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Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting With Pulse Shape Discrimination

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¹Introduction

Radiological characterization and monitoring is an important component of DOE's environmental management activities. Radionuclides which cannot easily be detected by gamma ray spectrometry, such as pure beta emitters and transuranics, pose special problems because their measurement generally requires labor intensive radiochemical separations procedures that are time consuming and not practical for field applications.

This project is concerned with a technology that combines ion exchange

chromatography, flow-cell scintillation counting, and pulse shape discrimination for the measurement of beta emitters and transuranics in environmental samples or waste samples. The technique is shown conceptually in Figure 1. First, samples are processed, if necessary, so as to yield an aqueous solution containing the radioactive constituents in ionic form. The radionuclides are then separated elementally by ion exchange chromatography and subsequently detected by a flow-cell scintillation system. The flow-cell detector is equipped with pulse discrimination circuitry that distinguishes between pulses due to alpha interactions and those due to beta interactions. This yields separate chromatograms for alpha emitters and for beta emitters and reduces alpha background in the beta chromatogram and beta background in the alpha chromatogram.

The actual chromatography system differs slightly from the simplified drawing in

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Figure 1 in that the radionuclides are first loaded onto a pre-concentration column. A variety of eluents then flow through the pre-concentration column and carry the ions to a separation column where the chromatographic separation occurs. The system is described in detail elsewhere (Reboul and Fjeld, 1994).

The technology development program consists of four tasks: (1) development of the flow cell detector, (2) identification of potential radiological and chemical interferences, (3) development of sample processing protocols, and (4) laboratory testing of a prototype system on surrogate or actual samples. Presented here are results of work focused on the testing and

evaluation of the pulse shape characteristics of potential scintillators and the identification of potential radiological and chemical interferences.

Objectives

1. To identify potential scintillator materials for the flow-cell detector and evaluate their pulse shape characteristics.
2. To identify potential chemical and radiological interferences.

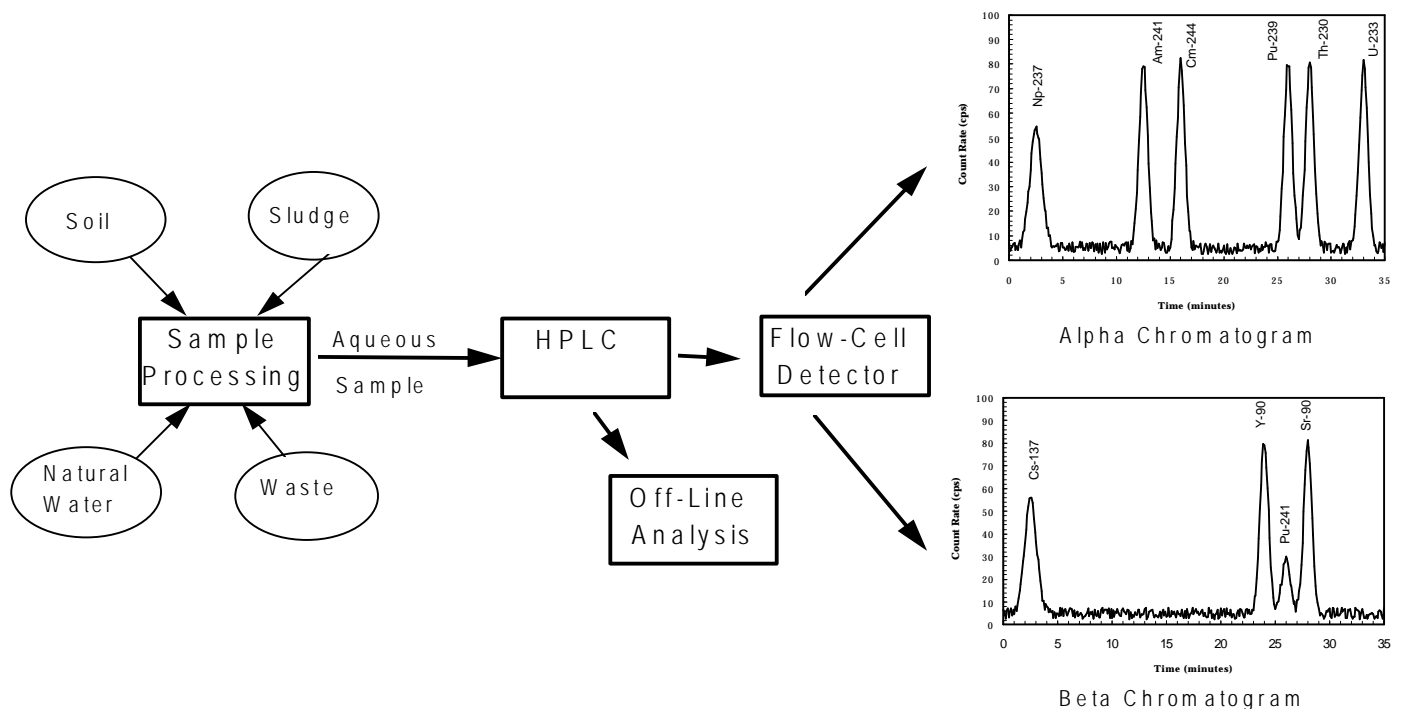


Figure 1. Technique for ion exchange chromatography, flow-cell scintillation counting, and pulse shape discrimination for the measurement of beta emitters and transuranics.

Project Description

Scintillator Testing

Although flow-cell scintillation detectors are commercially available, none are available with pulse shape discrimination. The advantages of pulse shape discrimination are 1) lower minimum detectable activity for alpha radiation, 2) reduced radiological interferences between co-eluted alpha- and beta- emitting radionuclides, and 3) possible isotopic information from the ion chromatography system. Pulse shape discrimination is possible if the light emitted following an alpha interaction has a component that is emitted faster than that emitted following a beta interaction (or vice versa).

A review of the literature was performed, and 21 scintillation materials having potential for pulse shape discrimination were identified. From this list, the following seven were selected for testing: BGO, GSO:Ce, YAG:Ce, uncoated CaF₂:Eu, fluorescent coated CaF₂:Eu, combination flow-cells of coated and uncoated CaF₂:Eu with ZnS:Ag, and a non-fluorescent polymer coated CsI:Tl. The test cell was a 1.5 mm inner diameter Teflon tube packed with scintillator particles (63-90 μm in diameter). Aqueous solutions containing ⁹⁰Sr/⁹⁰Y and ²³³U were passed through the cell. Light from the scintillator particles was collected by dual photomultiplier tubes. Both the dynode (fast) and anode (slow) were processed. The slow signal was split to allow simultaneous collection of pulse height (energy deposited) and pulse shape (type of incident radiation) data. These data could be recorded separately to yield single parameter pulse height or pulse shape spectra or simultaneously to yield a dual parameter spectrum.

The pulse shape characteristics of each scintillator was quantified by a figure of merit, FOM, defined by

$$\text{FOM} = \frac{|T_{\alpha} - T_{\beta}|}{W_{\alpha} - W_{\beta}}$$

Operationally, a figure of merit greater than one is considered to be acceptable for alpha/beta separation. Test results are given in Table 1.

CsI:Tl, with a figure of merit of 1.4, was the only scintillator to exhibit satisfactory pulse shape discrimination. The pulse shape spectrum for CsI:Tl is given in Figure 2. Alpha to beta and beta to alpha spillovers were both less than 5%. The detection efficiencies were 5%, 53% and 65% for ¹⁴C, ⁹⁰Sr/⁹⁰Y and ²³³U, respectively. The beta and alpha background count rates were 0.17 and 0.004 counts per second, and the corresponding minimum detectable activities for a 30 second counting time were 11, 1 and 0.2 Bq for ¹⁴C, ⁹⁰Sr/⁹⁰Y and ²³³U, respectively. Since CsI:Tl is soluble in aqueous media, the particles were coated to protect them from the existing eluents. The polymer coating thickness was approximately 3 μm, which is transparent to the scintillation light and sufficiently thin to allow the alpha radiation to pass without significant energy loss. With the coating, the rate of dissolution of the CsI particles is reduced but not eliminated.

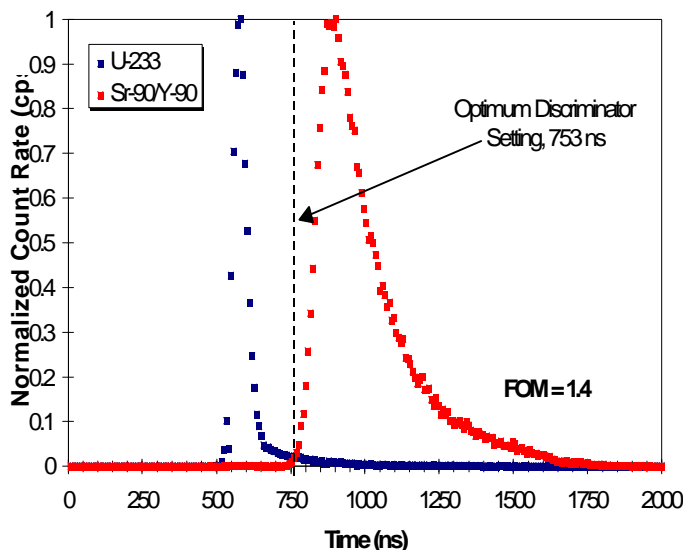


Figure 2. Pulse Shape Spectrum for CsI:Tl

Table 1. The Figure of Merit of Each Flow-Cell

SCINTILLATOR	FIGURE OF MERIT
BGO	0.18
GSO:Ce	0.23
YAG:Ce	0.32
CaF ₂ :Eu	0.44
CaF ₂ :Eu coated in Parylene C doped with Anthracene	0.28
ZnS:Ag+CaF ₂ :Eu in equal mass	*
CsI:Tl coated in Parylene C	1.4

* This cell contained ZnS:Ag and CaF₂:Eu particles. The hypothesis was that the ZnS:Ag would respond to alphas and the CaF₂ would respond to betas. However, there was significant response of CaF₂ to alphas (10% spillover) even though the FOM for the ZnS:Ag/CaF₂:Eu cell was good (FOM = 1.5).

Radiological and Chemical Interferences

A major consideration in the application of ion exchange chromatography to DOE samples is the effect of radiological and chemical interferences. Since interferences are sample specific, it is not possible to perform a comprehensive evaluation that can cover all types of samples. Instead, representative chemical and radiological interferences were identified for HLW supernatant and for groundwater. The testing of specific interferences should yield information on the general nature and types of effects to be expected. Based on published data regarding the composition of HLW supernatant (Ondrejcin, 1974) and groundwater (LANL, 1993) potential interferences were identified. The radiological interferences selected for testing were ³H, ⁶⁰Co, ¹³⁷Cs, ¹⁵²Eu, ^{Nat}U, and ²²⁸Th. The chemical interferences selected for testing were Al(NO₃)₃ * 9H₂O, Ca(NO₃)₂ * 4H₂O, NaOH, NaNO₃, NaHCO₃, NaNO₂, Na₂SO₄, KCl, NaCl, and uranium.

Interferences were defined quantitatively to be perturbations of the chromatogram which cause:

- 1) the peak elution time to vary by more than 3 standard deviations from the mean,
- 2) reduction in radionuclide detection efficiency by more than 3 standard deviations from the mean, or
- 3) the resolution parameter, R_s , to be less than 1.

For any two elution peaks, R_s is defined as

$$R_s = \frac{2(t_{E2} - t_{E1})}{w_1 + w_2}$$

where t_{E1} and t_{E2} are the elution times associated with the centroids of adjacent peaks and w_1 and w_2 are the peak widths at the baseline in units of time. Testing of each potential interferent was accomplished by comparison to a standard

chromatogram for a solution containing ^{63}Ni , ^{55}Fe , ^{90}Sr , ^{147}Pm , and ^{90}Y . This chromatogram is shown in Figure 3. All isotopes were NIST traceable and were obtained from either North American Scientific, Inc.² or Isotope Products Laboratories³. The radionuclides were wet-ashed and the residue was dissolved in 0.1 N HNO_3 to a concentration of approximately 300 Bq mL⁻¹ each.

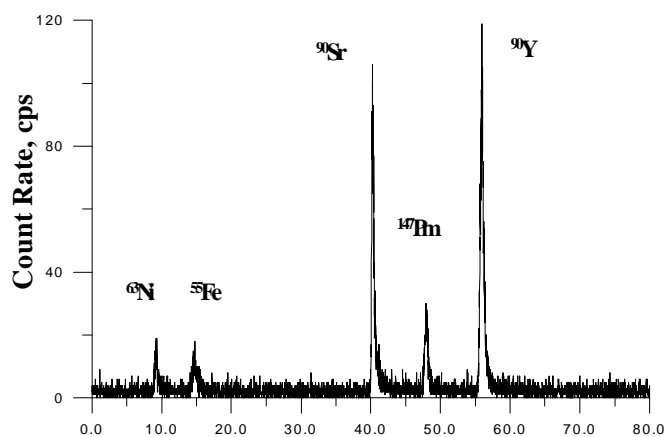


Figure 3. Chromatogram of the standard radionuclide solution

The method for testing the radiological interferences involved determination of the elution time of the potential interfering radionuclide and comparing the elution times of radionuclides in the standard solution. To verify that the potential radiological interference was indeed an interference, 0.5 mL (\approx 50 Bq) of the potential interference was mixed with 0.5 mL of the standardized radionuclide solution and the mixture was analyzed.

The method for testing the effects of chemical interferences involved preparation of simulated samples by mixing varying concentrations of the chemical of interest with the standard radionuclide solution. A 0.5 mL aliquot

of the standard radionuclide solution was mixed with 2.5 mL of varying concentrations of the chemical of interest and allowed to equilibrate for an hour prior to analysis. Elution times and peak areas for the simulated sample were compared to those for the standard.

Plots of detection efficiency as a function of the chemical molar concentration and plots of peak elution time as a function of chemical molar concentration were developed to determine levels of interference.

Results of the radiological interference studies with ^{60}Co , ^{152}Eu , and ^{137}Cs are shown in Figure 4. Tritium, as expected, was not retained in the pre-concentration column and was not an interference. The only interference, ^{137}Cs with ^{63}Ni , would not be a limitation in most DOE applications.

Natural uranium yielded a peak at approximately 40 minutes, which corresponds with the elution time for ^{90}Sr . It is not known if the peak is due to uranium or one or more decay products. If it is uranium, it will be removed when pulse shape discrimination is added to the detector. If it is a beta emitting decay product, it could pose a limitation in the application of the technique to DOE samples. Identification of the radionuclide(s) in the natural uranium peak is under investigation. ^{228}Th produced peaks at approximately 5 min. and 70 min., neither of which were an interference with the radionuclides in the standard.

² North American Scientific, Inc., 7345 Greenbush Avenue, North Hollywood, CA 91605.

³ Isotope Products Laboratories, 3017 N. San Fernando Blvd., Burbank, CA 91504.

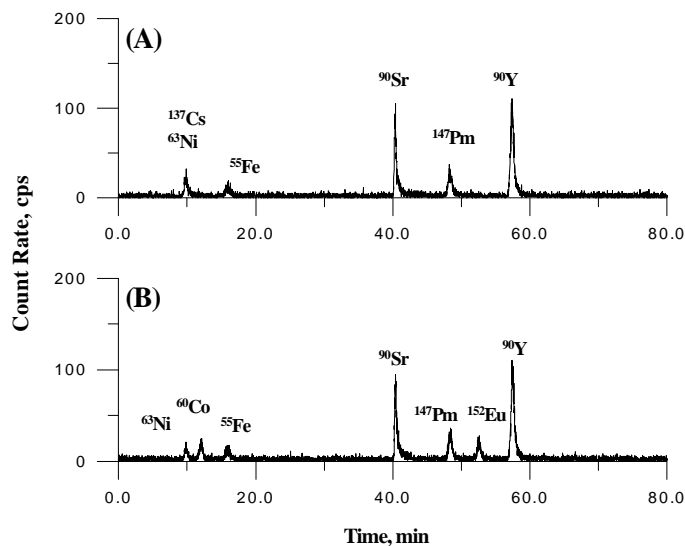


Figure 4. Effect of the radionuclides, ^{60}Co , ^{137}Cs , and ^{152}Eu on the elution of the standard radionuclide solution. Figure (A) shows the co-elution of ^{63}Ni from the standard solution with ^{137}Cs (47.8 Bq), while Figure (B) shows the elution of the standard radionuclide solution with Co-60 (48.0 Bq) and Eu-152 (50.2 Bq).

The types of effects seen in the chemical interference tests are illustrated in Figure 5 for $\text{Al}(\text{NO}_3)_3$, where chromatograms for various concentrations are compared to the standard chromatogram. Here, for example, it is seen that the peaks at 9 min (^{63}Ni) and 15 min (^{55}Fe) are affected (slight shift to a longer elution time) at the lowest concentration tested (0.43 mM), but the other peaks are not. The peak at 40 min. (^{90}Sr) begins to be affected (smaller peak area) at 1.7 mM. The peaks at 47 min. (^{147}Pm) and 56 min. (^{90}Y) are not affected at the highest concentration (3.5 mM) shown here.

Data from chromatograms such as these are displayed in summary form in Figures 6 and 7, where the former shows the effect on elution time and the latter on detection efficiency.

In Figure 6, for example, it is seen that the peak elution time for ^{63}Ni moved outside the 99%

confidence band at a concentration of 0.7 mM but the elution time for ^{90}Y was not effected at the highest concentration tested. In Figure 7, the detection efficiencies for all of the radionuclides decreased below the 99% confidence band at concentrations ranging from 1.7 mM (for ^{63}Ni) to 7 mM (for ^{90}Y). Graphs of this type were plotted for all of the chemicals that were tested. From these graphs, the maximum concentration at which effects were not observed was determined. This concentration was converted to a non-observable effects loading (NEL), which is defined as the number of moles of interferent chemical which produces no observable effect. The rationale for this measure is that the primary mechanism for chemical interferences is competition for sites on the pre-concentration column, which has a finite cation exchange capacity. Presented in Table 2 are NEL's for the chemicals tested. The lowest NEL's were observed for the doubly and triply charged cations, which is consistent with ion exchange theory. No interferences were observed for KCl, NaCl or Na_2SO_4 Therefore, the NEL's in Table 2 are the maximum loadings tested for these chemicals.

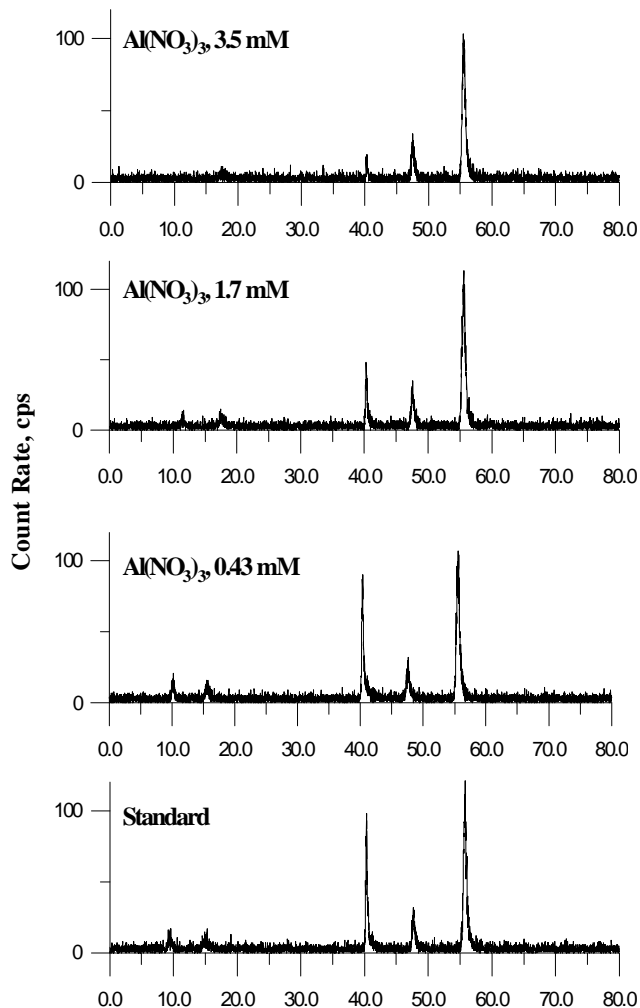


Figure 5. Sample chromatograms of the standard radionuclide solution with varying molar concentrations of $\text{Al}(\text{NO}_3)_3$. Note the changes in the ^{63}Ni , ^{55}Fe and ^{90}Sr peaks.

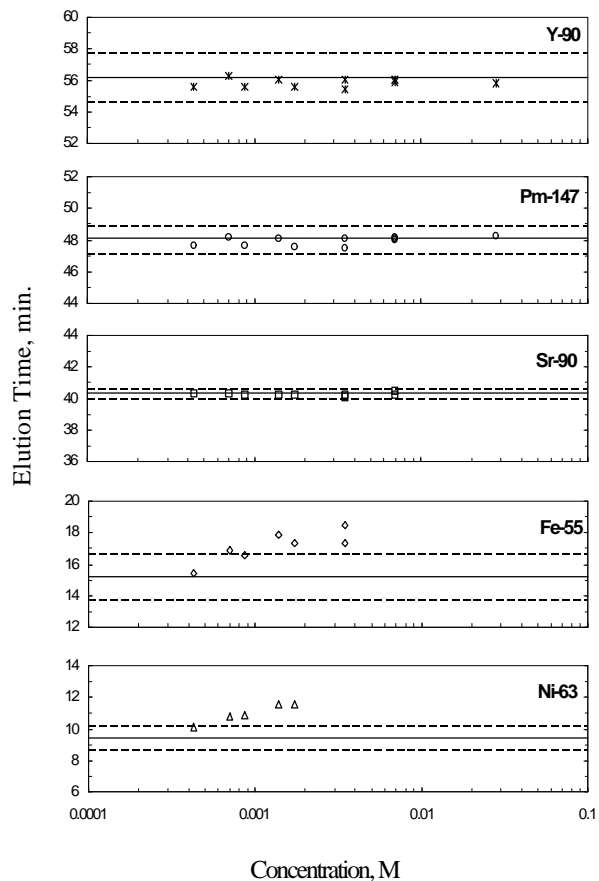


Figure 6. Effect of $\text{Al}(\text{NO}_3)_3$ on peak elution time.

The solid horizontal line represents the expected mean value while the dashed lines represent $\pm 3\sigma$. The absence of a peak elution time for a given concentration indicates the absence of the corresponding peak during the chromatographic analysis.

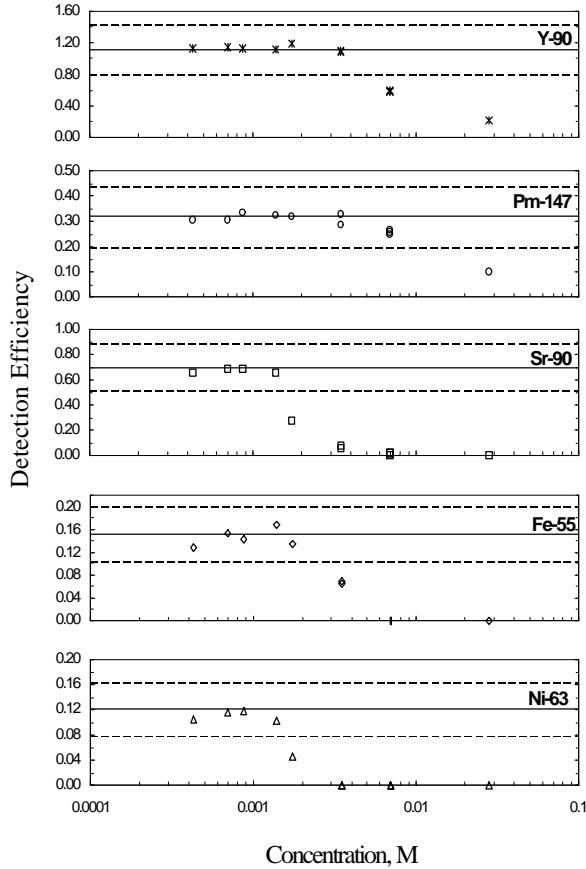


Figure 7. Effect of $\text{Al}(\text{NO}_3)_3$ on detection efficiency.

The solid horizontal line represents the expected mean value while the dashed lines represent $\pm 3\sigma$. Detection efficiency below the minimum detectable activity was assigned a detection efficiency of zero.

Summary

The principal conclusions are as follows:

1. CsI(Tl) provides sufficient pulse shape discrimination for use in the flow-cell detector. However, an improved method of coating is needed to extend the useful life of a detection cell.
2. Of the activation/fission products investigated, only the co-elution of ^{137}Cs and ^{63}Ni produced a radiological interference. Tritium (and presumably other non-ionic radioisotopes) can be separated

during the loading of the solution onto the pre-concentration column.

3. Natural uranium (and/or decay products) produced a radiological interference with ^{90}Sr . This is a potential problem in the application of the technique to DOE samples and will be the subject of additional study. No potential radiological interferences were observed with ^{228}Th .

4. Chemical interferences were observed to some degree for all the chemicals tested except for the chloride solutions, NaCl and KCl, and the sulfate solution, Na_2SO_4 . The specific interference effects were decreased detection efficiencies and changes in peak elution times. The NEL's are tentative targets for development of sample processing protocols, which is the next phase of the work.

Table 2. Non-observable Effects Loading (NEL) values for the chemicals used in this study.

Chemical	Detector Efficiency Criterion μmoles	Peak Elution Criterion μmoles
$\text{Al}(\text{NO}_3)_3$	4	1
$\text{Ca}(\text{NO}_3)_2$	4	1
NaOH	140	140
NaNO_3	350	280
NaHCO_3	34	34
NaNO_2	430	700
Na_2SO_4	60*	60*
KCl	12*	12*
NaCl	160*	160*

Chemical	Detector Efficiency Criterion Activity, Bq	Peak Elution Criterion Activity, Bq
Uranium	5	1

*Maximum loadings tested

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