AL-09-01-13-DD>). Our approach, which is illustrated in Figure 1, combines liquid chromatography and flow cell scintillation counting with alpha/beta pulse shape discrimination.

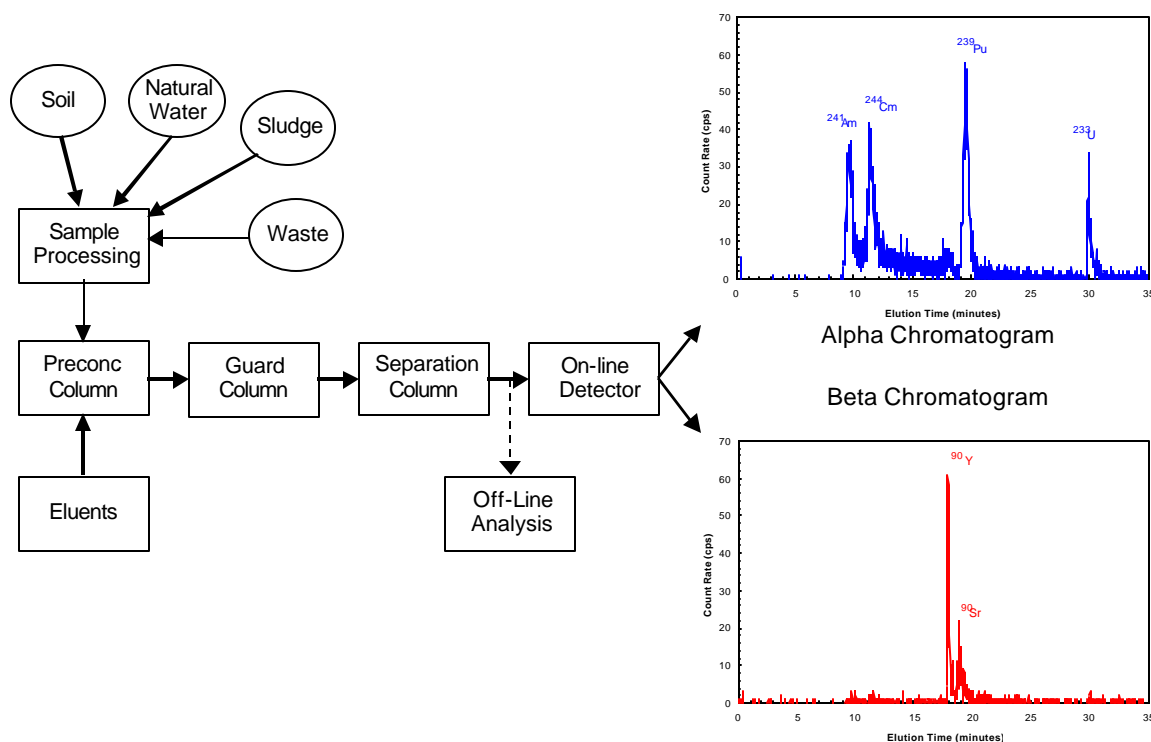


Figure 1. Simultaneous measurement of alpha and beta emitters by ion chromatography and the CsI:TI flow-cell pulse shape discrimination system of a groundwater sample spiked with radioactivity.



Samples are processed to yield an aqueous solution with the radionuclides in an ionic form. The ions are concentrated on an ion exchange column and subsequently removed to a separation column with chemical eluents. Through the selection and sequencing of the eluents, chromatographic separation of the constituents is achieved. A chromatogram of radioactive constituents is then produced by an on-line scintillation counter which yields separate chromatograms for alpha emitters and beta emitters through pulse shape discrimination. For low level applications, fractions containing selected radionuclides can be collected and counted off-line. Radionuclides are identified through characteristic elution times, and their concentrations are determined from the integrated counts under the peak of interest, the detection efficiency, the yield of the sample processing procedure, and the volume or mass of the original sample.

## TECHNICAL BACKGROUND

Below is a synopsis of the results from the Base Phase (Tasks 1-3) needed to understand the results of the Task 4. Additional information of the results of the base phase can be found in the final report for the base phase [Fjeld et al., 1998] and the publications listed in Appendix A.

### *Detector Development – Task 1*

An analog pulse shape discriminating electronic system was fabricated and used to evaluate heterogeneous and homogeneous flow-cell detectors and their respective scintillation materials. Granular CsI:TI coated with a hydrophobic polymer (Parylene C) was selected for use with the heterogeneous flow-cell detector. Modified Monoflow 5 and HiSafe 3 liquid scintillators were selected for use with the homogeneous flow-cell detector. Good alpha and beta particle discrimination was achieved for HiSafe 3 liquid scintillator with a 2.5% sample loading (Figure 2). Presented in Figure 3 is an illustrative chromatogram for step inputs of  $^{233}\text{U}$  and  $^{90}\text{Sr}$  as measured by the homogeneous flow-cell detection system for a 10% sample loading in HiSafe 3 liquid scintillation cocktail. Both heterogeneous and homogeneous detectors met the project goals for minimum detectable activity (Table 1), although a limitation of the CsI:TI based cell is a finite lifetime due to dissolution of the scintillation particles by water penetrating the polymer coating. Dual parameter (pulse shape and pulse height) analysis, which can reduce the minimum detectable activity (MDA) through reduced spillover, was successfully demonstrated for the flow-cell detectors. A typical dual parameter pulse shape discriminating spectrum for the CsI:TI heterogeneous flow-cell as measured by the analog data acquisition system is displayed in Figure 4. In addition, development of a state-of-the-art digital data acquisition system was initiated in Task 1 as a potential alternative to the conventional analog system. The digital system was subsequently completed and tested in Task 4.

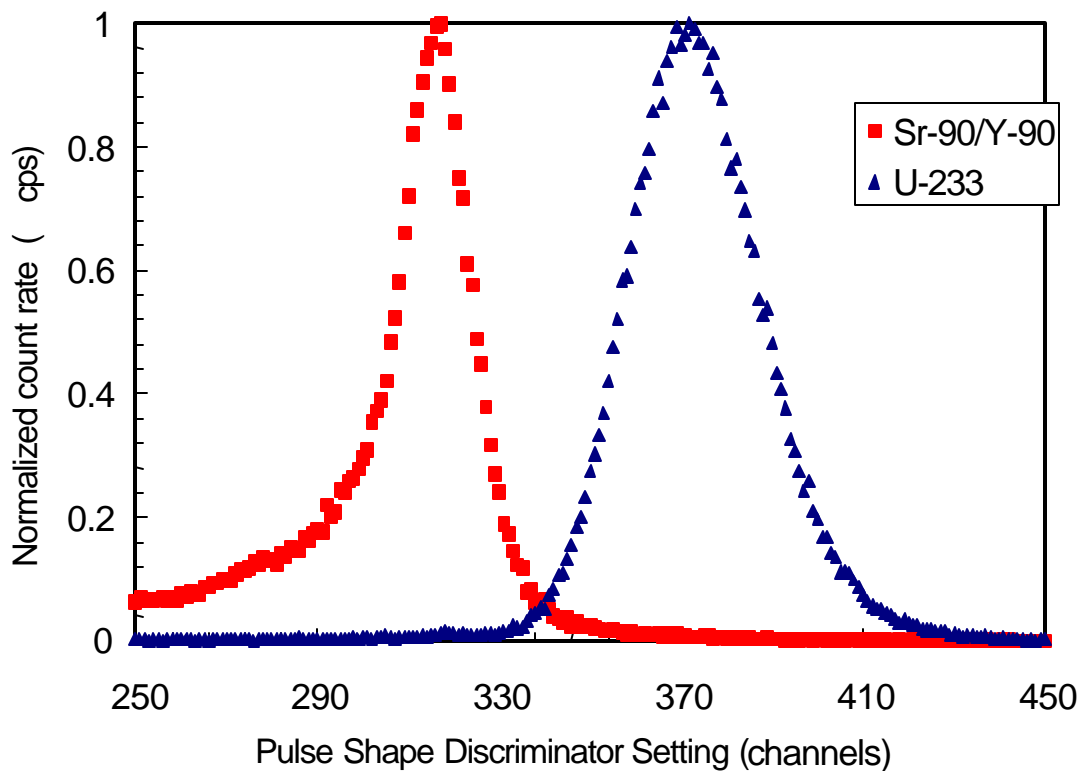


Figure 2. A typical pulse shape spectrum of HiSafe 3 at a 2.5% sample loading.

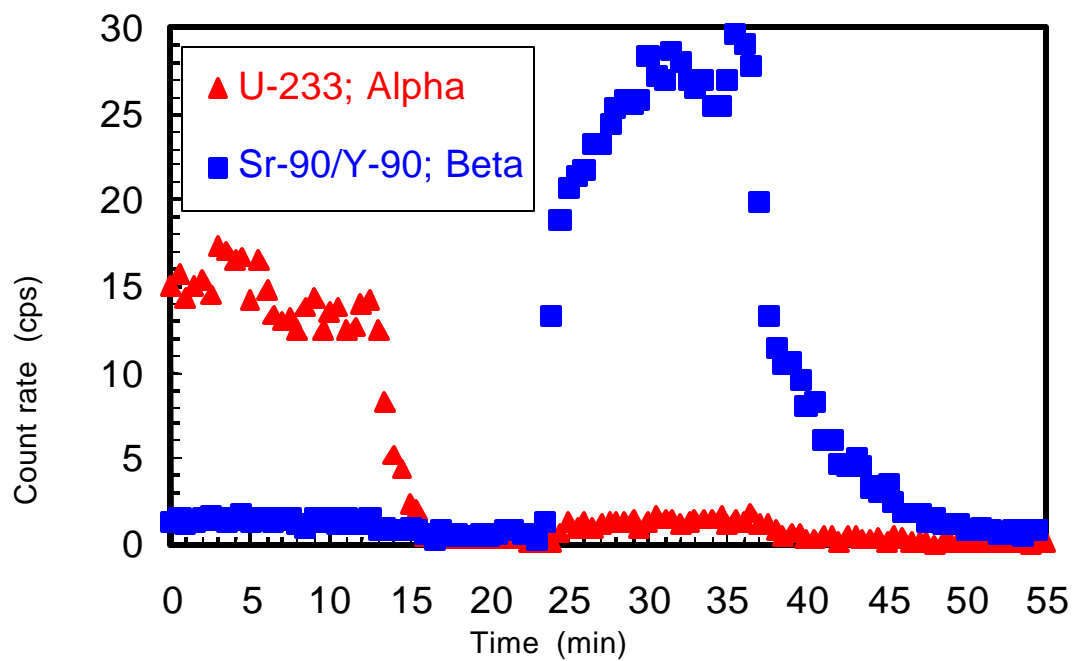


Figure 3. Flow test with HiSafe 3 for a 10% sample loading. The alpha emitter was  $^{233}\text{U}$  and the beta emitter was  $^{90}\text{Sr}/^{90}\text{Y}$ .

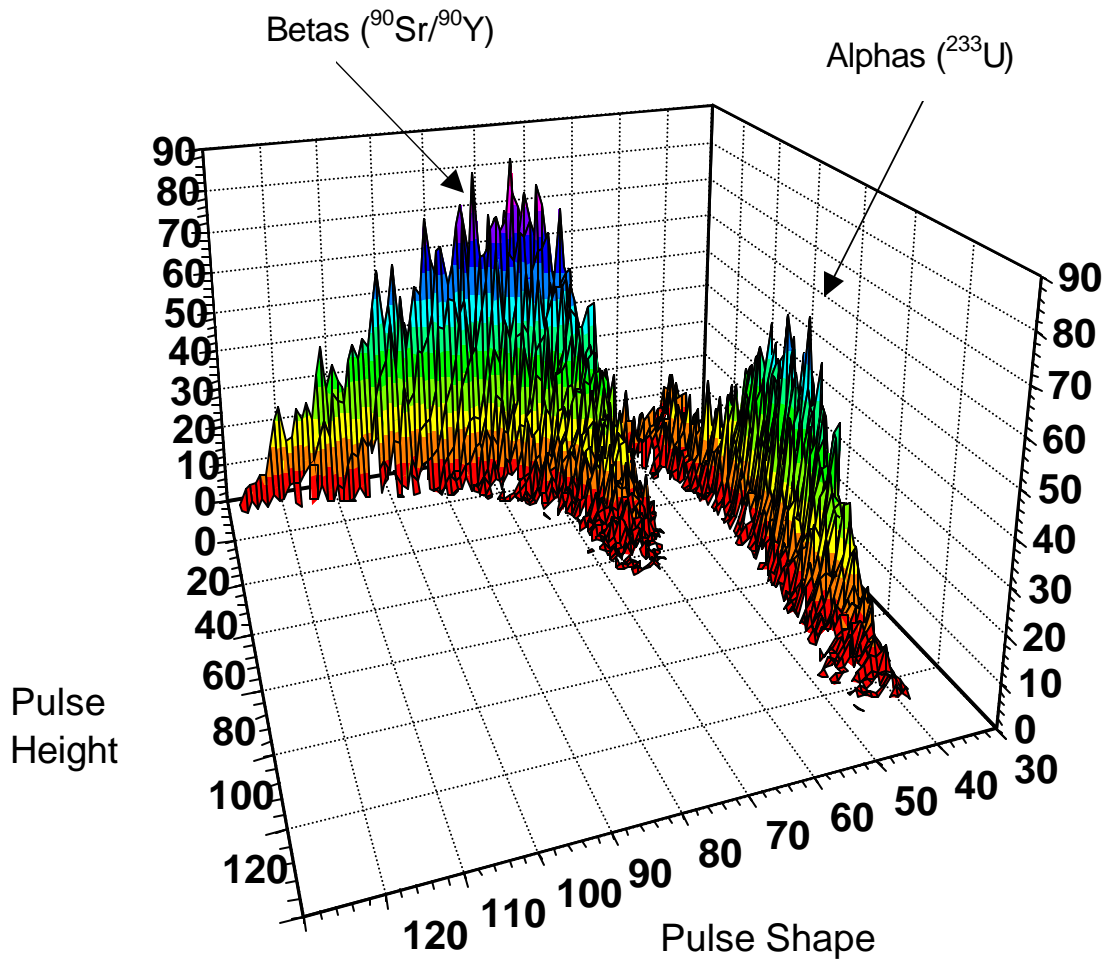


Figure 4. Heterogeneous CsI:TI dual parameter spectrum

TABLE 1. Results summary for Task 1.

	Heterogeneous <sup>1</sup>		Homogeneous <sup>2</sup>		Goals	
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$
Detection efficiency (%)	65	53	83	61	70	50
Background (cpm)	0.25	12	6	24.6	0.5	10
Spillover (%)	4.4	0.2	3.4	3.4	<5	<5
MDA (Bq)	0.2	0.9	0.46	1.1	0.5	5

<sup>1</sup> Parylene C coated CsI:TI (3% wall-to-core ratio)

<sup>2</sup> HiSafe 3 with a 10% sample loading

### Sample Interferences – Task 2

Chemical and radiological interferences were identified, and chemical interferences were quantified in terms of the non-observable effects loading (NEL). The NEL is operationally defined as the number of micromoles of interferent chemical which produces no observable effects on retention fraction and/or peak elution time. It has utility as a goal for sample clean-up procedures. Figure 5 contains a graph illustrating how the NEL was determined based on retention fraction while Figure 6 contains a graph illustrating determination of the peak elution time NEL. NELs were determined for a suite of ions (introduced in solution in the form of a chemical salt) commonly encountered in environmental and waste samples. Additional compounds were evaluated in Task 4. NELs for the various compounds tested under both Tasks 2 and 4 are given in Appendix B, and ion specific NELs inferred from these data are summarized in Table 2. The ion specific NELs ranged from a few hundred  $\mu\text{mole}$  for  $\text{Na}^+$  to 1  $\mu\text{mole}$  for multivalent cations such as  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$ . Iron and uranium are particularly problematic chemical interferences because they are likely to be encountered in samples at DOE sites.

No serious radiological interferences were identified.

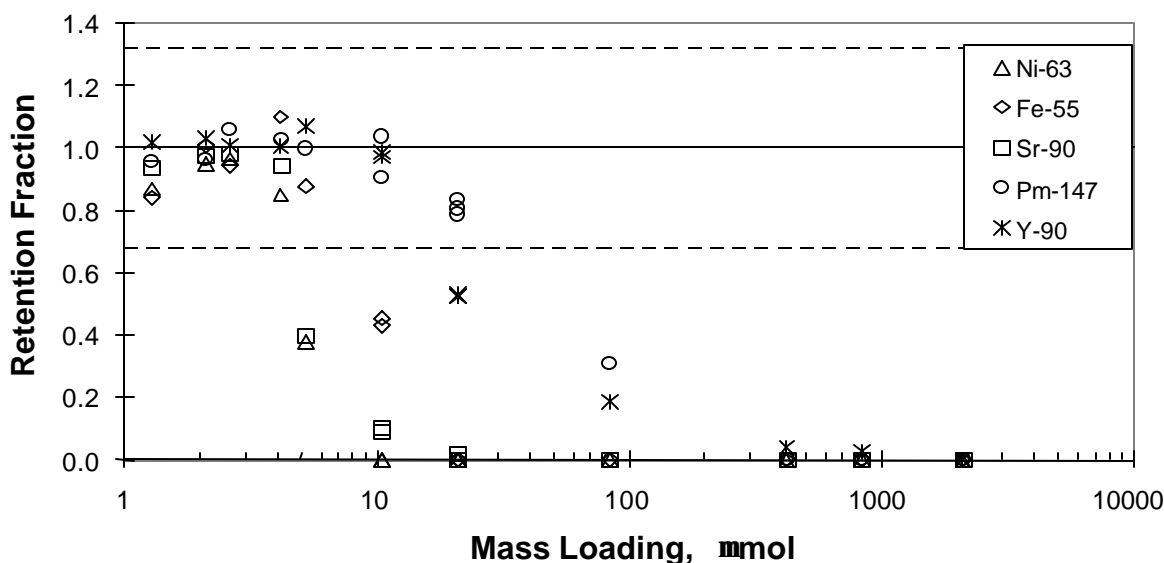


Figure 5. Effect of  $\text{Al}^{3+}$  on retention fraction. The solid horizontal line is the expected mean value while the dashed lines represent  $\pm 3$  standard deviations. Those retention fractions with radionuclide activities below the minimum detectable activity were assigned a retention fraction of zero.

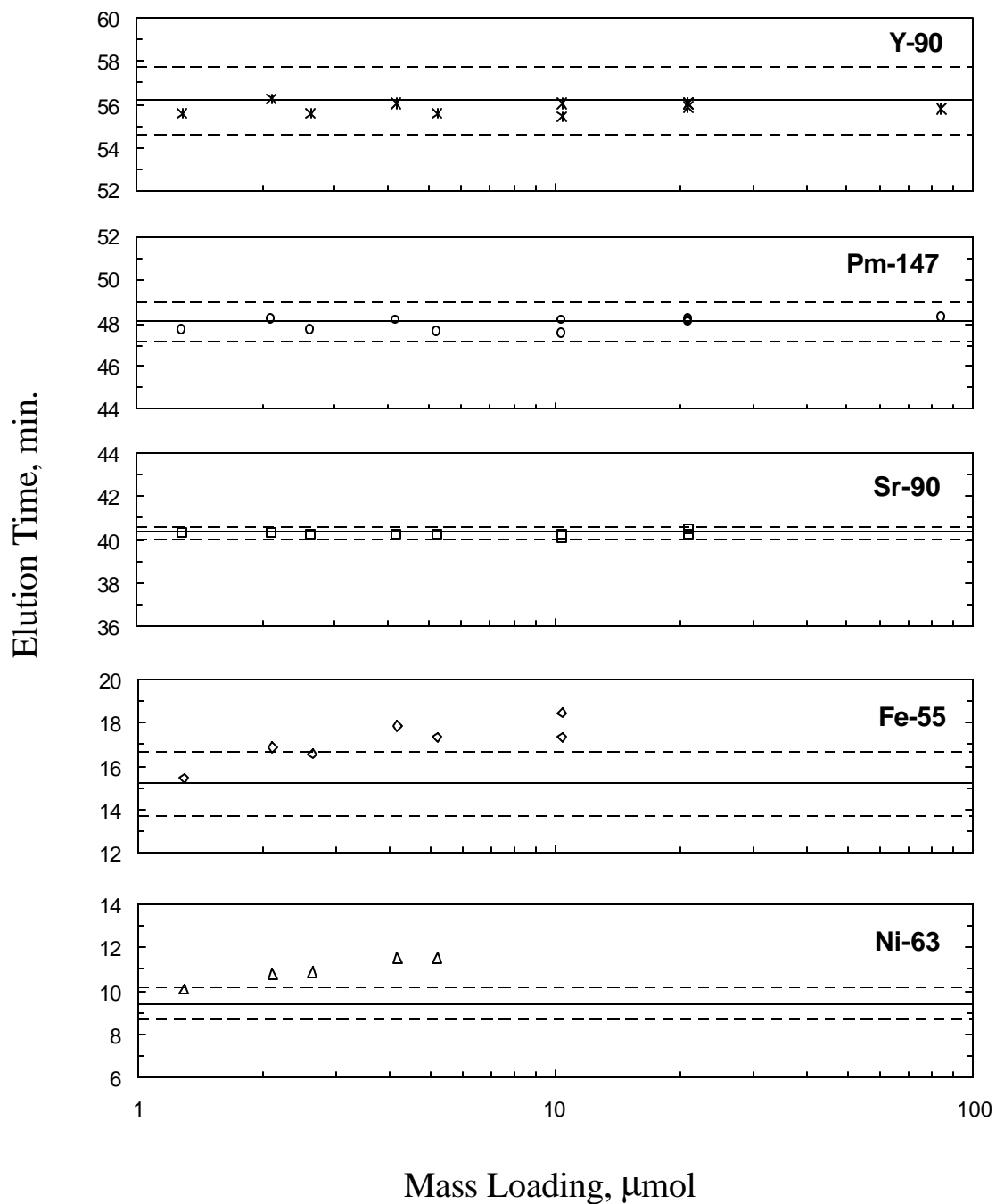


Figure 6. Peak elution time effects of  $\text{Al}^{3+}$  for mass loadings less than 100  $\mu\text{mol}$ . The solid horizontal line represents the expected mean and the dashed lines represent  $\pm 3$  standard deviations. The absence of a data point for a given mass loading (e.g.,  $^{63}\text{Ni}$ ,  $^{55}\text{Fe}$  and  $^{90}\text{Sr}$ ) indicates the absence of the corresponding peak during the chromatographic analysis or a peak activity that was below the minimum detectable activity.

TABLE 2. Values of non-observable effects loadings (NELs) for the ions investigated in this study

Ion	Retention Fraction Criterion	Peak Elution Criterion
	μmoles	μmoles
Na <sup>+</sup>	430	700
Al <sup>3+</sup>	4.2	1.3
Ca <sup>2+</sup>	3.6	0.9
OH <sup>-</sup>	140	140
NO <sub>3</sub> <sup>-</sup>	350	280
HCO <sub>3</sub> <sup>-</sup>	34	34
NO <sub>2</sub> <sup>-</sup>	430	700
SO <sub>4</sub> <sup>2-</sup> (1)	59	59
K <sup>+</sup> (1)	12	12
Cl <sup>-</sup> (1)	160	160
Fe <sup>3+</sup>	1.5	0.5
TiO <sup>2+</sup>	1.6	0.16
PO <sub>4</sub> <sup>-</sup>	0.32	1.9
Zn <sup>2+</sup>	0.75	0.75
ZrO <sup>2+</sup>	0.33	0.16
<sup>238</sup> U (2)	0.83 (5 Bq)	0.17 (1 Bq)

(1) No interference effect was observed using 2.5 mL of the solution at the concentration listed in Table 10.

(2) Does not include uranium progeny.

### *Sample Processing – Task 3*

Sample preparation procedures were developed for simple and complex matrices and applied to actual samples and to sample surrogates. A ground water sample spiked with a radioactive standard containing <sup>63</sup>Ni, <sup>147</sup>Pm, <sup>90</sup>Sr/<sup>90</sup>Y, and <sup>55</sup>Fe was processed by filtration and oxidation. Yields ranged from 40% for <sup>63</sup>Ni to 100% for <sup>90</sup>Y and <sup>147</sup>Pm. A generic sample processing procedure based on microwave assisted digestion was developed for complex matrices such as soil or high level waste tank sludges or supernatant. A subsequent extraction/concentration procedure based on Eichrom resins was developed for strontium and transuranics (Figure 7). The digestion/ extraction/

concentration procedure was tested on soils spiked with a standard containing radionuclides relevant at DOE sites ( $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{90}\text{Sr}$ , and  $^{233}\text{U}$ ) (Figure 8). Yields generally ranged between 70 and 100% (Table 3). An actual liquid sample from the high-activity drain tanks at the Savannah River Technology Center (SRTC) was obtained. Analyses were performed on an unprocessed sample, an oxidized sample, and a fully processed (digestion/extraction/concentration) sample. Results were compared to analyses performed at SRTC using traditional techniques. Our analyses were within 10% of the SRTC results for the unprocessed sample, 15% for the oxidized sample, and 40% for the fully processed sample. The project goal for sample preparation time was met for simple matrices requiring filtration and oxidation but was not met for complex matrices requiring digestion/extraction/complexation.

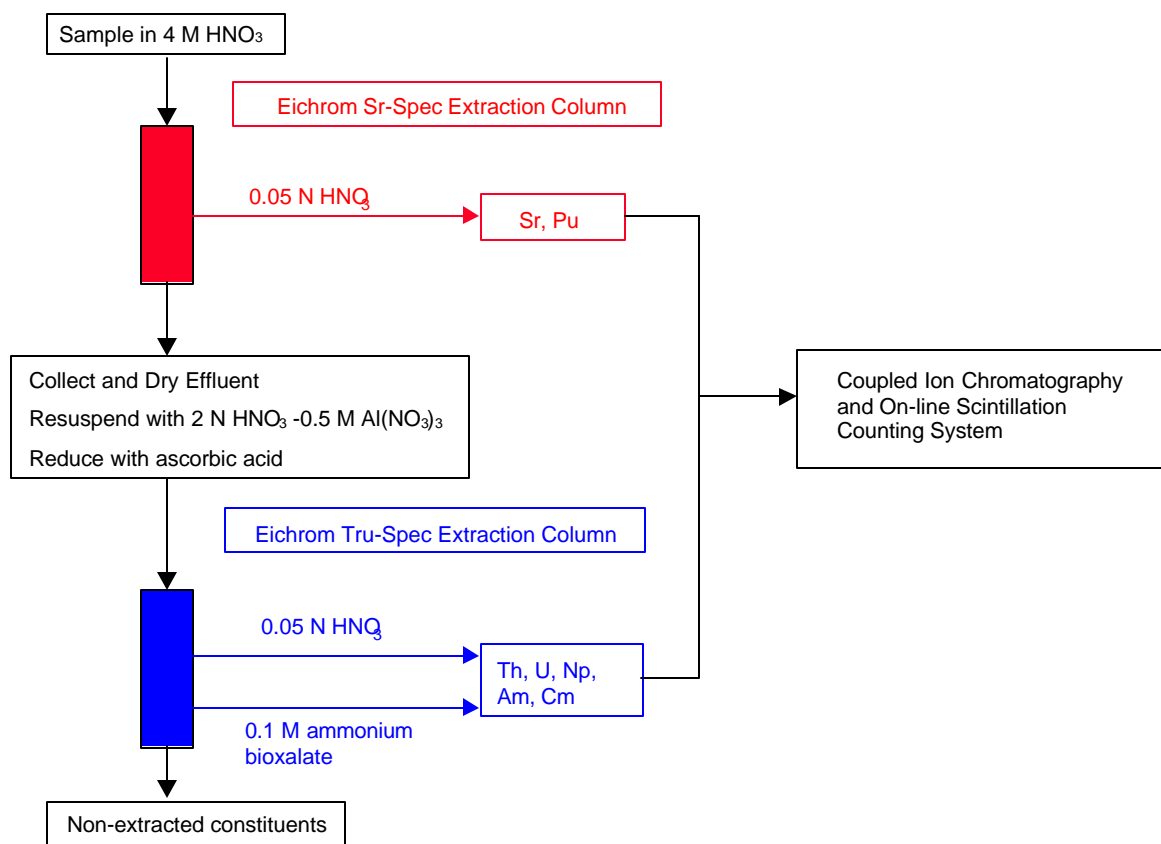


Figure 7. Sample chemical preparation scheme.



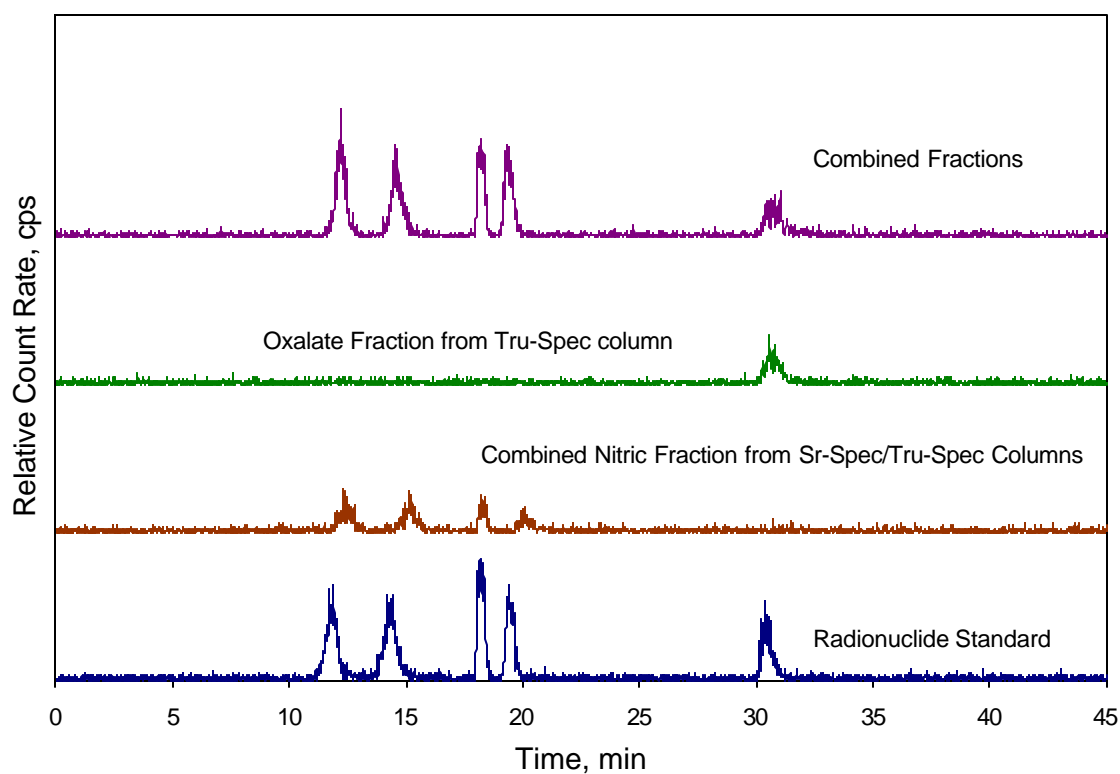


Figure 8. Extracted fraction chromatograms from samples of spiked Blanton series soil.

TABLE 3. Radionuclide yields for Blanton series soil and SRTC high activity drain tank samples.

	Blanton A - Soil	Blanton B - Soil	Blanton C -Soil	Unprocessed Drain Tank	Oxidized Drain Tank	Processed Drain Tank
<sup>241</sup> Am	101%	91%	n.a.	90%	90%	78% ± 4%
<sup>244</sup> Cm	91%	77%	n.a.	99%	87%	64% ± 10%
<sup>90</sup> Sr	70%	91%	92%			
<sup>233</sup> U	83%	81%	84%			

n.a. ≡ not available

## RESEARCH APPROACH FOR TASK 4

Objective: Integration and testing of a laboratory prototype system.

Sub-task 4.1: Integration of the sample processing, chromatographic separation, and radiation detection components into a prototype bench-scale system.

Sub-task 4.2: Perform analyses on the environmental water and waste tank surrogates which contain targeted radionuclides.

Sub-task 4.3 Perform analyses on actual environmental water and waste tank samples.

The ultimate goal of this project is development of a field deployable system using ion chromatography with a flow cell pulse shape discriminating data acquisition system. The purpose of the three tasks in the base phase of the project was to determine if the approach was technically feasible. The purpose of Task 4 was to integrate ion chromatography and sample processing with the pulse shape discriminating flow-cell data acquisition system to demonstrate the capabilities of the combined system in a laboratory setting.

Once the systems were integrated, the laboratory prototype was used to characterize the following: spiked groundwater, spiked basalt from the Idaho National Engineering and Environmental Laboratory, a supernatant from the SRTC high activity drain tank, and sludge from a high level waste tank at the Savannah River Site. These types of samples are representative of those encountered within the DOE complex. Groundwater represents a simple matrix from the standpoint of potential chemical interferences while soils, waste tank supernatant, and HLW sludge samples represent complex matrices.

## RESULTS AND DISCUSSION

### **Task 4.1 Systems Integration and Digital PSD**

Sub-task 4.1 involved integration of the ion chromatography and the analog pulse shape discriminating flow-cell detection system into a transportable laboratory prototype. Based on the outcome of the research conducted under Task 1, it was decided that the granulated Parylene C coated CsI:TI would be used for the flow-cell and that additional development work on the digital data acquisition system was warranted.

#### *Systems Integration*

Three transportable equipment cabinets were used to house the sample processing, ion chromatography, and data acquisition components of the laboratory prototype (Figure 9). The sample processing cabinet (left cabinet in Figure 9) houses the microwave oven, hot plates, and extraction chromatographic columns. The ion chromatography cabinet (middle cabinet in Figure 9) houses the chemical eluents, gradient pump, and ion chromatography unit. The electronics cabinet (right cabinet in Figure 9) houses the analog pulse shape discrimination.



Figure 9. Photograph of the laboratory prototype. The left cabinet is for sample processing, the middle cabinet houses the ion chromatography system and the right cabinet contains the analog pulse shape discrimination system. The flow-cell is housed in the black box that is atop the middle and right cabinets.

### *Parylene C Coated CsI:TI*

The coating thickness of the Parylene C coated CsI:TI particles is expressed as the ratio of coating mass to particle mass. Coating thicknesses of 3%, 4%, and 5% were evaluated to determine cell half life and radiation detection efficiencies. This was accomplished by monitoring the count rate from the flow-cell as a function of time following a semi-infinite step input of a radionuclide standard. The integrity of the coating was quantified through the half life, which is the time required for the efficiency to decrease by a factor of two. The alpha-particle detection efficiency  $\epsilon_{\alpha}$  was the average of the first 10 minutes of three flow-cell lifetime tests. The beta-particle detection efficiency,  $\epsilon_{\beta}$ , was determined from the chromatograms of radionuclide standards. Tests were conducted for two particle sizes, 63 – 90  $\mu\text{m}$  and 90 – 125  $\mu\text{m}$  particles. The results for these tests are given in Table 4. Significant differences in lifetimes and detection efficiencies were not observed for the 63 – 90  $\mu\text{m}$  and the 90 – 125  $\mu\text{m}$  diameter particles. The 4% and 5%-coated particles have a half life on the order of two – three hours. This is less than we obtained previously for 3% coated particles, which is cause for some concern, but we have characterized the detection efficiency as a function of time to be able to correct for this variable.

TABLE 4. Summary of detection efficiency and half life of the Parylene C Coated CsI:TI data for the 63-90  $\mu\text{m}$  and 90-125  $\mu\text{m}$  granules.

	CsI(Tl) coated with 3% Parylene C			CsI(Tl) coated with 4% Parylene C			CsI(Tl) coated with 5% Parylene C		
	$\epsilon_{\alpha}$	$\epsilon_{\beta}$	$\tau(\text{hr})$	$\epsilon_{\alpha}$	$\epsilon_{\beta}$	$\tau(\text{hr})$	$\epsilon_{\alpha}$	$\epsilon_{\beta}$	$\tau(\text{hr})$
63-90 $\mu\text{m}$	67%	34%	5.2	41%	24%	3.4	32%	11%	4.0
90-125 $\mu\text{m}$	59%	31%	5.1	42%	21%	2.0	30%	11%	4.1

$\alpha$  is  $^{241}\text{Am}$ ,  $\beta$  is  $^{90}\text{Y}$ , and  $\tau$  is the flow-cell half life as determined for an alpha emitter. The degradation curve had two components. The half life reported above is for the long-lived component.

### *Digital PSD System*

In Task 4, work continued on development of a digital pulse shape discrimination system that condenses the data acquisition system to a computer card and computer (Figure 10). A program was written using National Instruments, Inc. LabVIEW V 5.1 for pulse shape discrimination of the summed coincident pulses (Figure 11). The program involves three integrated steps. First, if the leading edges of the individual PMT pulses are within 100 ns of one another, the pulses are considered to be in coincidence. Second, if the pulses are coincident, they are aligned in time and summed. Third, the summed pulse is processed to produce pulse shape and pulse height spectra. On-line and off-line analyses of the data are available to optimize the alpha and beta regions-of-interest in the single parameter pulse shape and dual parameter spectra. The software has a real-time indicator which displays the total (alpha + beta) count rate, thus providing a real-time chromatogram for qualitative analysis. The dual-parameter spectrum and



Figure 10. Photo of Digital Data Acquisition System. The digital oscilloscope resides in the computer.

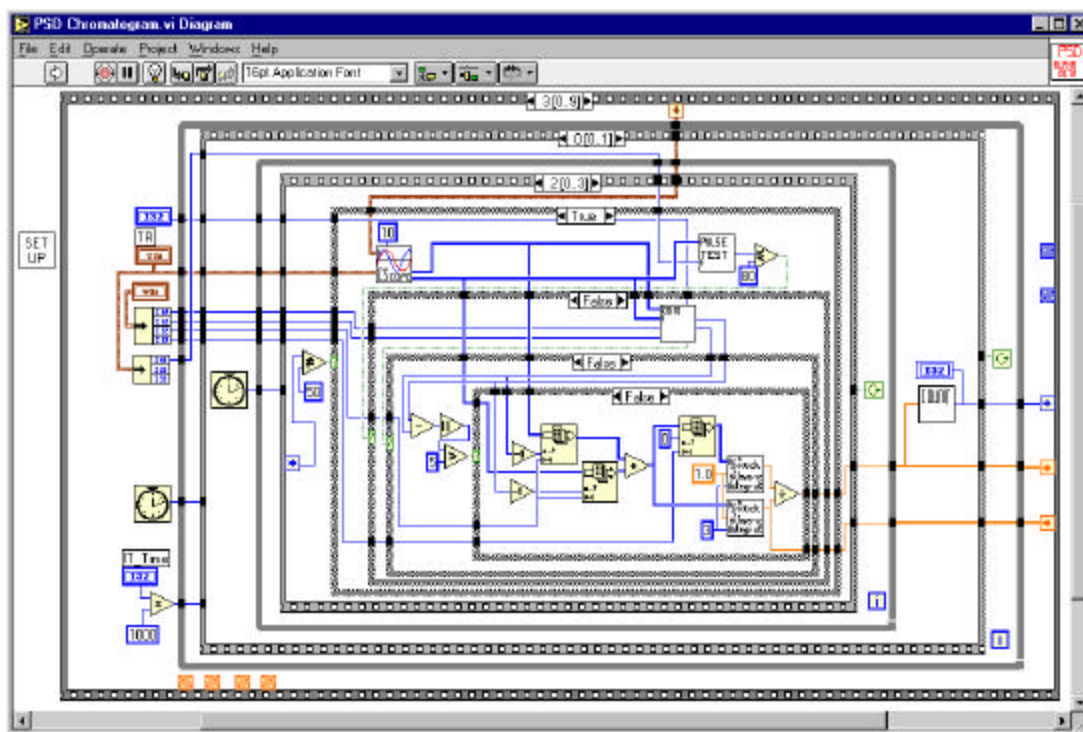


Figure 11. One subroutine of the digital data acquisition software in the object oriented programming environment.

alpha/beta chromatogram are subsequently generated by post-processing the data stored in computer memory after the chromatograph run finishes (Figure 12). The digital system thus provides the following features: (1) real-time count rate; (2) pulse height and pulse shape spectra; (3) 2D and 3D dual-parameter spectra; (4) alpha and beta chromatograms.

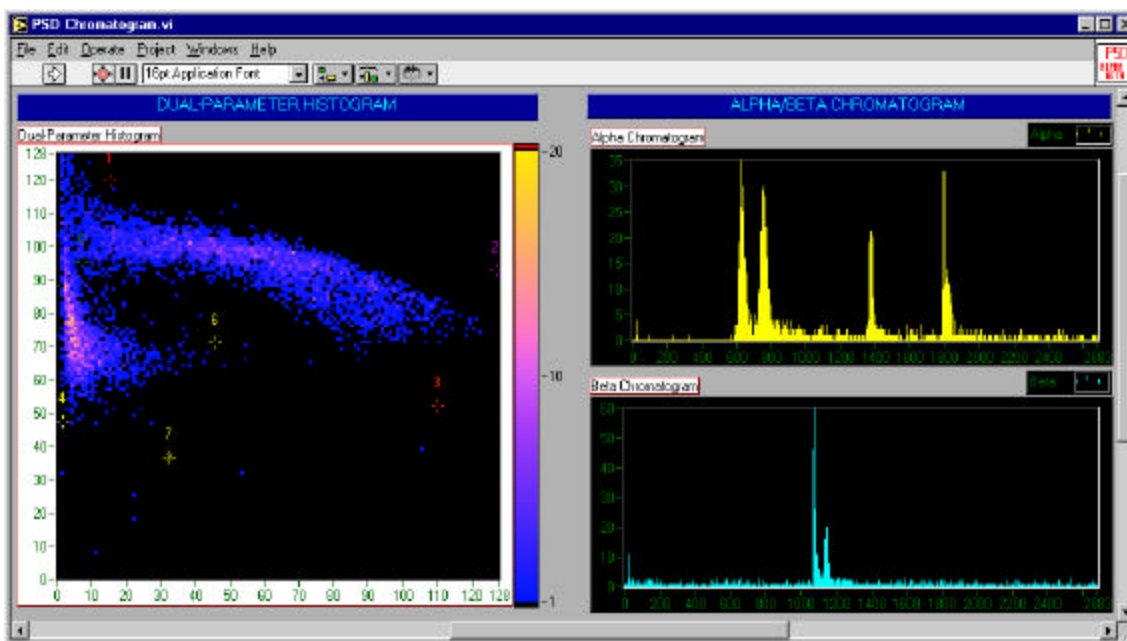


Figure 12. Data display for the digital dual parameter pulse shape discriminating data acquisition system.

The digital system was successfully benchmarked against the analog data acquisition system. Pulse height chromatograms from CsI:TI,  $\text{CaF}_2\text{:Eu}$ , and scintillating glass (GS-20) flow cells for the two systems were compared. Good correlation between the digital system and the analog system were obtained.

A disadvantage of the digital system is the dead time, which is due primarily to the transfer of digitized data from the oscilloscope memory to the computer memory and software processing and display of the digitized data. To decrease the dead time the digital system was modified by upgrading from LabVIEW 4.1 to 5.1 and upgrading the computer from P5 – 200 MHz to PIII – 450 MHz. These modifications reduced the dead time by a factor of 2 – 3. Modification of the LabVIEW code interface node (CIN) expedited data acquisition and dead time was reduced by an additional factor of two to approximately 2 ms. Additional reductions could be achieved by hardware implementation of the data processing. A summary of the operational specifications of the digital system used in conjunction with the CsI:TI detector is given in Table 5.



TABLE 5. Characterization of the digital data acquisition system with CsI:TI and aqueous solutions of  $^{90}\text{Sr}/^{90}\text{Y}$  and  $^{233}\text{U}$

Property		Single Parameter	Dual Parameter
FOM	$^{90}\text{Sr}/^{90}\text{Y}$ $^{233}\text{U}$	1.65	—
Detection Efficiency (%)	$^{90}\text{Sr}/^{90}\text{Y}$	26.4	26.0
	$^{233}\text{U}$	31.3	30.4
Background Count Rate (cps)	$\alpha$	0.31	0.05
	$\beta$	0.84	0.69
Spillover (%)	$\alpha$ to $\beta$	2.1	1.3
	$\beta$ to $\alpha$	1.4	0.3

## Tasks 4.2 and 4.3 Laboratory Prototype Testing

### *Additional Potential Chemical Interferences*

At the conclusion of Task 3, there was an unidentified interference associated with INEEL interbed. The problems associated with the interference could be circumvented by reducing the amount of digested, prepared sample (10 mL) introduced into the chromatography unit from 5- mL to 0.5-mL. Although the dilution appeared to solve the interference problem, it also raised the minimum detectable concentration. Therefore, as part of Task 4.2, soil samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). INEEL interbed and basalt materials were either digested with a mixture of nitric, hydrochloric, and hydrofluoric acids (5:1 : 5) in a microwave oven or they were leached with nitric acid. The samples were then processed using the protocol in Figure 7 and the resulting solution was analyzed by ICP-MS for metals. The concentrations are given in Table 6.

TABLE 6. ICP-ES and ICP-MS analyses of microwaved assisted digestion and nitric acid leached INEEL interbed and basalt after sample processing. The values are micromoles in 0.5 grams of interbed or basalt.

Metal	INEEL Interbed		INEEL Basalt
	Digested	Acid Leached	Digested
Al	8.1	1.3	3.2
Fe	0.6	0.1	0.1
Ca	0.7	0.1	bd
Zn	bd	bd	0.2
Ti	0.11	bd	1.4
Sr	0.34*	0.23*	bd
Zr	bd	0.08	0.3
B	0.13	bd	1.1
P	0.42	0.38	1.1
La	0.08*	0.09*	-
Ce	0.14*	0.17*	-
Nd	0.5*	0.5*	-

\*Indicates measurement with ICP-MS, other values are by ICP-ES  
bd – below detection

NEL's were determined for several of the potential interferences identified in Table 5. Experiments were conducted to test the effect of  $\text{Na}^+$ ,  $\text{PO}_4^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{ZrO}^{2+}$ , and  $\text{TiO}^{2+}$  on the chromatographic separation of the radionuclide standard. The values for NEL as determined by the retention fraction and peak elution criteria were given previously in Table 2 and Appendix B.

### *Sample Analyses*

The laboratory prototype was tested for two surrogate samples and two actual samples that are representative of the spectrum of matrices encountered at DOE sites. The surrogates, a groundwater from the southeastern U.S. and basalt from INEEL, were spiked with the strontium/actinide standard developed under Task 3 (Figure 13). The actual samples were supernatant from the high activity drain tank at SRTC and sludge from a waste tank at SRS.

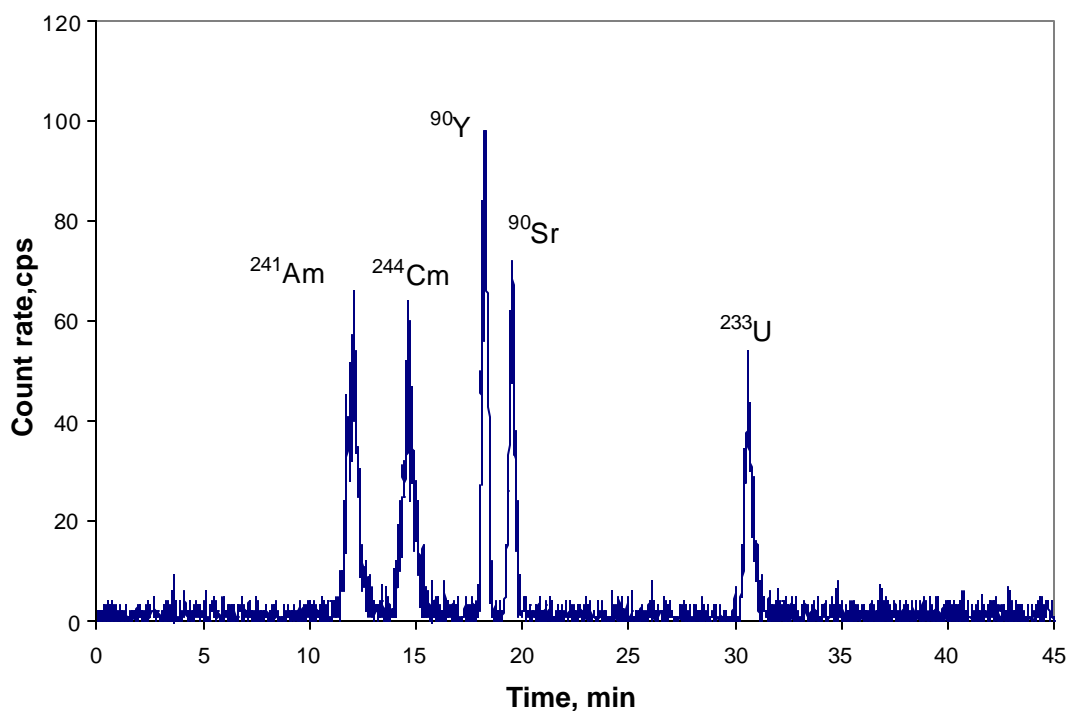
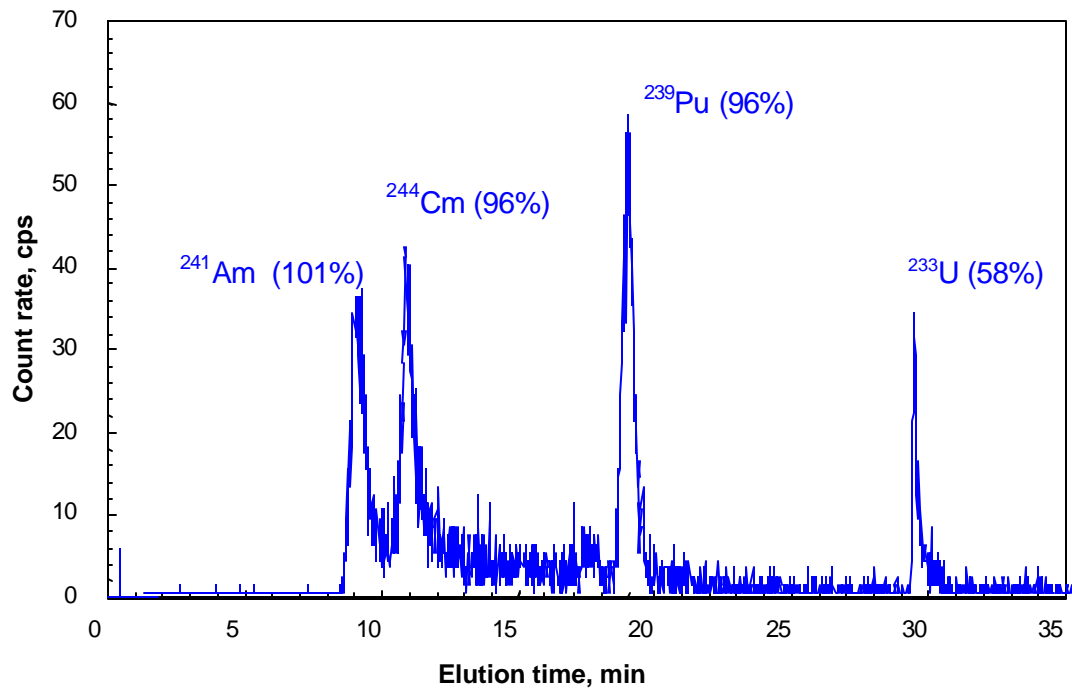


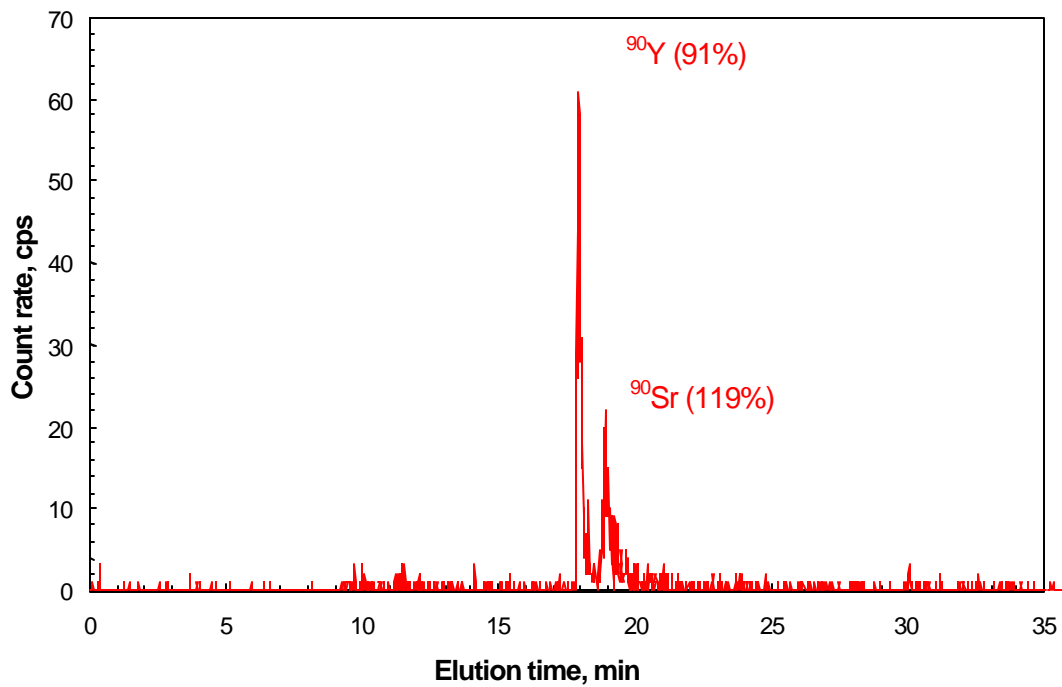
Figure 13. Chromatogram of Strontium / Actinide Standard

Groundwater from the southeastern U.S. was spiked with both the strontium/actinide standard and with plutonium. Plutonium was added because its elution time in the chromatography column is the same as strontium, and we wanted to test the ability of the PSD detector to discriminate between the two. The alpha and beta chromatograms for the sample are presented in Figure 14 (a) and (b), respectively. The data were obtained using a 4% 90-125  $\mu\text{m}$  Parylene C coated CsI:TI flow-cell. The resolution of these chromatograms was essentially the same as the standard (Figure 13), and the recoveries exceeded 90% for all of the radionuclides except for uranium. Basalt from INEEL was also spiked with the strontium/actinide standard. However, analyses of digested samples were unsuccessful, and the decision was made to leach the samples with nitric acid rather than to digest them. In this test, 0.5 g. of basalt was leached with nitric acid and processed. The resulting solution was diluted by a factor of ten. The combined alpha/beta chromatogram (obtained using a glass flow cell) is presented in Figure 15. The resolution was excellent, but the recoveries were poor, especially for uranium. Extensive efforts to identify the uranium interference were unsuccessful. The inability to analyze the digested sample and the problem with the

recoveries are consistent with our finding from Task 3 that the processing protocol may need to be modified for some complex matrices.



(a)



(b)

Figure 14. Alpha (a) and beta (b) chromatograms from a spiked groundwater sample. Recoveries (in percent) are given in parentheses.

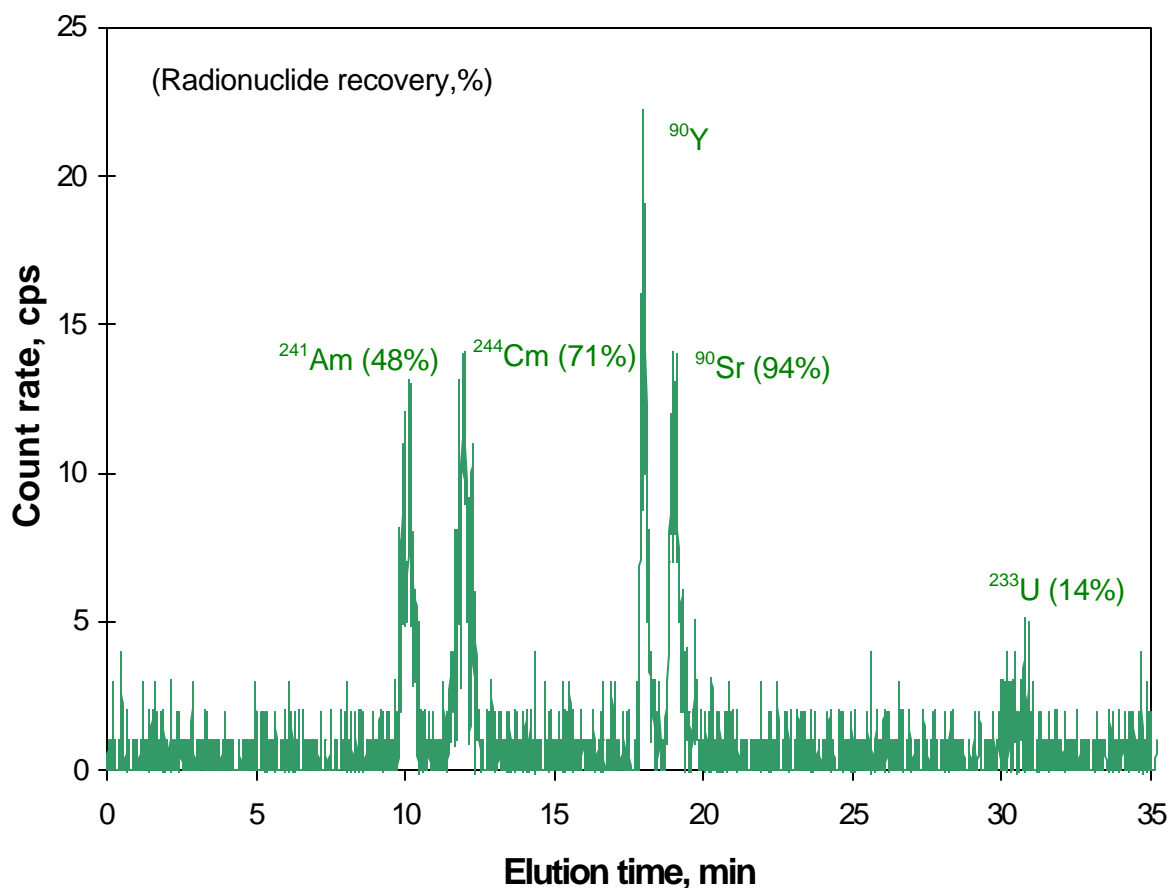


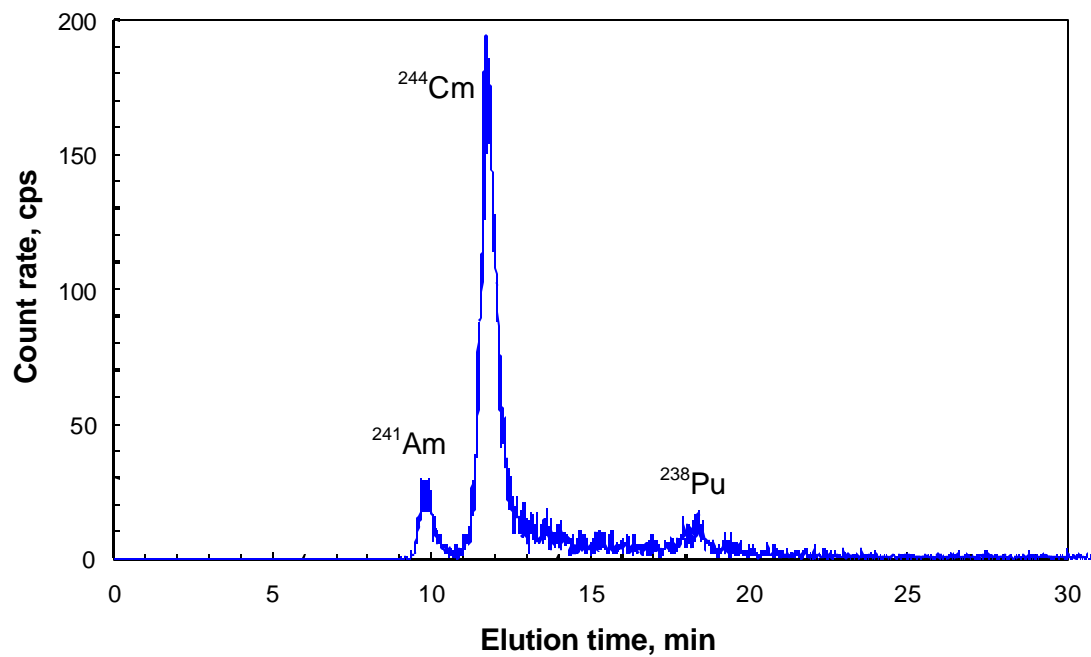
Figure 15. Chromatogram for a nitric acid leached spiked INEEL basalt material obtained with a glass scintillation flow-cell.

The SRTC high-level drain tank receives liquid laboratory wastes. A 0.25 mL sample was analyzed without processing. The chromatograms are presented in Figure 16. Based on elution times, plutonium, americium, and curium were detected in the alpha chromatogram; and cesium, strontium, and yttrium were detected in the beta chromatogram. There was some spillover of curium in the beta chromatogram. Presented in Table 7 is a comparison of concentrations as measured in our system and as measured at SRTC. Our analyses were all within 20% of those from SRTC.

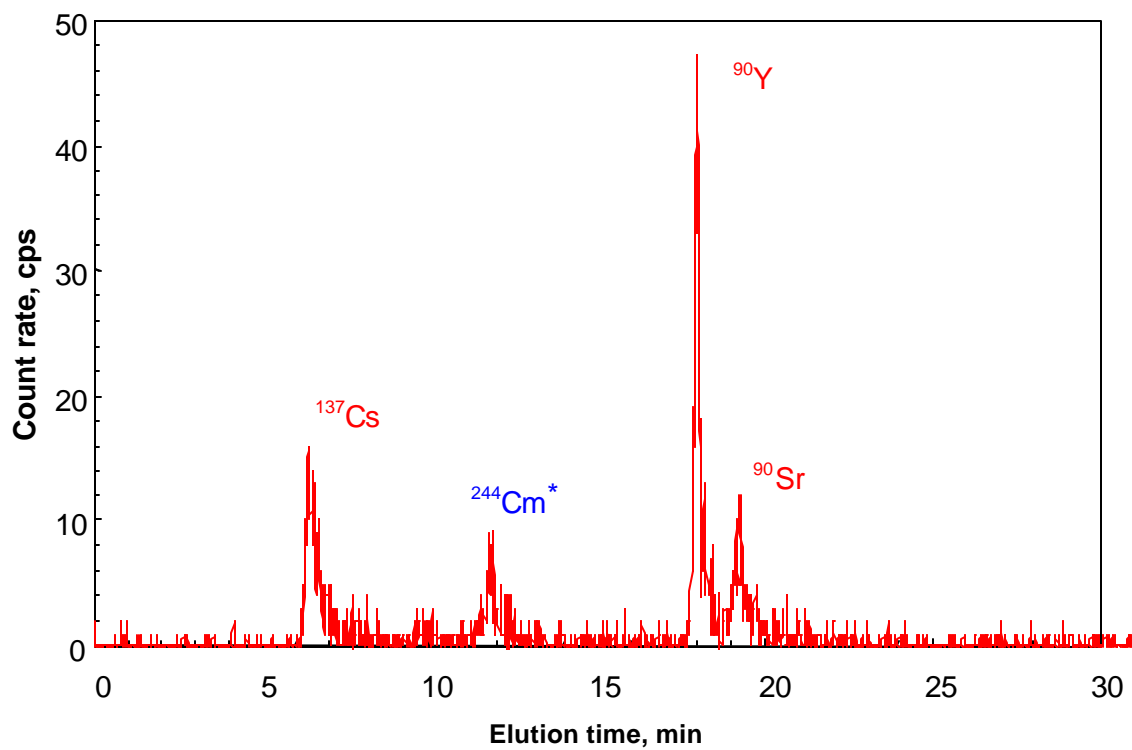
TABLE 7. Summary of High Activity Drain Tank Sample. Data obtained using a 4% 90-125  $\mu\text{m}$  Parylene C coated CsI:TI flow-cell.

Radionuclide	SRTC Measurement (Bq mL <sup>-1</sup> )	Our Measurement (Bq mL <sup>-1</sup> )
<sup>90</sup> Sr	-	1130
<sup>137</sup> Cs	1557	1880
<sup>238</sup> Pu	828	690
<sup>241</sup> Am	1165	1080
<sup>244</sup> Cm	10656	10020

A sample of sludge was obtained from SRS HLW Tank 8. At SRTC, 0.125 grams of the sample was dissolved into 100 mL of 0.1 M HNO<sub>3</sub> of which 10 mL was shipped to our laboratory. A 0.25 mL aliquot was analyzed without processing. The chromatograms are presented in Figure 17. Cesium, strontium and yttrium were detected in the beta chromatogram; and plutonium, americium and curium were detected in the alpha chromatogram. The comparison of the analyses is presented in Table 8. Our analyses were within 15% of the SRTC analyses for strontium, americium and curium and within 30% for cesium and plutonium.

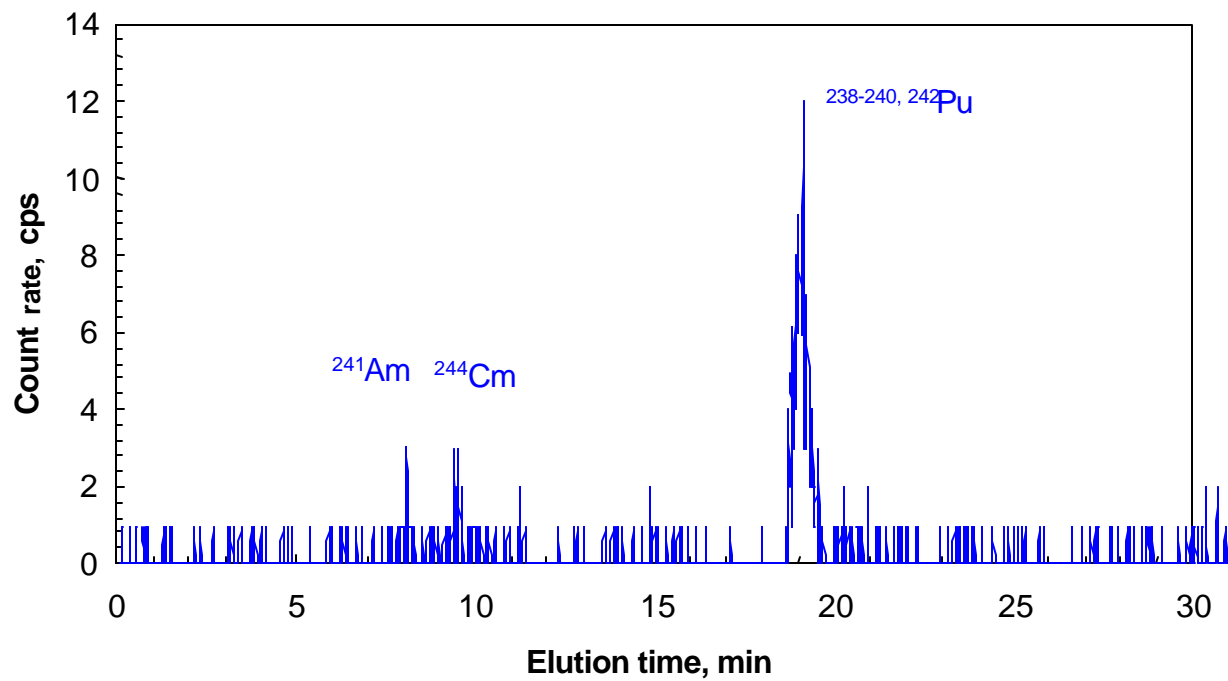


(a)

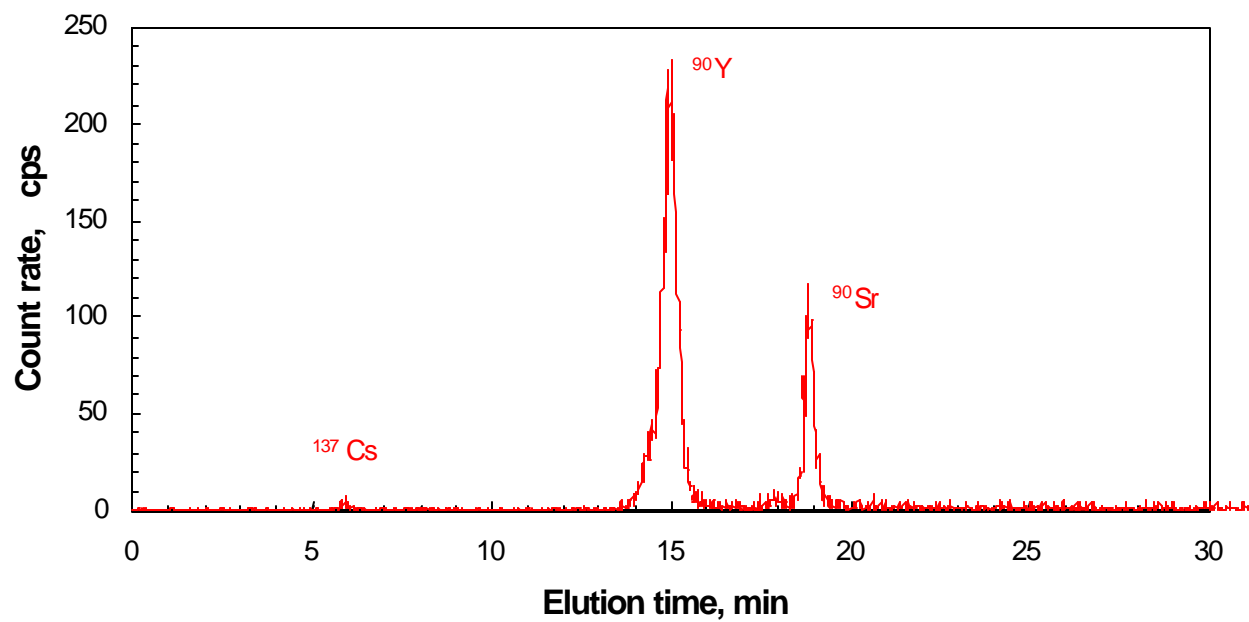


(b)

Figure 16. Alpha (a) and beta (b) chromatograms for the supernatant form the high activity drain tank at SRTC.



(a)



(b)

Figure 17. Alpha (a) and beta (b) chromatograms from a SRS HLW sludge.



TABLE 8. Summary of the HLW sludge sample analysis. Data obtained using a 3% 63 - 90  $\mu\text{m}$  Parylene C coated CsI:TI flow-cell.

Radionuclide	SRTC Measurement (Bq mL <sup>-1</sup> )	Our Measurement (Bq mL <sup>-1</sup> )
<sup>90</sup> Sr	33,300	28,410
<sup>137</sup> Cs	1170	850
<sup>238-240,242</sup> Pu	920	640
<sup>241</sup> Am	45	41
<sup>244</sup> Cm	60	54

#### *Comparison with Existing Technology*

A direct comparison of analysis costs between this system and existing techniques is difficult because there is not an existing technique which is capable of simultaneously analyzing for multiple alpha and beta emitters in a sample. However, an estimate of the relative costs can be inferred from the time required to perform the analyses. Presented in Table 9 is the time required for us to analyze the two actual samples from SRS compared to the analysis times contained in the SRTC Laboratory Information Management System.

TABLE 9. Comparison of analysis times.

SAMPLE	SRS Lab Information Management System	Our System
SRTC High Activity Drain Tank	15.5 hours	3 hours
SRS Sludge	8.5 hours	3 hours

## CONCLUSIONS

Based on the results of Task 4, it is concluded that the system, with some limitations, is capable of analyzing alpha and beta emitters in samples that are representative of many of those encountered in the DOE complex. Based on analyses of both surrogate samples and actual samples from DOE sites, radionuclide concentrations obtained using this technology were generally within 20% of those obtained using standard laboratory protocols. In addition, analysis times were much less (by a factor of 3-5 for liquid wastes). Estimates of the capabilities of the system, in terms of analysis time and minimum detectable concentration, are presented in Table 10.

The principal advantages of the technology are (1) its ability to analyze a mixture of alpha and beta emitters in a relatively short period of time, much less than that required by traditional techniques, and (2) its relatively small size makes it amenable to field deployment. This translates into both a cost advantage and an operational advantage, especially in field applications. The limitation is that modifications of the sample processing protocol may be required for complex matrices such as soils. For example, we found that our sample processing protocol worked well for a specific soil at SRS (Blanton series) but would need to be modified to reduce interferences in basalt from INEEL.

TABLE 10. Summary of expected detection limits and analysis times for aqueous and solid samples.

	Aqueous Sample		Solid Sample
	4 hour analysis (on-line counting)	24 hour analysis (off-line counting)	48 hour analysis (off-line counting)
Strontium-90	4000 pCi L <sup>-1</sup> (160 kBq/m <sup>3</sup> )	12 pCi L <sup>-1</sup> (0.4 kBq/m <sup>3</sup> )	5 pCi g <sup>-1</sup> (0.2 kBq/Kg)
Transuranics	1500 pCi L <sup>-1</sup> (60 kBq/m <sup>3</sup> )	3 pCi L <sup>-1</sup> (0.1 kBq/m <sup>3</sup> )	1 pCi g <sup>-1</sup> (0.04 kBq/Kg)

The original goal of this project was to develop a technology for the rapid analysis of waste samples and environmental media containing multiple non-gamma emitting radionuclides. This goal was clearly achieved for liquid waste samples in which radionuclide concentrations on the order of 100's of kBq/m<sup>3</sup> (1000's of pCi/L) can be analyzed in a few hours. For complex matrices such as soil or for typical environmental

concentrations, the analysis time can extend to a couple of days. Although this is not rapid compared to the few hours required for liquid waste samples, it is considerably quicker than typical analysis times using current techniques. The next step in the path toward commercialization could be a site demonstration involving liquid waste samples such as those from the laboratory drain tank at SRTC or supernatant from high level waste tanks at SRS, ORNL or Hanford.

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R. A. Fjeld, T. A. DeVol, and J. D. Leyba, "Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting with Pulse Shape Discrimination: Final Report for Base Phase," Clemson University, 1998.

## APPENDIX A

### Presentations / Publications

R. A. Fjeld, T. A. DeVol, and J. D. Leyba, "Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting with Pulse Shape Discrimination: Final Report for Base Phase," Clemson University, 1998.

DeVol, T.A., Tan, H., and Fjeld, R.A., "Dual Parameter Analysis of CsI:TI/PMT with a Digital Oscilloscope," *Nucl. Instr. and Meth.*, A435, (1999).433-436

T. A. DeVol, S. B. Chotoo, R. A. Fjeld, " Evaluation of granulated BGO, GSO:Ce, YAG:Ce, CaF<sub>2</sub>:Eu and ZnS:Ag for alpha/beta pulse shape discrimination in a flow-cell radiation detector," *Nucl. Instr. and Meth.*, A425 (1999) 228-231.

J. E. Roane, T.A. DeVol, J.D. Leyba and R.A. Fjeld, "Effects of Ionic Radiological and Chemical Interferences on the Chromatographic Separation of a Radionuclide Standard Solution," *J. Radioanalytic and Nuclear Chemistry* Vol. 240, No. 1 (1999) 197-208.

K. H. Hastie, T.A. DeVol and R.A. Fjeld, "Development of a Homogeneous Pulse Shape Discriminating Flow-Cell Radiation Detection System," *Nucl. Instr. and Meth.*, A422 (1999) 133-138.

S. D. Chotoo, T. A. DeVol and R. A. Fjeld, "Development of a Heterogeneous Pulse Shape Discriminating Flow-Cell using Polymer Coated CsI:TI," *IEEE Trans. Nucl. Sci.*, Vol. 44, No. 4 (1997) 1630-1634.

Tan, H., Fjeld, R.A., and DeVol, T.A., "Digital Alpha/Beta Pulse Shape Discrimination of CsI:TI for On-Line Measurement of Aqueous Radioactivity," accepted for publication in *IEEE Trans. Nuc. Sci.*.

## APPENDIX B

Table B-1. Values of non-observable effects loadings (NEL) for the ions investigated in this study. Ions were introduced to solution in the form of chemical salts. By comparing the NEL values for the different chemical species resulted in the determination of the interfering ion, which is listed here and in Table 2.

Ion	Chemical	Retention Fraction Criterion	Peak Elution Criterion
		μmoles	μmoles
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub>	4.2	1.3
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	3.6	0.9
OH <sup>-</sup>	NaOH	140	140
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	350	280
HCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	34	34
NO <sub>2</sub> <sup>-</sup>	NaNO <sub>2</sub>	430	700
SO <sub>4</sub> <sup>2-</sup> (1)	Na <sub>2</sub> SO <sub>4</sub> (1)	59	59
K <sup>+</sup> (1)	KCl (1)	12	12
Cl <sup>-</sup> (1)	NaCl (1)	160	160
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	1.5	0.5
TiO <sup>2+</sup>	TiOCl <sub>2</sub>	1.6	0.16
PO <sub>4</sub> <sup>-</sup>	KH <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	0.32	1.9
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	0.75	0.75
Zr <sup>2+</sup>	ZrO(NO <sub>3</sub> ) <sub>2</sub>	0.33	0.16
	Uranium(2)	0.83 (5 Bq)	0.17 (1 Bq)

(1) No interference effect was observed using 2.5 mL of the solution at the concentration listed in Table 10.

(2) Does not include uranium progeny.