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Separation and Collection of Iodine, Sulfur, and Phosphorous Anion Complexes for Subsequent Radiochemical Analysis (U)

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SEPARATION AND COLLECTION OF ANION COMPLEXES FOR SUBSEQUENT RADIOCHEMICAL ANALYSIS

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SUMMARY

We have developed a method to separate anion complexes of radioactive sulfur, iodine, and phosphorus to enable determination by radiochemical techniques. This method involves ion chromatographic separation of the anion complexes from other highly emitting radioactive species such as cesium-137 and strontium-90 which interfere with radiochemical analysis. We essentially use the ion chromatograph as a sample pretreatment method. The samples are injected onto a cation exchange column which allows the anions to pass through while retaining the positively charged species. If more than one negatively charged radionuclide is present, the sample is injected onto an anion exchange column and the individual anions are separated from each other as well as from the cations. These anions are collected in the column effluent and measured by nuclear counting methods.

The method was developed to enable measurement of trace radionuclides in radioactive waste and in environmental samples. Trace radionuclides which are present in concentrations of only a few hundred disintegrations per minute per milliliter can be separated and then analyzed using liquid scintillation counting analysis. This paper establishes the separation and collection protocol, collection efficiencies for sulfur, iodine, and phosphorus anion standards, and overall efficiencies and detection limits for the separation and subsequent radiochemical analysis of iodine-129 from both environmental level and high salt waste samples.

INTRODUCTION

Our laboratory provides analytical support for many different types of research programs within the Savannah River Technology Center and throughout the Savannah River Site. A wide variety of sample types including ground water, organics, laboratory waste, process control, sludge, soils, and others are received for many different analyses. These samples are both radioactive and non-radioactive and may contain hazardous materials such as RCRA metals, organics, and flammable solvents. Often these analyses involve measurement of trace constituents in the presence of higher concentrations of interfering species. This is especially common when measuring trace radionuclides in the presence of high concentrations of radioactive cesium and strontium.

We have developed a method for analysis of low levels of radioactive phosphorus, sulfur, and iodine in waste and environmental samples. This method involves ion chromatographic separation from radioactive cesium and strontium isotopes by passage through a cation exchange column. The cesium and strontium (cations) are retained by the column while the iodine, sulfur, and phosphorus, present as anion complexes pass through unretained. The radionuclides of the separated species are then measured using liquid scintillation counting and gamma spectroscopy.

Currently available methods for determination of low-level radionuclides involve chemical separation of each element individually and subsequent radioichemical analysis using nuclear counting techniques. The ion chromatographic method separates all of the elements simultaneously including ones which cannot be determined using existing wet chemical methods. This decreases the length of time required for analysis and the amount of waste generated, as well as limiting personnel radiation and chemical exposure.

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 plumbed for a 500 uL sample size. The large sample size (10 times larger than the standard injection size of 50 uL) was necessary to recover a sufficient volume of the separated sample for subsequent analysis by LSC.

The columns used were CG3/CS3 separator columns for cation separation and AG5/AS5 separator columns for anion separation, both from Dionex. The columns 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 the column.

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 an electrochemically generated regenerant solution running counter current to the eluent stream.

Radioactive samples were separated chromatographically into ion fractions. These fractions were collected and subsequently analyzed using LSC and gamma spectroscopic analysis. 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). The separation and collection method is diagrammed in Figure 1.

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

Nonradioactive IC anion standards were prepared by volumetric dilution with ultrapure deionized water 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. The eluent used was 50 mM sodium carbonate/50 mM sodium bicarbonate for anion separation and 1.6 mM HCl for cation separation. The sample was injected at 0.5 minutes with an eluent flow rate of 1 mL per minute and allowed to elute for 15 minutes. Figure 2 is an ion chromatogram showing the retention times for standard anion complexes including iodate, sulfate, and phosphate. The location and intensity of the peak are dependent upon both the identity and concentration of the eluent solution. The separation protocol and column conditions are listed in Figure 2.

During the chromatographic separation of nonradioactive standards, eluted ions were detected using conductivity detection. The radionuclides separated from the waste solutions were collected by hand in 1 mL (1 minute) fractions and subsequently analyzed using LSC. For LSC, the fractions were collected directly into vials containing 14 mL of Optifluor.

DISCUSSION

Principle of the Method and Experimental Details

The method essentially uses the ion chromatograph as a sample preparation tool. The sample is injected onto the column and the different ions in solution are separated. The separated ions are collected as they exit the column in eluent fractions. These fractions are collected into liquid scintillation coctail and the radionuclides present are measured by liquid scintillation counting.

Two routes for separation were pursued. The first involved injecting the sample onto a low capacity anion exchange resin column and collecting the individual ions as one-minute fractions. The collection efficiency of nonradioactive standards of iodate, sulfate, and phosphate ranged between 93 and 97% (see Table 1). The collection efficiency for an iodine-129 standard collected was 94% overall, including the collection and subsequent liquid scintillation analysis. The liquid scintillation spectrum from the I-129 fraction is shown in Figure 3.

The other separation strategie was to inject the sample onto a low capacity cation exchange resin column. Anions are unretained on this column and pass through in the column void volume. The cations are retained on the column and thus separated completely from the anions. This strategie was used when the anion radioisotopes did not interfere with each other's detection. The collection efficiency of non-radioactive standards is between 97 and 99% using this method (see Table 2). The collection efficiency for an iodine-129 standard collected was 97% overall, including the collection and subsequent liquid scintillation analysis.

Preparation of a Standard Curve

For nonradioactive elemental analyses, standard curves are prepared by plotting the concentration of known standards versus the peak height in conductivity 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 instruments memory. These calibration curves are verified by running a check standard each time the analysis is run. For radioactive standards, the overall efficiency is determined by measuring sample spike recoveries using standards of known activity.

Length of Time Required for Analysis

The length of time for analysis depends on the elution times for the individual anion. After a sample has been properly prepared, the chromatographic run to elute all 3 anions takes 10 minutes. Liquid scintillation measurements were made using a 10 minute count.

Separation of Interfering Species

Samples which contain many different species present in widely differing concentrations are particularly difficult to analyze. As stated earlier, this chromatographic method was developed to be used in the analysis of high activity SRS waste. This waste contains low levels of radioactive iodine, phosphorus, and sulfur in the presence of high levels of radioactive cesium and strontium. Tables 3 and 4 show the activity and half lives of various radioisotopes present in SRS waste. Two of these isotopes, Cs-137 and Sr-90, are high energy beta emmiters. This activity masks the signal from these low-level isotopes and thus prevent their detection and quantitation. Qualitative identification of the radionuclides in the separated ion fractions was done by liquid scintillation counting. Standards and spiked samples were run to determine collection efficiency, counting efficiency, and overall recovery of radioisotopes. After the chromatographic separation was complete, the column was flushed with concentrated eluent to remove any remaining species which may have been retained by the column. This wash was counted by LSC and no activity was found.

The major difficulty encountered with this analysis is the nature of the samples. High level nuclear waste contains many cationic and anionic species at widely differing concentration levels including chemicals from plant separation processes, laboratory waste, fission products, neutron activation products, uranium, plutonium, and other actinides. Environmental samples often contain high levels of nitrates and chlorides. The high concentrations of individual anions and cations prevent the trace constituents from completely interacting with the column stationary phase and thus inhibit separation into discrete fractions. To counteract this effect, nonradioactive carriers (10 uL of the 1000 ppm standards of stable elemental isotopes per 1 mL of sample) were added to the samples. This enabled the trace constituents to more effectively compete with the column surface.

For radionuclide analysis, ion chromatography was used only to separate the ions into discrete fractions for subsequent analysis by liquid scintillation counting and gamma spectroscopy. The ions were collected in 1 mL fractions. Since only a 50 uL 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 uL injection loop, thus increasing the amount of sample injected onto the column and then recovered by ten-fold. Comparison of chromatographic runs using 1-ppm nonradioactive standard solutions showed no effect in precision of accuracy of the data or the effectiveness of the separation.

Analysis of Waste Tank Samples

Increasing the size of the sample loop proved problematic when analyzing waste samples of sample with high salt content. The large amount of anions exceeded the separation capacity of the column and prevented the collection of discrete anion complexes. A waste tank sample with high salt content which had been spiked with a known activity of I-129 was injected onto an anion separation column. The I-129 did not elute in a discrete fraction, as was seen with the I-129 standard. Instead, the I-129 activity bled out over several minutes and could not be collected efficiently. The anion separation method is not suitable for high salt content samples.

The same sample was injected onto a cation separator column using a 0.5 mL sample loop and much better results were obtained. The I-129 eluted in the column void volume (the first minute after sample injection) and was recovered with an overall recovery of 84%.

CONCLUSION

We have developed a method which can separate low levels of radioactive anions from high levels of radioactive cations which would otherwise prohibit their analysis. The method can be used for both environmental and waste samples which are very difficult to analyze because of the wide variety of species found in them in varying concentrations. 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 liquid scintillation counting and gamma counting. Future work includes measuring the separation and collection efficiencies of S-35 and P-32.

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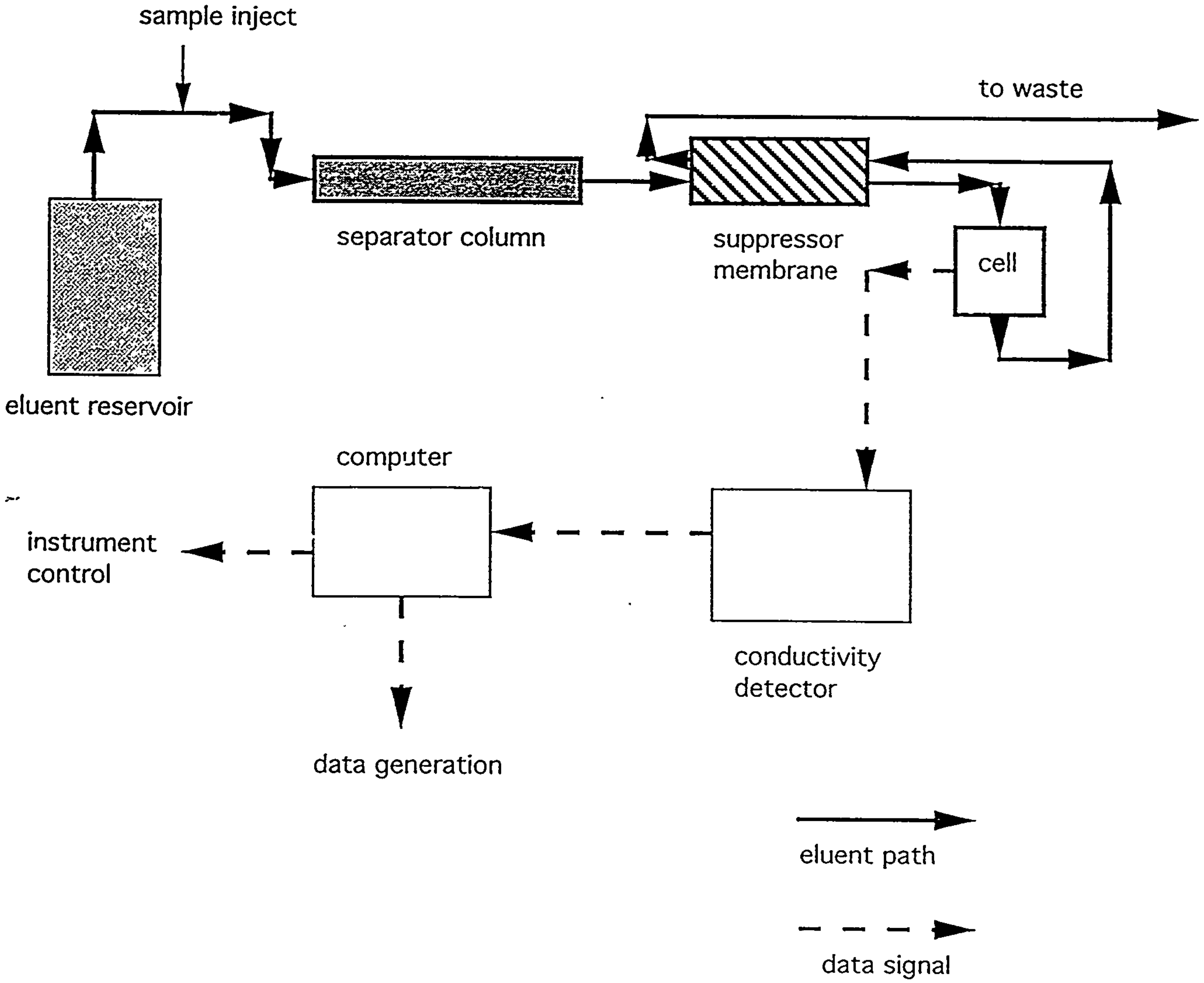
Figure 1: Basic Ion Chromatography Instrument Diagram - Eluent is pumped through a separator column. The sample is injected into this stream and passes through the column which separates the anions in the sample. The separated anions pass through a conductivity cell, the conductivity is recorded and the chromatogram generated. When collecting anion fractions for LSC, the column is disconnected from the conductivity cell and the effluent is collected into LSC cocktail.



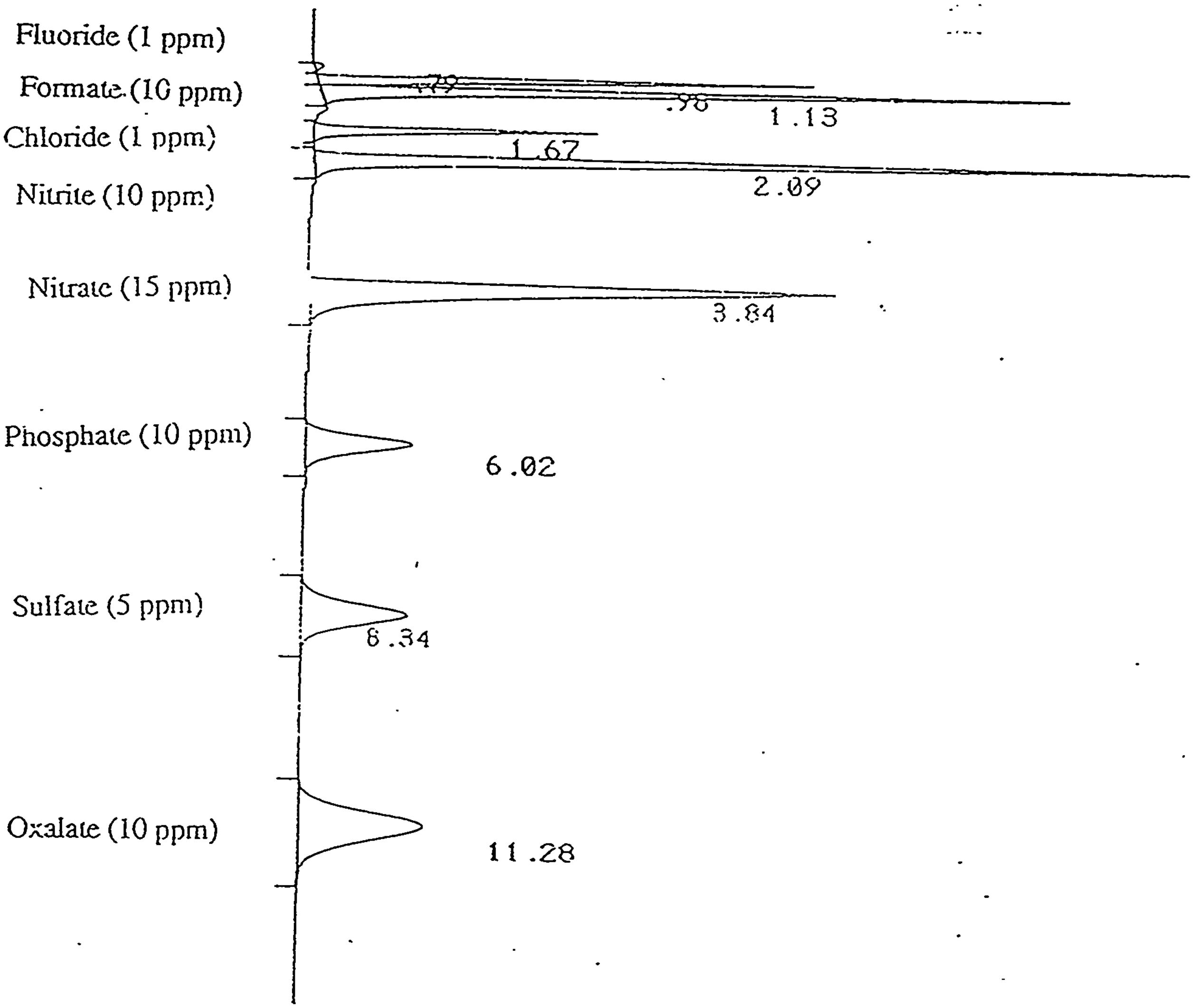


Figure 2: Ion Chromatogram of Nonradioactive Anion Standards.

detector range = 30 uS
integrator attenuation = 1024

Figure 3: LSC Spectrum of I-129 Fraction - Standard was injected onto cation column and the first 1 minute of eluent was collected.

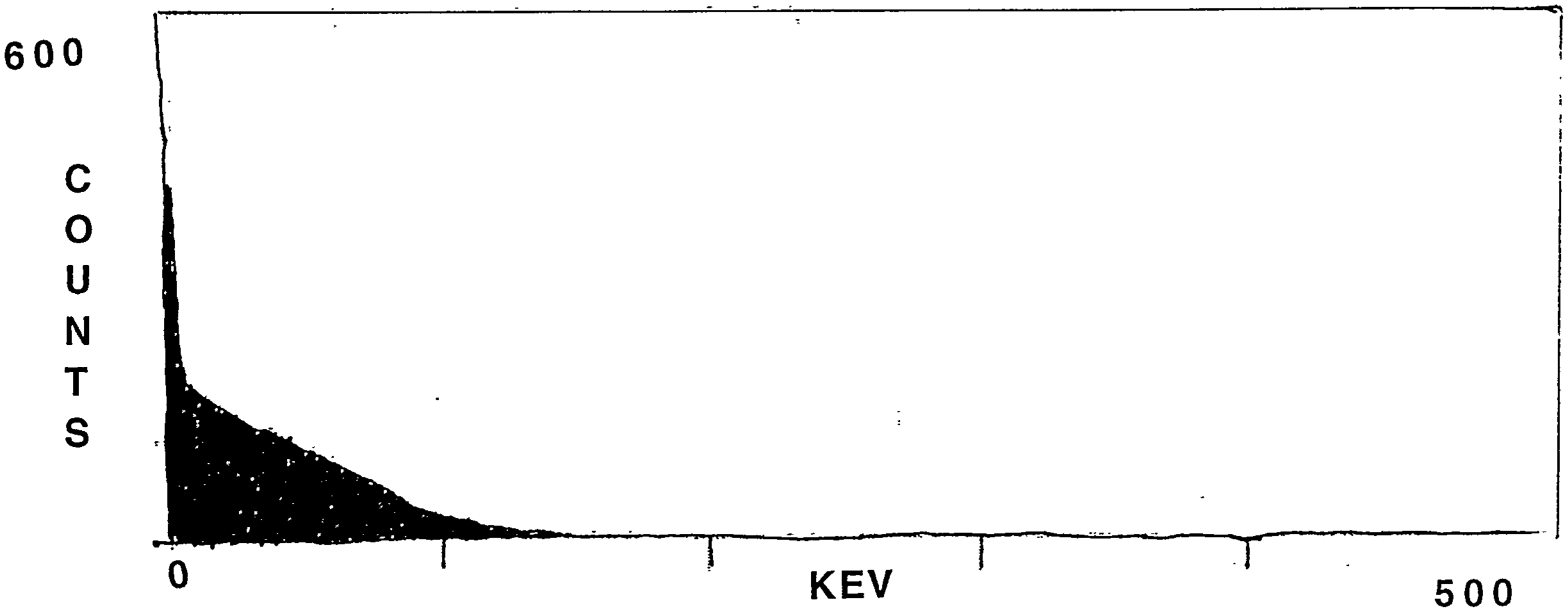


Table 1: Collection Efficiencies of Anion Complexes as Measured by Ion Chromatography, Anion Exchange Column.

Anion Complex	Efficiency	%RSD on 5 Reps.
I -	94	3.8
SO4-2	93	4.6
PO4-3	97	2.9

Table 2: Collection Efficiencies of Anion Complexes as Measured by Ion Chromatography, Cation Exchange Column.

Anion Complex	Efficiency	%RSD on 5 Reps.
I -	97	2.3
SO4-2	99	2.8
PO4-3	98	2.1

Table 3: Radionuclides Required to be Measured in SRS

NUCLIDE	HALF LIFE years
Ni-59	8E04
Ni-63	92
Se-79	7E04
Sr-90	28
Nb-93m	12
Zr-93	1E06
Tc-99	2.1E05
Pd-107	7E06
Sn-126	1E05
Cs-135	2E06
Cs-137	30
Sm-151	93
Th-230	80
U-234	2E05
U-238	5E09
Np-237	2E06
Pu-238	89
Pu-239	2E04
Pu-240	7E03
Pu-241	13
Pu-242	4E05
Am-241	5E02
Am-243	8E03
Cm-244	18

Table 4: Radinuclide Concentrations Measured in SRS Sludge

Isotope	Concentration
Ni59	19
Sr90	1.9
Zr93	1.1
Tc99	2.8
Pd107	12.4
Sn126	0.01
Cs135	1.2
Cs137	7.0
Sm151	0.2
Th230	0.0
U234	1.4
U238	10,9
Np237	106
Pu239	36
Pu240	3
Am243	0.3
Cm244	0.09
Pm147	2.5
Eu154	0.0