

SEQUENTIAL DETERMINATION OF  
THORIUM, URANIUM, NEPTUNIUM, PLUTONIUM  
AMERICIUM AND CURIUM IN WATER

by

Terry F. Rees

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## ABSTRACT

A procedure for the sequential separation of thorium, uranium, neptunium, plutonium, americium and curium from groundwater has been developed. The procedure first uses a chloride anion exchange step to isolate plutonium, neptunium, and uranium from the sample matrix. Each element is then sequentially eluted from the ion exchange column and mounted on individual stainless steel counting discs. The effluent from the first ion exchange column is converted to the nitrate form, and then thorium is sorbed on a nitrate ion exchange column. The effluent, which contains americium and curium, is extracted with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione in xylene to separate the americium and curium from the sample matrix. This extract is mounted on a single disc containing both americium and curium. Thorium is eluted from the ion exchange column and mounted on a separate disc. Accuracy and standard deviations for the sequential separation are comparable to values for single element separations in the literature.

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## INTRODUCTION

One of the major questions yet to be answered concerning the nuclear industry is how to safely handle the radioactive wastes which are generated. At the present time, there are seventy-two nuclear power reactors on line. Assuming a 30 megawatt (MW) power production, a burnup of 33000 MW days/ton and an average flux of  $2.93 \times 10^{13}$  neutrons per  $\text{cm}^2\text{-sec.}$ , each metric ton of uranium fuel charged into the reactor core will, upon reprocessing, result in the generation as waste of 482 g of neptunium-237, 0.835 g plutonium-238, 26.3 g plutonium-239, 10.8 g plutonium-240, 5.04 g plutonium-241, 44.7 g americium-241, and 91.6 g americium-243, as well as large quantities of mixed fission products (1). The half-lives for the fission products are relatively short, approximately 30 years for cesium-137 and strontium-90, while the actinide elements have very long lives, ranging from 86 years for plutonium-238 to 24,400 years for plutonium-239 to  $2.14 \times 10^6$  years for neptunium-237. (One half-life is the time required for one half of the original radioactive atoms to decay.) What this means is that for the first several hundred years, the radioactivity of the fission products predominate, after which the actinide and radium activities dominate. This is graphically illustrated in Figure 1 (2).

Current nuclear waste management philosophy is based on the concept that the wastes must be isolated from the biosphere for a period sufficiently long as to allow the radioactivity to decay to some "safe" level. There are six areas which have in the past or are presently being considered which might meet this requirement. The

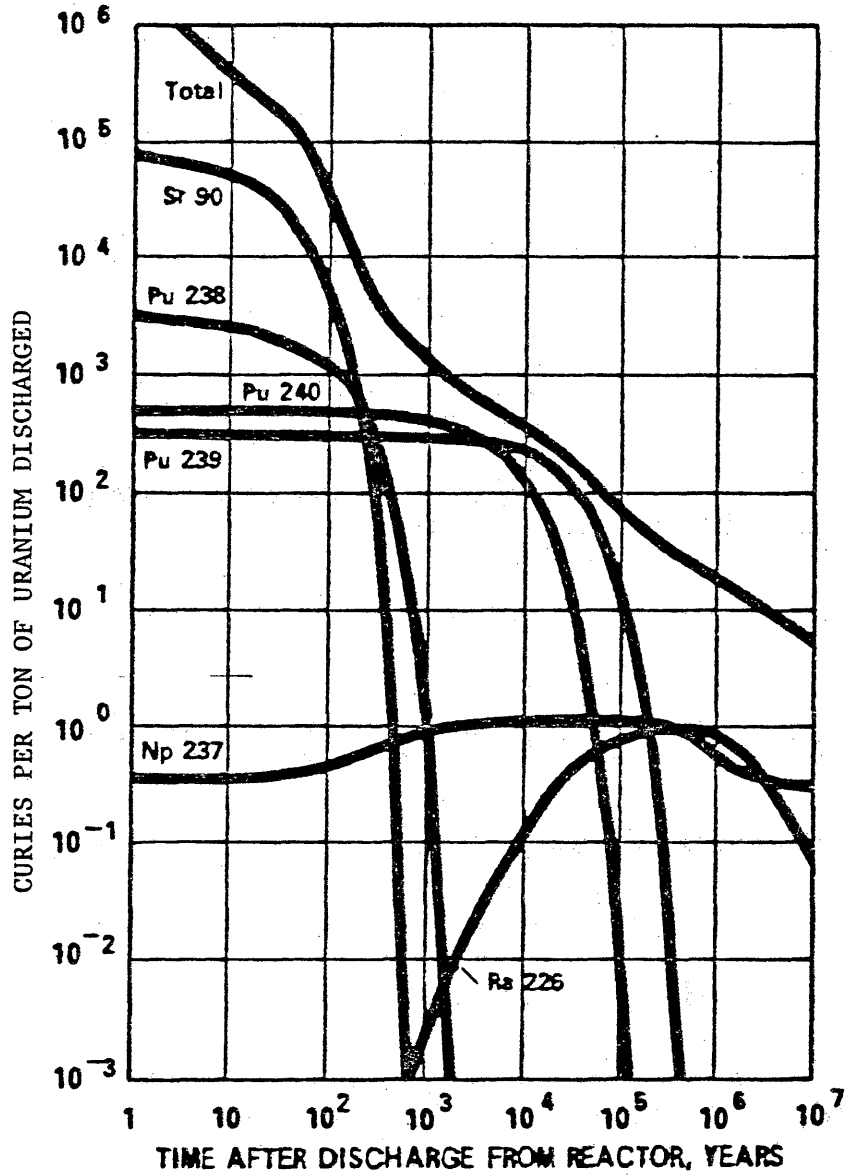


FIGURE 1: Nuclear reactor waste decay with time

first would be to load all the wastes into rockets and then shoot them into space. This would permanently remove the waste from the biosphere, but should a radwaste rocket blow up or have a malfunction, the clean-up operation would be monumental. A second approach is very glamorous, scientifically. The wastes would be partitioned into various element groups. These groups would then be fed into specially designed reactors and be "transmuted" into other radioisotopes. These new radioisotopes would hopefully have shorter half-lives and would be allowed to decay into some innocuous substances. These would then be disposed of in traditional fashion. While this is very attractive, the technology is not yet refined, and this solution is decades away. The third option is surface storage under careful surveillance. Human civilization as we know it has existed for perhaps six thousand years. Since the wastes must be isolated for perhaps millions of years, there is no way to assure that the necessary societal controls will last long enough for the radiation to decay. Three approaches involve placing the wastes into geologic formations which would be expected to stay intact for a sufficiently long period. One such approach would be to bury the waste in glaciers or continental ice sheets. Another would be to dispose of the wastes on or beneath the ocean floor in the middle of tectonic plates where they would remain undisturbed for perhaps millions of years. The final option, and the one receiving the most attention at the present time is that of disposing of the

wastes in deep geologic formations such as salt domes or beds, granite, basalt, or shale. These formations have been around for millions of years, and there is no reason to expect that some specific deposits would not remain undisturbed for millions of years more.

Disposal in deep geologic formations will require an understanding of both the geologic processes which might affect the formations as well as an understanding of the long-term geochemical behavior of the wastes themselves. The geological factors include the possibility of earthquakes or volcanic activity breaching the repository site, the effects of any future glaciation or erosion, the mechanisms of ground water transport and the prediction of any change in ground water flow in the future. The geochemical factors to be considered include the leachability of the selected waste form, the present ground water chemistry, the mechanisms of nuclide removal from groundwaters, and what mechanisms would allow the nuclides in solution to get to the biosphere for uptake in plants and animals, including man.

The current philosophy, then, is the Multiple Barrier Concept. This basically means that there will be a series of independent barriers which will keep the waste from reaching the biosphere. These independent barriers should, as much as possible, remain intact, even if all other barriers are breached, and each barrier should independently be capable of preventing the waste nuclides from reaching the biosphere. This will be accomplished by converting the waste into some dense, non-leachable form. This waste form would then be placed into a

thick, non-corrodible container. This container would be embedded in some clay that would retard water flow and also sorb any radionuclides which might leach from the waste canister. Finally, this entire system would be placed inside some buried geologic formation that would have little or no ground water, and would tend to retard its flow.

In order to evaluate each potential barrier, it will be necessary to develop analytical procedures to test the barriers ability to provide protection. It will be necessary to determine the leachability of the waste forms. It will be necessary to measure distribution coefficients and decontamination factors for various elements on various clay and rock minerals. It will be necessary to have very sensitive techniques for analyzing radionuclides in groundwaters to both assure no migration of radionuclides is occurring, and to monitor the rate and direction of migration if it does occur.

Almost all procedures in the literature are for single element separation and because they optimize conditions for the element of interest, are not amenable to separation of more than one element from a single aliquot of sample. Those procedures which do allow multielement separations have been designed for soils and require steps not necessary for groundwaters. This thesis, then, reports a procedure which has been developed for analyzing all the lower actinides, elements 90 through 96, from a single aliquot of water associated with nuclear waste disposal sites. This procedure will reduce the costs of evaluation of the multiple barriers by speeding the analytical time and reducing the amount of sample which must be collected for analysis.

## ANALYTICAL BACKGROUND

There are a variety of techniques available for the analysis of the lower actinides. These range from direct techniques, where no chemical separations are necessary, to techniques which require great care to insure separation of the analyte from the matrix. The direct procedures include gamma spectrometry and gamma spectrometry in association with X-ray analysis (3-4). They are of limited utility, however, because of an inability to measure adequate sized aliquots and the necessity to maintain an accurate sample-detector geometry. Detection systems used for those procedures requiring careful separations because of high solute concentrations and the resulting degradation of spectra include gamma spectrometry (3-4), mass spectrometry (5-7), alpha spectrometry (8-38), and liquid scintillation (39-40). Most of the purification schemes have been developed for surface features such as soils, surface waters, sediments and biological samples. Only a few of these procedures allow more than one element to be analyzed from an aliquot and most are not directly applicable to groundwater analysis.

Actinide group separations from the sample matrix can be accomplished using coprecipitation and solvent extraction techniques. The common precipitates are fluorides (22,41), hydroxides (16, 18, 22), sulfates (8,14,15,23,35), manganese oxides (42-43), and phosphates (44). All of these procedures must be followed by further purification prior to counting. The major classes of compounds used for solvent extraction are the amines (14,15,22,28,32,36,45-48), the organic phosphates (13,19, 25,29-31,36,41,45,50-54), the ketones and B-diketones (41,55,56), and

the polyglycols (57). These procedures can be used both for group separations and for final purification from other actinides.

A large number of analytical techniques are based on the tendency of the actinides to form stable anionic complexes. These complexes are then separated by anion exchange. Aqueous nitrate complexation accounts for most of the ion exchange techniques (9,10,20,21,27,35,56) followed by alcoholic nitrate procedures (32,36,38). The alcoholic procedures are used to separate the +3 oxidation states which are not efficiently isolated from aqueous media. Thiocyanate complexes are also used to separate the +3 elements (36). Chloride complexes are often used to separate uranium and neptunium which form relatively weak nitrate complexes (16,41).

Final preparation of a planchet for counting can be accomplished either through evaporation of a purified solution or electrodeposition of the analyte from solution. The efficiency of electrodeposition depends on the electrolyte, current, pH and purity of the plating solution. The common electrolytes include oxalate (11,28), sodium sulfate-bisulfate mixtures (17), chlorides (20,27), various ammonium salts (11), and organics (58).

The procedure, which could be applied to any water suspected to be contaminated, is based on ion exchange, solvent extraction and electrodeposition. The individual properties exploited for each element include the following:

Thorium is present in aqueous media almost exclusively as Th(IV). It forms stable nitrate anionic complexes, but does not form stable chloro complexes. Thorium extracts quantitatively into the xylene solution of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyl-

trifluoroacetone, or TTA) from aqueous nitrate solutions above pH 1.

Protactinium is not included in the separation scheme since the only long-lived isotope, Pa-231, is not formed from common decay schemes and therefore would not be expected in significant amounts in groundwaters associated with waste sites. However, because the chemistry of protactinium closely mimics that of neptunium, it is predicted that protactinium would follow neptunium through the separation.

Uranium can exist as U(III), U(IV), U(V), and U(VI). However, U(VI) is the most mobile and is the state expected in groundwaters. Uranium forms stable U(VI) chloro complexes and is easily separated by anion exchange. It also extracts into TTA-Xylene solutions from aqueous nitrate solutions above pH 5.

Neptunium can exist as Np(III), Np(IV), Np(V), Np(VI), and Np(VII). Neptunium (V) is the most stable under normal aqueous conditions. Both Np(IV) and Np(VI) form chloro complexes which are useful for ion exchange. Neptunium is efficiently electrodeposited anodically as the hydroxide from 4 M ammonium chloride solution at approximately pH 5.

Plutonium, like uranium and neptunium, exists in +3 to +6 oxidation states. Unlike uranium and neptunium, however, the couples between the various oxidation states are close to each other, and therefore plutonium tends to disproportionate. All four states can be present in a given solution. Both Pu(IV) and Pu(VI) form chloride anionic complexes useful for ion exchange. Plutonium, like neptunium, can be electrodeposited from ammonium chloride solutions at around pH 5.



Americium and curium are considered together since their chemistries make it nearly impossible to separate one from the other. Both exist entirely in the +3 oxidation state under normal conditions. Both form complexes which are generally not useable for anion exchange. Both americium and curium extract weakly from nitrate solutions above pH 3.5 into the xylene solution of TTA. Even though it is nearly impossible to separate these two elements, by using alpha spectrometry, individual analyses can be obtained because the alpha particles which they emit have different energies.

## SEQUENTIAL SEPARATION

This procedure allows Th-228, Th-230, Th-232, U-234, U-238, Np-237, Pu-238, Pu-239,40, Am-241 and Cm-244 to be analyzed from a single aliquot of groundwater sample. Each element is separated sequentially, then mounted on a stainless steel disc for alpha spectrometric analysis (see Appendix A). The individual isotopes are calculated from the resulting alpha spectra.

Reagents and Apparatus

All chemicals used were reagent grade. Dilute acids were made by diluting reagent grade concentrated acids with deionized water. Nitric acid,  $\text{HNO}_3$ ; 16 N, 8 N, 1 N, and 0.1 N. Hydrochloric acid,  $\text{HCl}$ ; 12 N, 9 N, and 1 N. Hydrofluoric acid,  $\text{HF}$ ; 30 N. Perchloric acid,  $\text{HClO}_4$ ; 70%. Ammonium hydroxide,  $\text{NH}_4\text{OH}$ ; 1 N. Neptunium strip solution; 4 N  $\text{HCl}$ --0.1 N  $\text{HF}$ . Plutonium strip solution; 9 N  $\text{HCl}$ --0.05 M  $\text{NH}_4\text{I}$ . Uranium strip solution; 0.4 N  $\text{HCl}$ --1 N  $\text{HF}$ . Ammonium acetate buffer, pH 5: mix 100 mL 1.5 N  $\text{CH}_3\text{COOH}$  and 100 mL 3 M  $\text{CH}_3\text{COONH}_4$  and adjust the pH to 5 with dilute acetic acid or ammonium hydroxide. 4,4,4-trifluoro-1-(2-thienyl)-1,3-butane dione (TTA); 0.5 M in xylene. Ammonium chloride,  $\text{NH}_4\text{Cl}$ ; 4 M. Anion exchange resin, Biorad AG 1 X 8, chloride form, 100-200 mesh. Tracer solutions of Th-229, U-232, Np-239, Pu,-242, and Am-243, prepared according to Sill (14)

Ion exchange columns, 0.7 X 15 cm. Electroplating cells, Teflon. Glass vials, 7 mL.

Standardization

Chemical yields were determined by the method of isotopic dilution. Known quantities of calibrated tracer isotopes were added

to the sample prior to digestion. The added tracers have alpha energies different from the isotopes of interest (with the exception of Np-239 which emits beta particles and must be counted using a beta proportional counter to determine recovery). Since the alpha spectrometer can resolve the different energies, and since the added tracers are subjected to the same chemical reactions as the analyte isotopes, it can be assumed that the recovery of the tracer isotopes is the same as the analyte isotopes. Reagent blanks were found to be contamination free.

#### Procedure

Figure 2 is a schematic representation of this separation procedure. A known volume of the groundwater is measured into a Teflon beaker. Calibrated quantities of Th-229, U-232, Np-239, Pu-242, and Am-243 are added. Sufficient concentrated  $\text{HNO}_3$  is added to render the solution at least 1 N. One mL  $\text{HClO}_4$  is added for each liter of sample taken. The sample is evaporated to dryness on a hot plate and the residue is dissolved in 9 N  $\text{HCl}$ . A repeated treatment with nitric and perchloric acids may be needed if there are high levels of organics in the sample and recovery is low.

Plutonium, neptunium and uranium separation. An anion exchange column is prepared by pouring a slurry of Biorad AG 1 X 8 resin, chloride form, into a Teflon-wool-plugged column. The excess water is allowed to drain from the column. The resin bed, which should be approximately 2 cm deep, is rinsed with 50 mL 9 N  $\text{HCl}$ . The prepared sample is eluted through the prepared column which is then rinsed with 10 mL 9 N  $\text{HCl}$ . The eluate and rinses are collected into a clean Teflon beaker. This

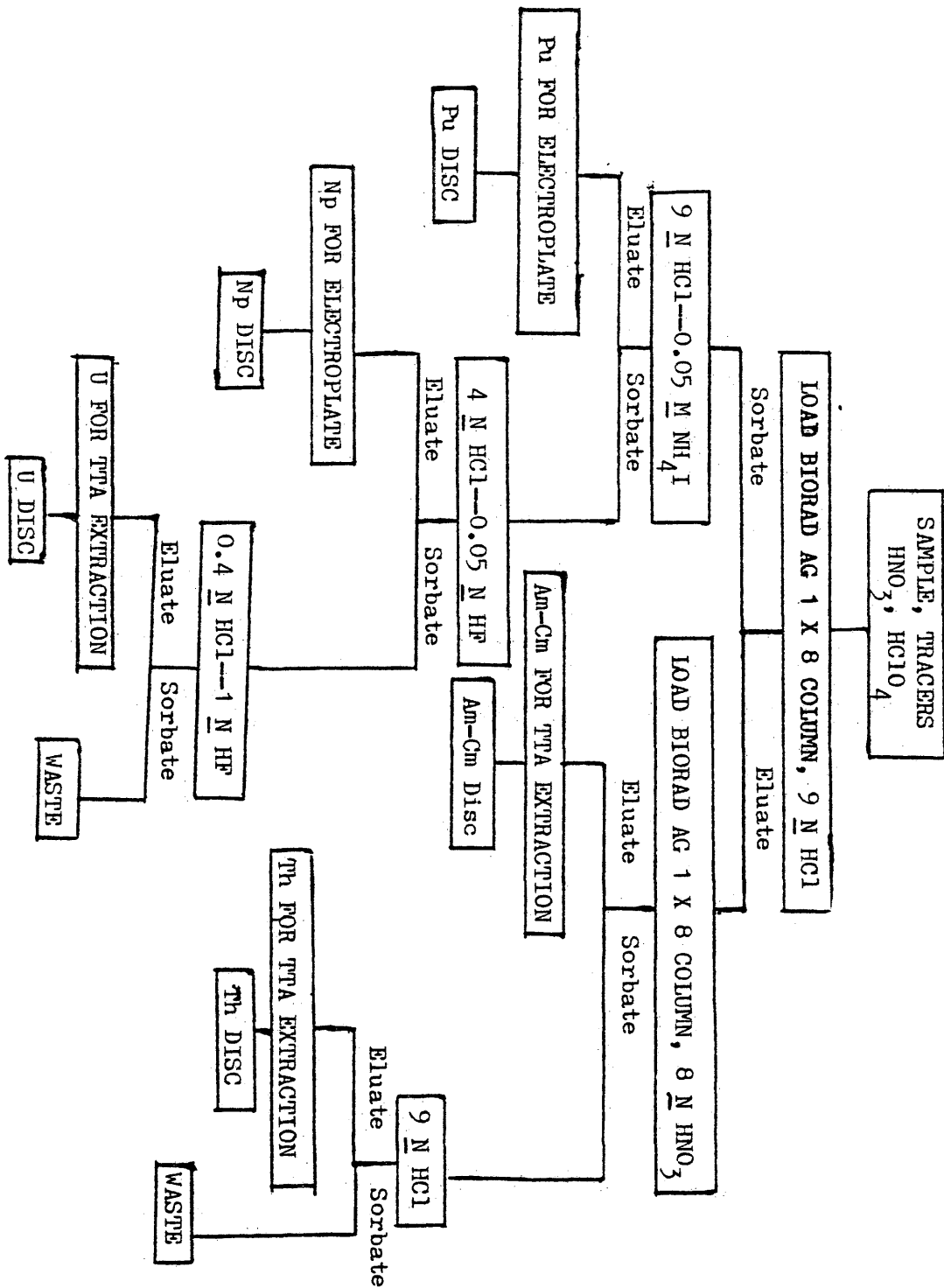


FIGURE 2: Sequential Separation Schematic

solution is evaporated to dryness and the residue is used for the Thorium-Americium separation below.

Plutonium is eluted from the column using the plutonium strip solution. The eluate is collected in a separate clean Teflon beaker. Neptunium is eluted from the column next using the neptunium strip solution. This eluate is also collected into a separate clean Teflon beaker. Finally the uranium is eluted from the column using the uranium strip solution and this eluate is collected into a separate, clean Teflon beaker. The plutonium, neptunium and uranium eluates are evaporated to dryness. The plutonium and neptunium fractions are electroplated onto stainless steel discs in the same fashion. The evaporated residues are treated by adding 16 N  $\text{HNO}_3$  and 0.25 mL  $\text{HClO}_4$  and evaporated to dryness. The residue is dissolved in 9 N  $\text{HCl}$  and again evaporated, this time to approximately 0.25 mL. This drop is then diluted with 2.5 mL 4 M  $\text{NH}_4\text{Cl}$ , the pH is adjusted to around 5 using dilute  $\text{HCl}$  and/or  $\text{NH}_4\text{OH}$ , and the resulting solution is transferred to a Teflon plating cell. The analyte is then electroplated at 0.6 ampere for 1 hour. Before the current is turned off, the solution is made basic with 1 N  $\text{NH}_4\text{OH}$  and electroplated for one additional minute. The current is stopped, the plating cell rinsed with 1 N  $\text{NH}_4\text{OH}$ , and the plated disc is removed, dried, and analyzed by alpha spectrometry.

The uranium fraction is treated as follows: The dried residue is dissolved in 16 N  $\text{HNO}_3$  and evaporated to dryness. This residue is dissolved in 0.1 N  $\text{HNO}_3$  and transferred to a small glass vial. One

milliliter of the ammonium acetate buffer is added. Two milliliters of the 0.5 M TTA is added and the solution is extracted. The two phases are allowed to separate, and the organic phase is removed with an eyedropper and evaporated onto a stainless steel disc. The dried disc is flamed to remove residual organics before being counted.

Thorium-ameridium separation. The dried residue from the first ion exchange separation is dissolved in 16 N HNO<sub>3</sub> and evaporated to dryness. This residue is dissolved in 8 N HNO<sub>3</sub>. An anion exchange column is prepared as before, only it is pretreated by eluting 50 mL 8 N HNO<sub>3</sub> through the resin bed. The prepared thorium-ameridium fraction is eluted through the column which is then rinsed with 10 mL 8 N HNO<sub>3</sub>. The eluate and rinses are collected into a clean Teflon beaker. This fraction, which contains the ameridium and curium, is evaporated to dryness, dissolved in 16 N HNO<sub>3</sub> and again evaporated to dryness. The residue is dissolved with 0.1 N HNO<sub>3</sub> and is transferred to a small glass vial. One mL of the ammonium acetate buffer and 2 mL of the 0.5 M TTA are added, and the solution is extracted. The phases are allowed to separate and the organic phase is evaporated onto a stainless steel disc in the same fashion as the uranium. The disc is then flamed and counted.

Thorium is eluted from the column using 12 N HCl. The eluate is evaporated to dryness, dissolved in 16 N HNO<sub>3</sub> and again evaporated to dryness. The residue is dissolved in 0.1 N HNO<sub>3</sub> and is transferred to a small glass vial. Two mL of the 0.5 M TTA is added and the solution is

extracted. The phases are allowed to separate and the organic phase is evaporated onto a stainless steel disc. The disc is flamed and then counted on the alpha spectrometer.

## DISCUSSION

Since no standard solution of the lower actinides was available, and since we could not do an inter-laboratory comparison study, the accuracy of the sequential separation procedure was evaluated by comparing its analytical results to results obtained using standard techniques, and by comparison to the method of additions result. The procedures selected as being "state of the art" were published by Sill (15). His procedures have been widely referred to, and are accepted by the radiochemical community. The standard additions technique involved making a series of measurements on an unknown sample. First, each isotope was analyzed by the sequential method on an unmodified aliquot of sample. Then replicate aliquots of the sample were analyzed using the sequential technique after the addition of calibrated quantities of analyte isotope. The data set was then plotted with the nominal added value on the abscissa and the analytical result on the ordinate. The least squares fit was then applied. The intercept was taken to be the analytical value of the unknown. This technique was used for two unknown samples which are described in Appendix B.

Bias was also investigated by plotting curves of nominal concentrations (concentrations added to the sample) vs the analytical values as determined by the sequential separation over several orders of magnitude. Once again, the intercept was used to determine any bias which might have been present. These regression curves were also used to determine a linear range for the procedure for each isotope.

Precision was determined for each element by calculating a pooled standard deviation over the entire concentration range of linearity.



This pooled standard deviation was then compared to that reported by Sill(15). This is true for thorium, uranium and plutonium. No published standard deviation for neptunium analyses was found. The procedures for separating americium and curium are included in the procedure for completeness. However, no evaluation work was possible, since before this phase could be completed, we received notice that the site which receives our waste would no longer accept americium and curium.

All concentrations reported in the following pages are given in the radiometric terms of disintegrations per minute per liter (d/m/L). These values can easily be converted to molar concentrations using the specific activity for each isotope, which can be calculated from Equation 5 in Appendix A. All statistical results are at the 95% confidence level.

#### Thorium Results

The accuracy of the thorium separation was determined as described above. Analysis by the recognized procedure gave values of  $17 \pm 2$  d/m/L and  $19 \pm 2$  d/m/L for Unknowns 1 and 2 respectively. Analysis by the sequential procedure gave results of  $20 \pm 2$  and  $19 \pm 2$  d/m/L. Finally, the method of additions technique yielded results of  $20 \pm 10$  d/m/L for Unknown 1 and  $21 \pm 5$  d/m/L for Unknown 2. The curves for these analyses, as well as the confidence interval plots as described in Kleinbaum and Kupper, chapter 5(59), are given in Figures 3 and 4. As can be seen from the standard deviations, there are no statistically significant differences in the three analyses.

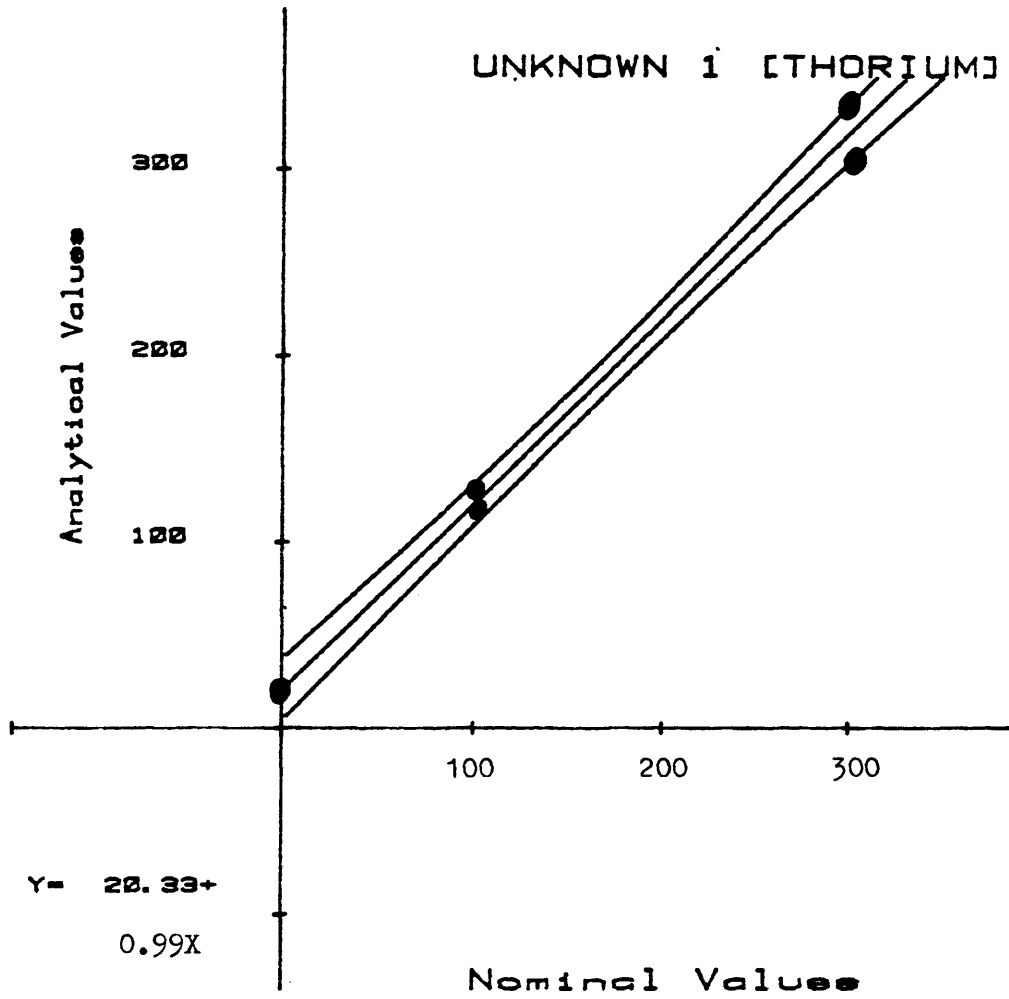


FIGURE 3: Thorium analysis of Unknown 1 by the method of additions. (Values are d/m/L)

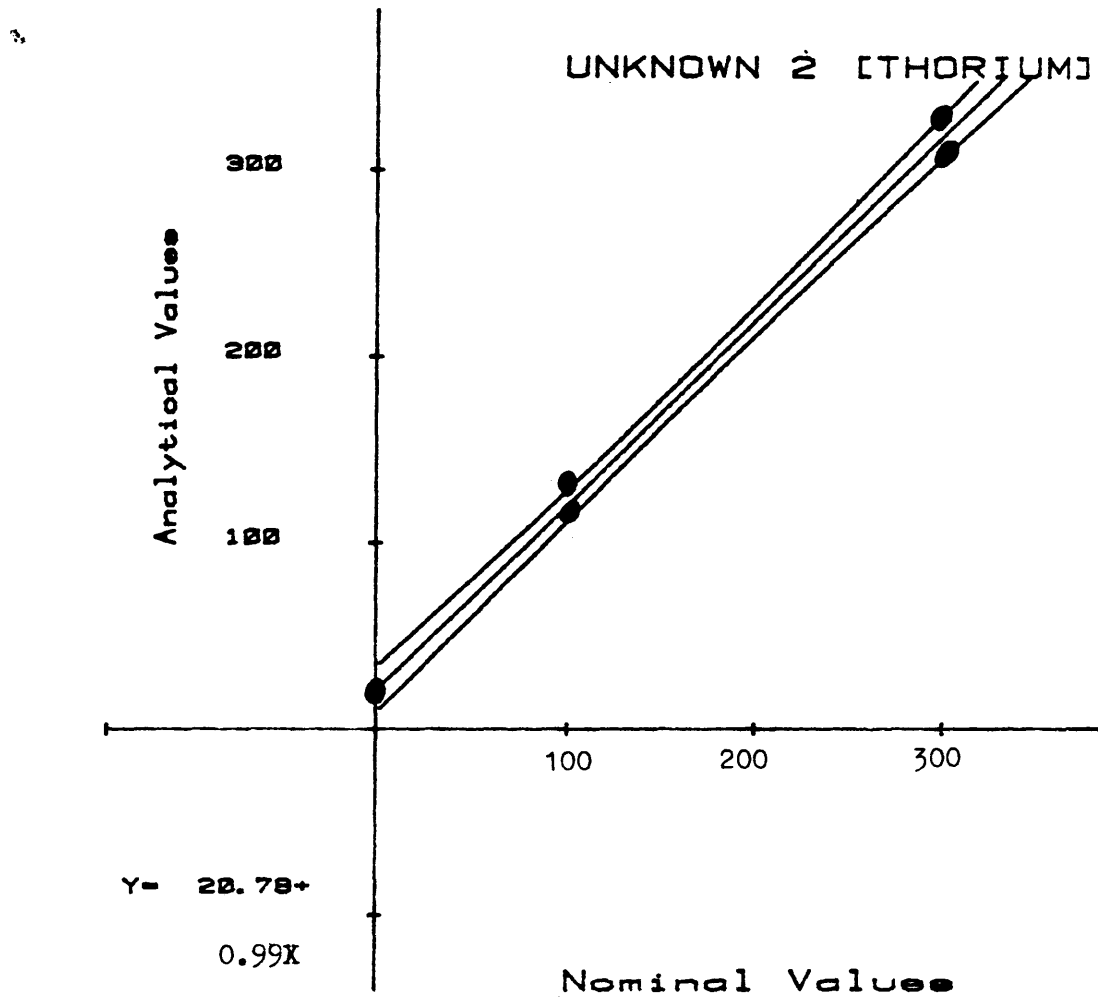


FIGURE 4: Thorium analysis of Unknown 2 by the method of additions. (Values are d/m/L)

The regression line for the analysis over a concentration range of three orders of magnitude is shown in Figure 5. Table 1 is the analysis of variance table for the thorium regression line. The intercept value of -2.11 is not statistically different from zero using a t-statistic with 22 degrees of freedom, suggesting there is no apparent bias in the thorium separation. The slope is equal to one.

The extent of linearity was determined by analyzing replicate aliquots of a relatively high level sample and seeing if the regression equation would predict its actual analytical value. The regression equation predicted a value of  $30017 \pm 178$  d/m/L. The actual analytical value was  $29457 \pm 3$  d/m/L. Since the confidence intervals overlap, these values are not significantly different, and the procedure appears linear at least over the range of zero to 30000 d/m/L.

One additional measure of accuracy is to determine the recovery of the added tracer. Our measured recovery of  $100 \pm 5\%$  agrees well with the published recovery of 98% for the single element analysis.

The pooled standard deviation based on 21 separate analyses (giving 18 degrees of freedom) was 15 d/m/L. This compares to the reported standard deviation of 11 d/m at 265 d/m reported by Sill.

#### Uranium Results

Analysis of uranium by the recognized procedure (15) gave a value of  $< 1$  d/m/L for Unknown 1 and  $70 \pm 5$  d/m/L for Unknown 2. Analysis by the sequential procedure gave results of less than 1 and  $64 \pm 3$  d/m/L for Unknowns 1 and 2, respectively. Analysis by the method of additions gave values of less than 1 and  $62 \pm 2$  d/m/L. The curves for these analyses are given in Figures 6 and 7. As can be seen from the standard

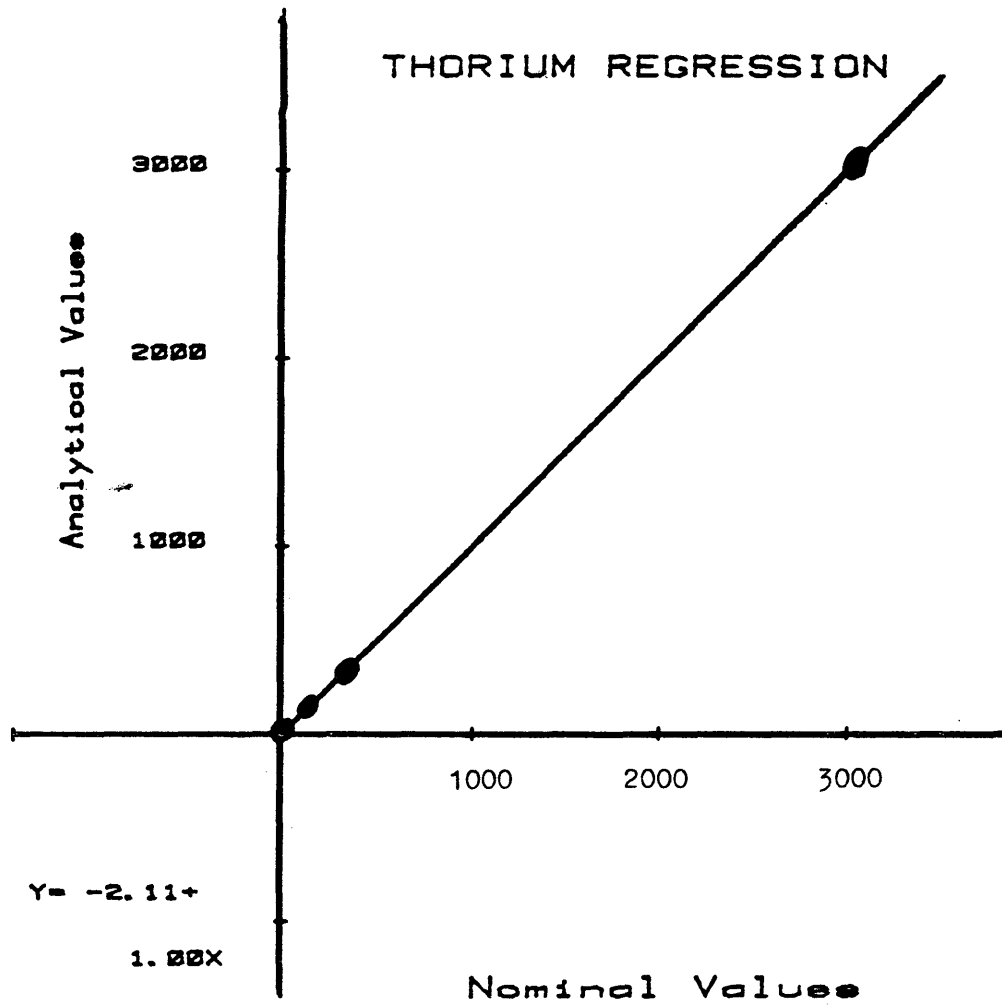


FIGURE 5: Regression line for the Thorium analysis (Values are d/m/L)

TABLE 1: Analysis of Variance Table for the Thorium Regression Line.

SOURCE OF VARIATION	SUM OF SQUARES	DEG. OF FREEDOM	MEAN SQUARE
Total	34572295	22	1571488
Regression	34588726	1	34588726
Residual	3575	1	3575

F STATISTIC = 203052

DF Num = 1

DF Den = 21

$R^2 = 1.00$

deviations, there are no statistically significant differences in the three sets of analyses.

The regression line for the analysis over a concentration range of approximately three orders of magnitude is shown in Figure 8. Table 2 is the analysis of variance table for the regression line for uranium. The intercept value of 1.33 is not statistically different from zero using a t-statistic with 21 degrees of freedom, indicating there is no apparent bias in the uranium separation. The slope is equal to one.

The extent of linearity was evaluated in the same fashion as for thorium. The regression equation predicted a value of  $41700 \pm 182$  d/m/L. The actual analytical value was  $41538 \pm 1197$  d/m/L. These values are not significantly different, and the procedure appears linear over the range of zero to 40000 d/m/L.

The recoveries of the added tracer were  $100 \pm 10\%$ . This agrees well with the published recovery of 94% for the single element analysis of uranium.

The pooled standard deviation based on 20 separate analyses (giving 15 degrees of freedom) was 15 d/m/L. The published value of 40 d/m at 6020 d/m is comparable.

#### Neptunium Results

Analysis of neptunium by the recognized procedure gave values of  $5 \pm 4$  d/m/L and  $102 \pm 6$  d/m/L for Unknowns 1 and 2, respectively. Analysis by the sequential procedure gave results of  $9 \pm 3$  and  $93 \pm 5$  d/m/L for Unknowns 1 and 2, respectively. Analysis by the method of additions gave values of  $10 \pm 8$  and  $93 \pm 12$  d/m/L. The curves for these analyses are given in Figures 9 and 10. As can be seen by the

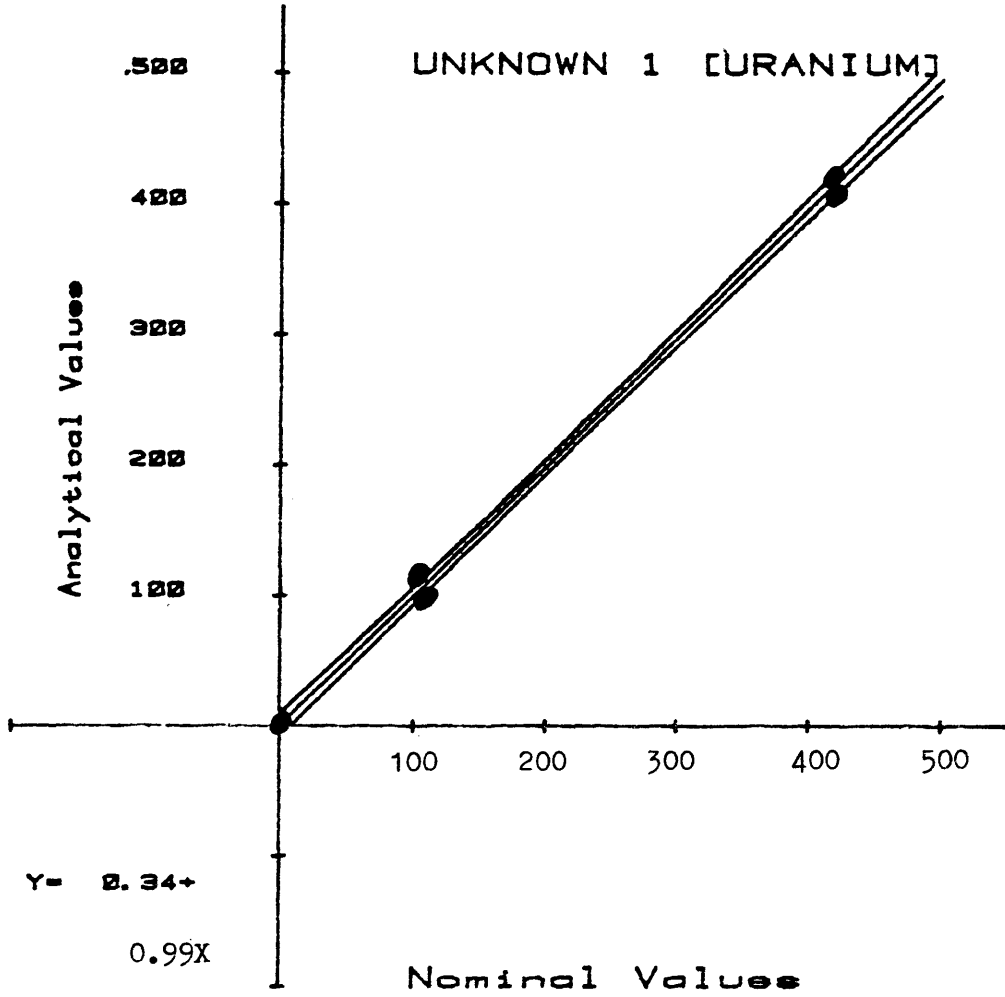


FIGURE 6: Uranium analysis of Unknown 1 by the method of additions. (Values in d/m/L)



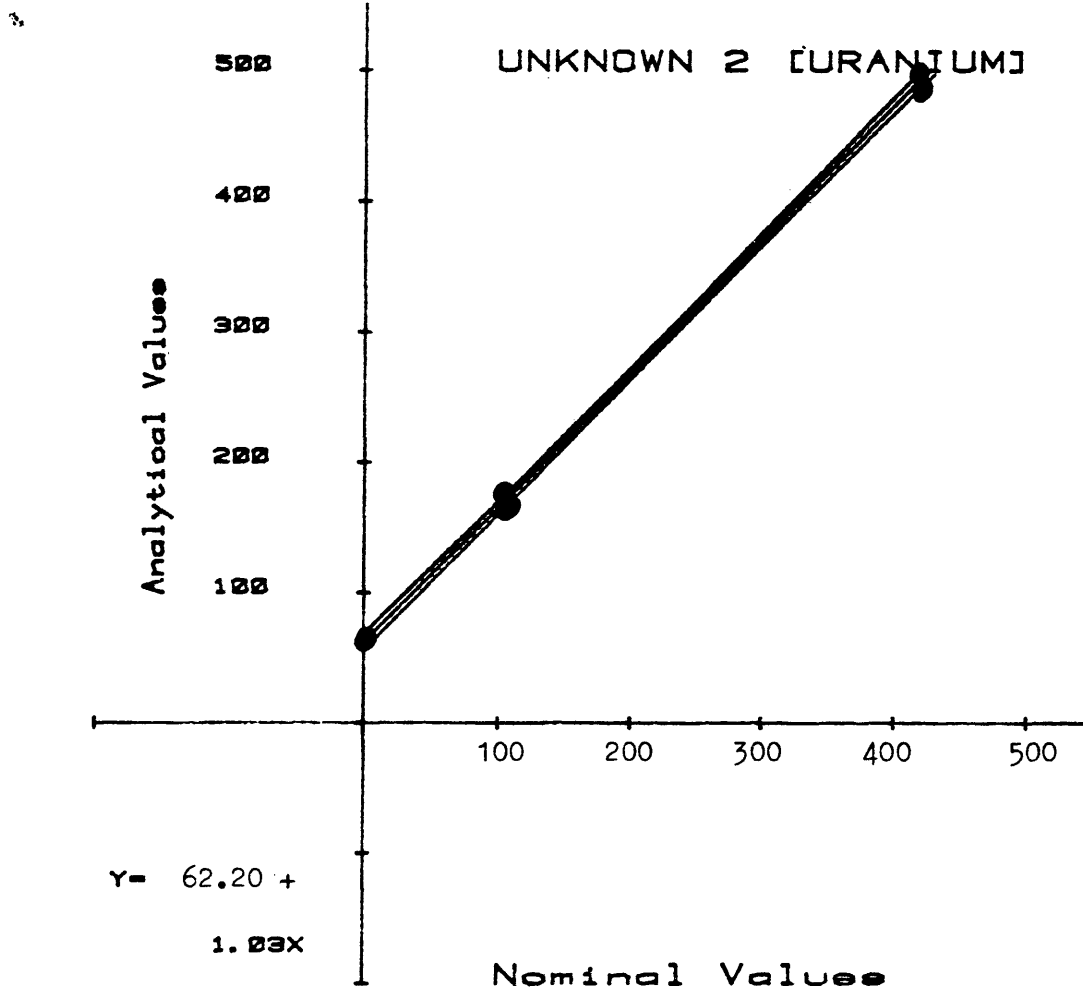


FIGURE 7: Uranium analysis of Unknown 2 by the method of additions. (Values in d/m/L).

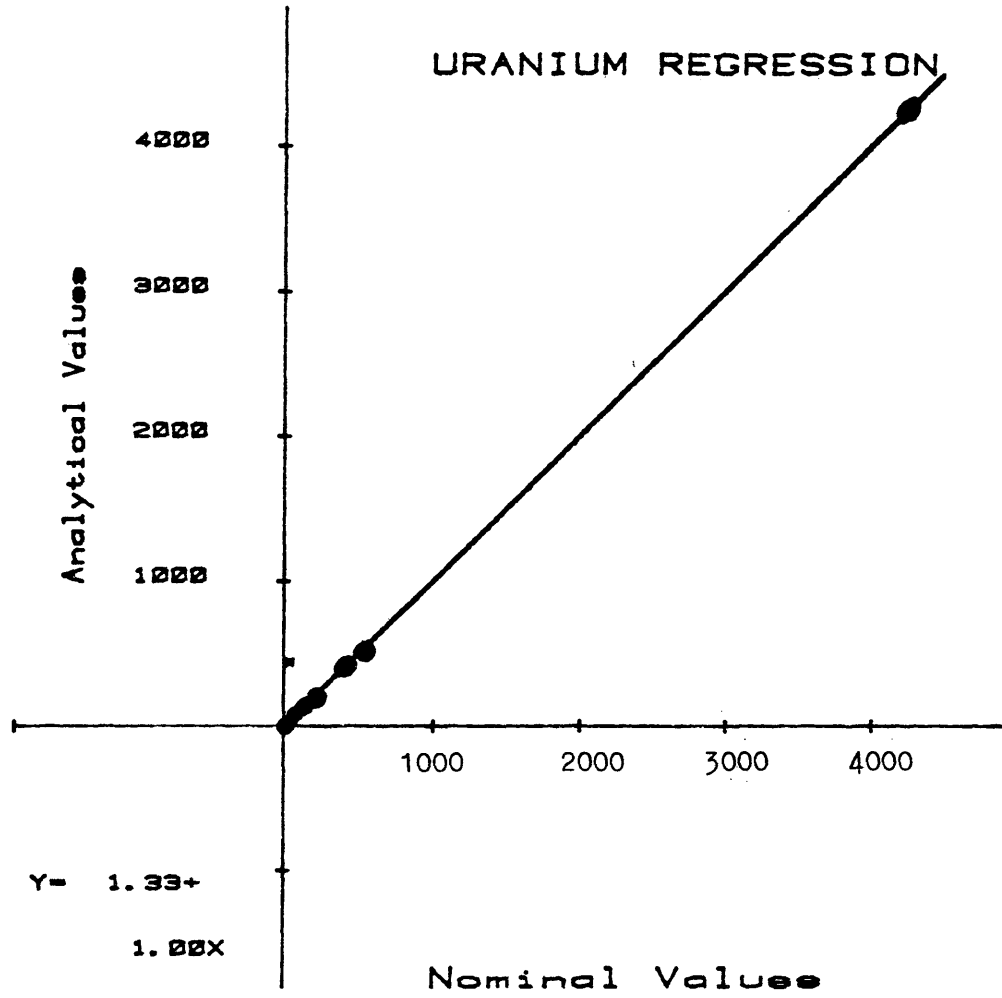


FIGURE 8: Regression line for the Uranium analysis.  
(Values in d/m/L)

TABLE 2: Analysis of Variance Table for the Uranium Regression Line

SOURCE OF VARIATION	SUM OF SQUARES	DEG OF FREEDOM	MEAN SQUARE
Total	57597597	21	3223695
Regression	57594964	1	57594964
Residual	2696	20	131

F STATISTIC = 514196

DF Num = 1

DF Den = 20

$R^2 = 1.00$

standard deviations, there are no statistically significant differences in the three sets of analyses.

The regression line for the analysis over a concentration range of approximately three orders of magnitude is shown in Figure 11. Table 3 is the analysis of variance table for the regression line. The intercept value of  $-3.74$  is not significantly different from zero using a  $t$ -statistic with 22 degrees of freedom, indicating there is no apparent bias in the neptunium separation. The slope is equal to one.

The extent of linearity was determined as described earlier. The regression equation predicted a value of  $8493 \pm 120$  d/m/L. The actual analytical value was  $8433 \pm 231$  d/m/L. These values are not significantly different, and the procedure appears linear in the range of zero to approximately 10000.

The recoveries of the added tracer were  $72 \pm 3\%$ . While relatively low, it compares well with the published value of 77%. Apparently the neptunium is slowly reduced on the ion exchange column, eluting into the waste solution. This results in low recovery. It is important, therefore, to keep the residence time on the column as short as practical.

The pooled standard deviation based on 23 different analyses (giving 18 degrees of freedom) was 14 d/m/L. A published value of the standard deviation for the analysis of neptunium could not be found.

#### Plutonium Results

Analysis of plutonium by the recognized procedure gave values of  $200 \pm 5$  and  $710 \pm 15$  d/m/L for Unknowns 1 and 2, respectively.

Analysis by the sequential procedure gave results of  $189 \pm 5$  and  $704 \pm 8$

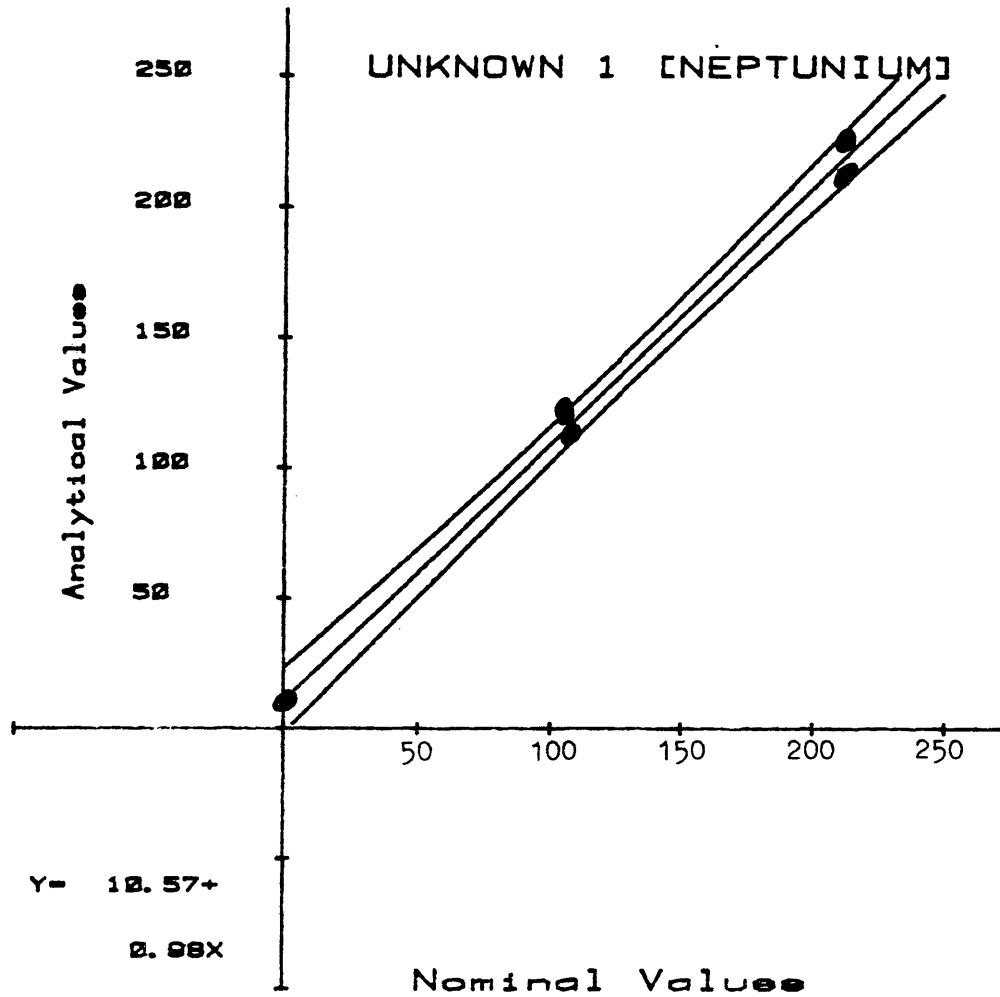


FIGURE 9: Neptunium analysis of Unknown 1 by the method of additions. (Values are d/m/L)

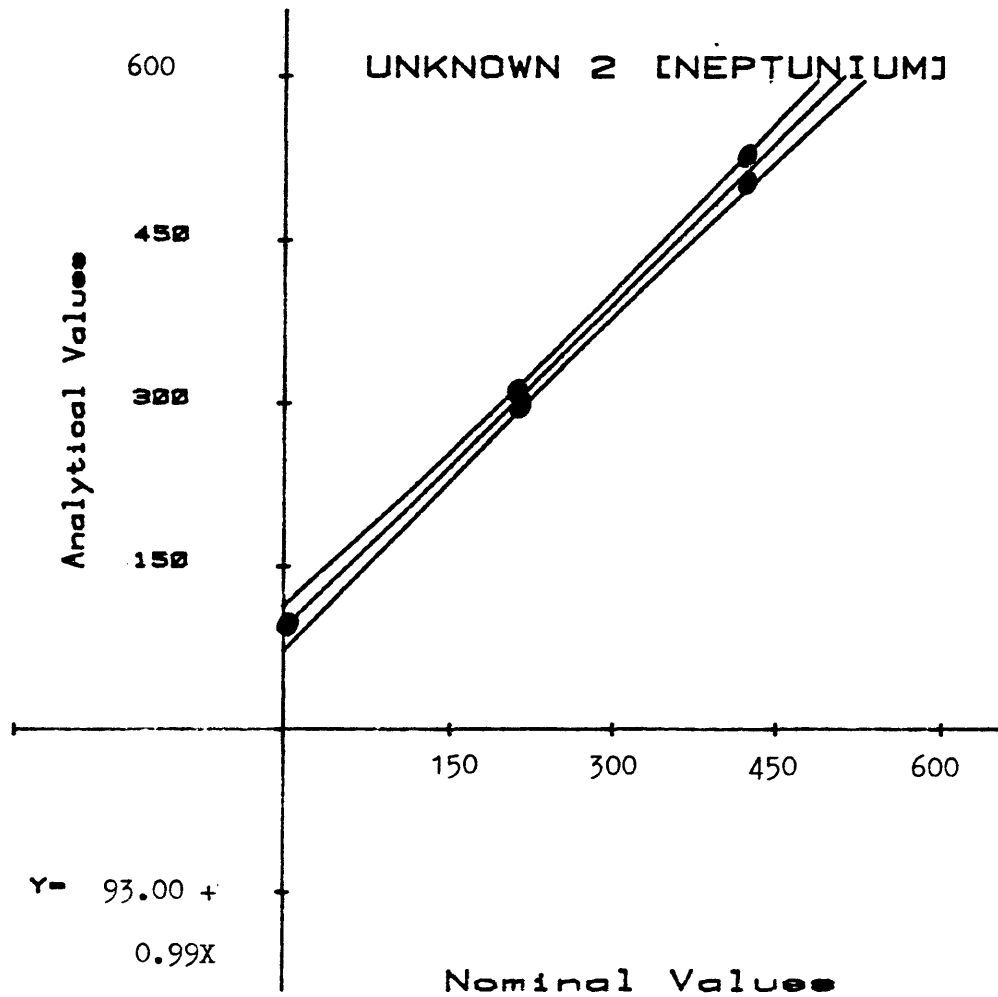


FIGURE 10: Neptunium analysis of Unknown 2 by the method of additions. (Values are d/m/L)

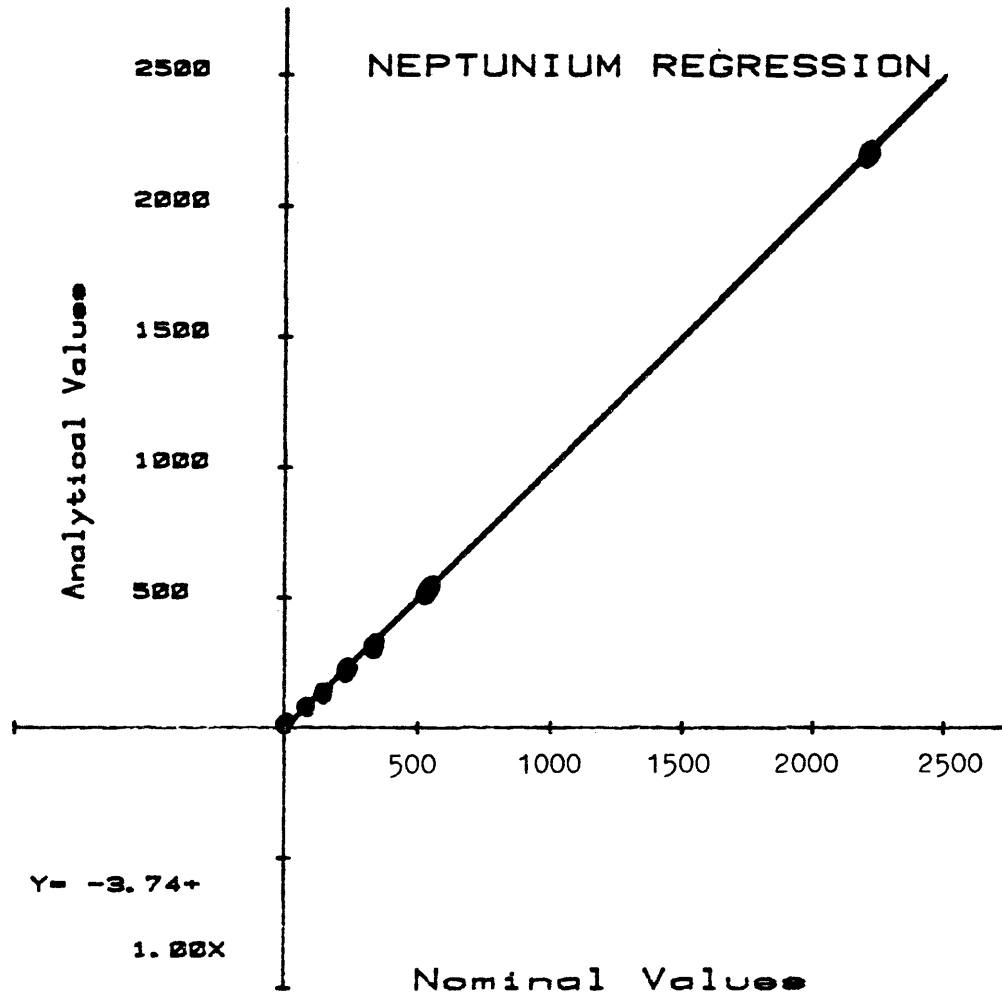


FIGURE 11: Regression line for the Neptunium analysis.  
(Values are d/m/L)

TABLE 3: Analysis of Variance Table for the Neptunium Regression Line.

SOURCE OF VARIATION	SUM OF SQUARES	DEG. OF FREEDOM	MEAN SQUARE
Total	17315385	22	787868
Regression	17312826	1	17312826
Residual	2515	1	2515

F STATISTIC = 144574

DF Num = 1

DF Den = 21

$$R^2 = 1.00$$



d/m/L for Unknowns 1 and 2, respectively. Analysis by the method of additions gave values of  $189 \pm 15$  and  $694 \pm 100$  d/m/L. The curves for these analyses are given in Figures 12 and 13. As can be seen by the standard deviations, there are not statistically significant differences in the three sets of analyses.

The regression line for the analysis over a concentration range of approximately four orders of magnitude is shown in Figure 14. Table 5 is the analysis of variance table for the regression line. The intercept of 5.73 is not significantly different from zero using a t-statistic with 24 degrees of freedom, indicating no apparent bias in the plutonium analysis. The slope is equal to one.

Since linearity over nearly four orders of magnitude had been investigated in the regression model, it was felt unnecessary to extend the linear range further.

The recovery of the added tracer was  $100 \pm 5\%$ . This agrees well with the published value of 95% for single element analysis for plutonium.

The pooled standard deviation based on 20 separate analyses (giving 15 degrees of freedom) was 26 d/m/L. This compares to the published value of 24 d/m at 6000 d/m.

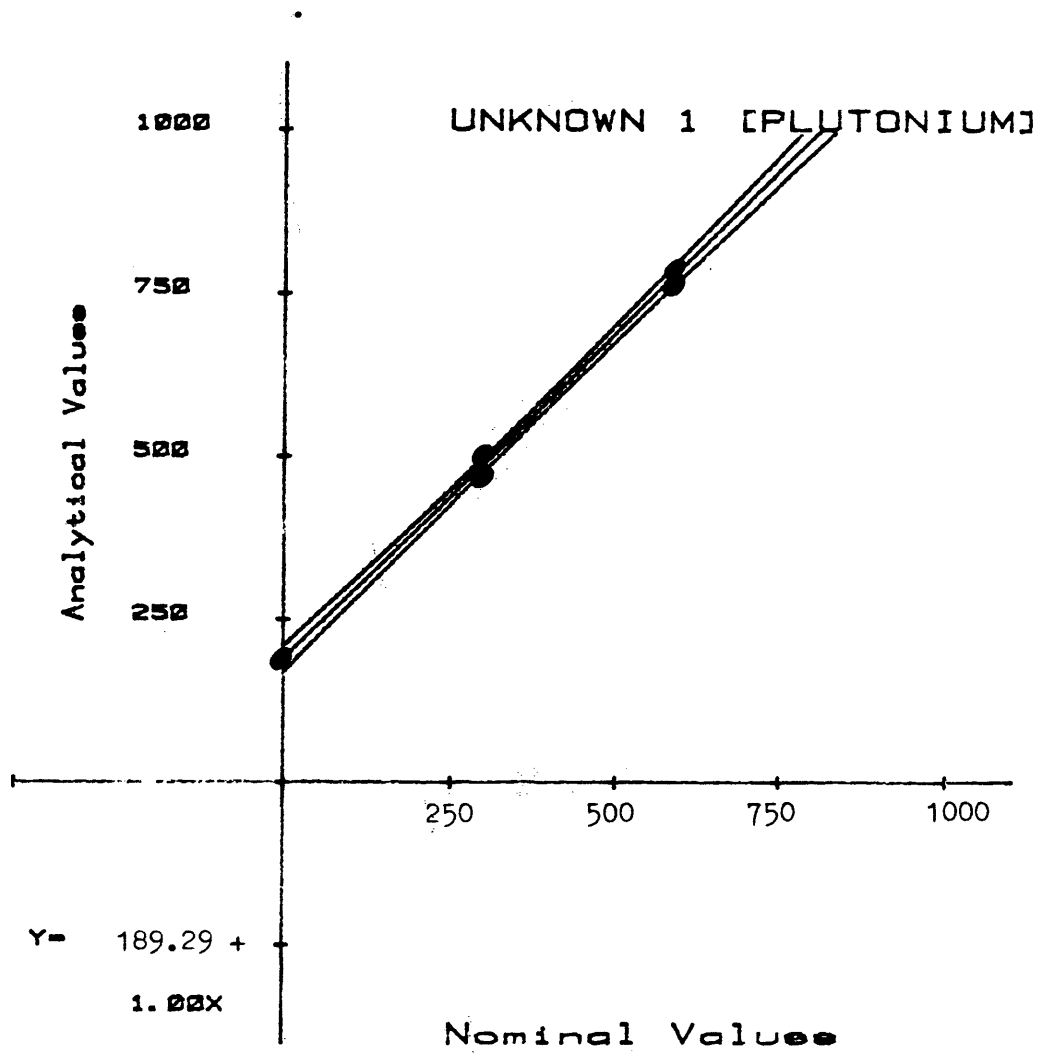


FIGURE 12: Plutonium analysis of Unknown 1 by the method of additions. (Values are d/m/L)

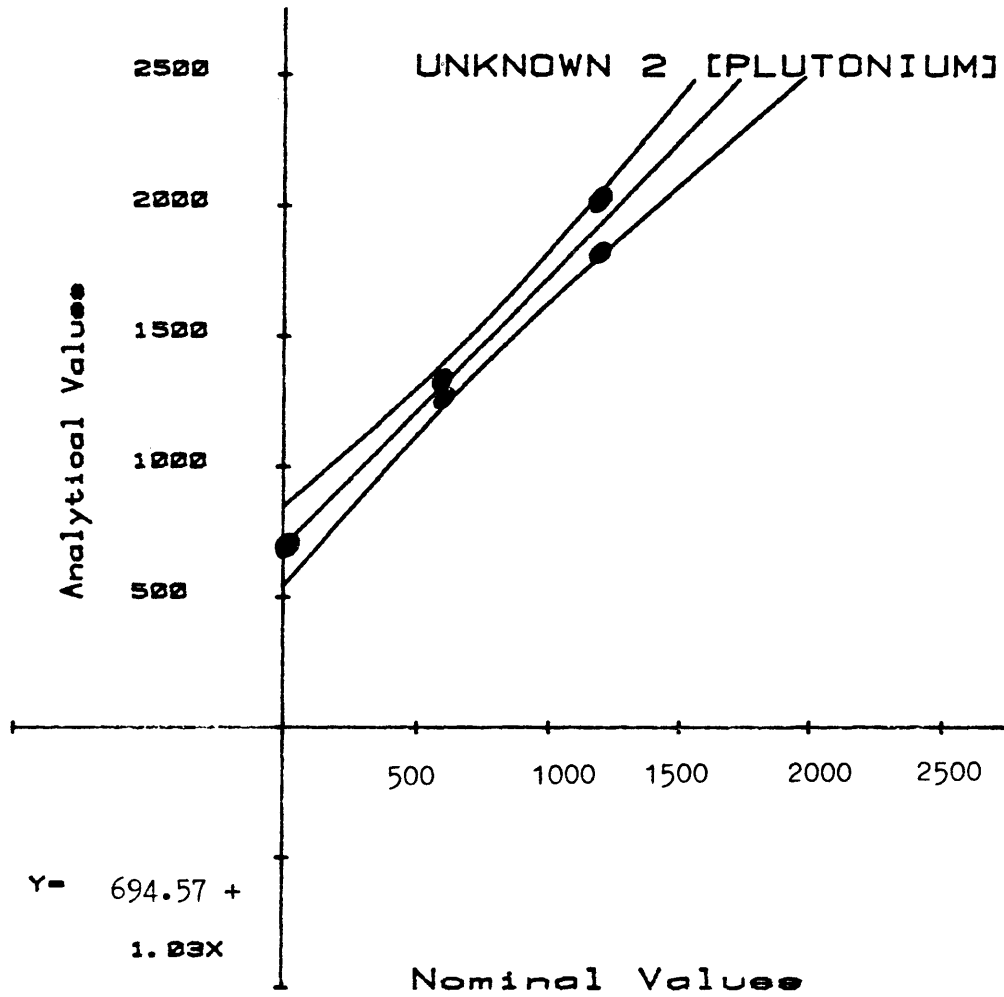


FIGURE 13: Plutonium analysis of Unknown 2 by the method of additions. (Values are d/m/L)

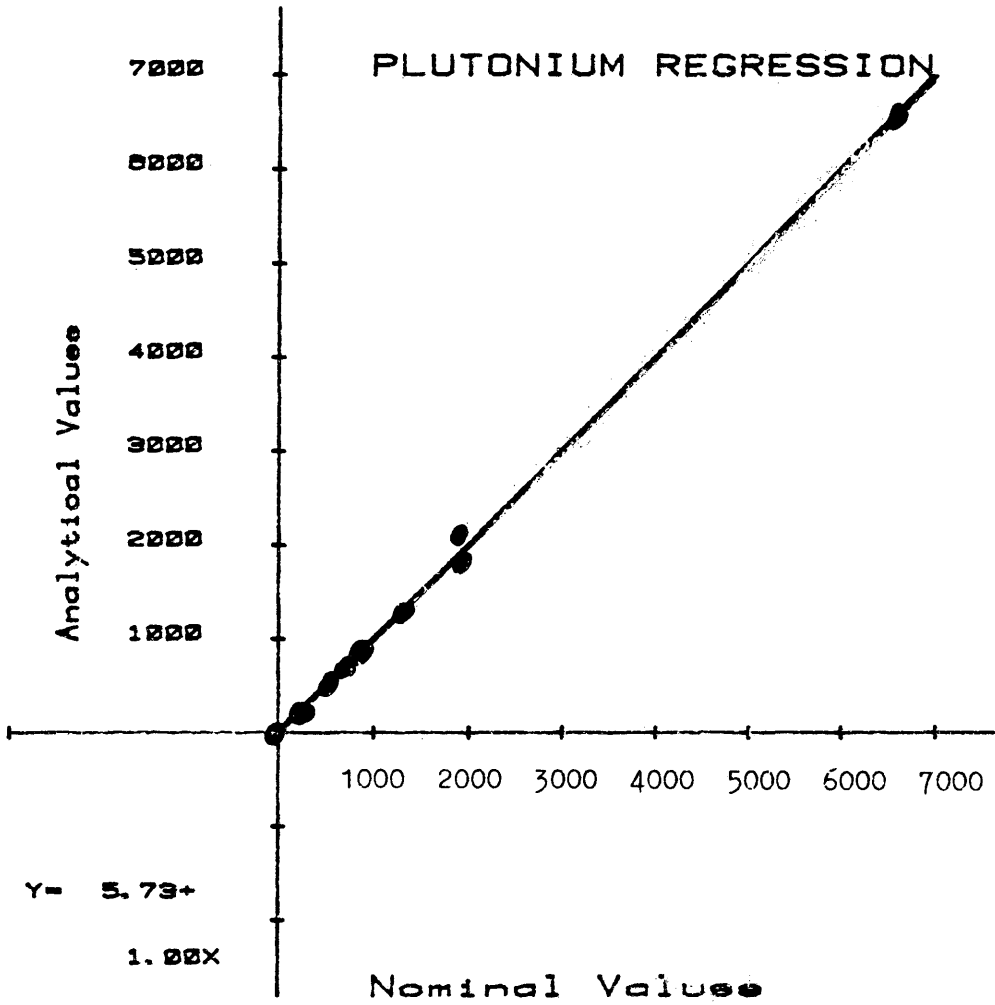


FIGURE 14: Regression line for the Plutonium analysis.  
(Values are d/m/L)

TABLE 4: Analysis of Variance Table for the Plutonium Regression Line.

SOURCE OF VARIATION	SUM OF SQUARES	DEG. OF FREEDOM	MEAN SQUARE
Total	182198858	24	7587535
Regression	182068714	1	182068714
Residual	37143	1	37143

F STATISTIC = 112738

DF Num = 1

DF Den = 23

$R^2 = 1.00$

## SUMMARY

A procedure has been developed which allows thorium, uranium, neptunium, plutonium, americium, and curium to all be analyzed from a single aliquot of groundwater sample. This procedure has accuracies and precisions comparable to those reported in the literature for separate analyses. A summary of these results are given in Table 5. This developed procedure has several advantages: It is relatively fast, capable of completion in approximately two to three days, whereas the same analyses on separate aliquots would take about a week. Because of the speed, the cost per analysis should be less. Since all five elements can be analyzed from the same sample, less sample needs to be collected in the field, reducing field time, and the cost of sample transportation. This procedure also has some disadvantages: The biggest disadvantage is that highly trained personnel are needed since the procedure gets complex as many things must be done simultaneously. Also, relatively pure isotopic tracers must be used, since contamination with any of the analyte isotopes would give erroneous analytical results.

TABLE 5: Summary of Analytical Results. All results are d/m/L.

<u>UNKNOWN</u>	<u>SINGLE ELEMENT</u>	<u>TECHNIQUE</u>	
		<u>ADDITIONS</u>	<u>SEQUENTIAL</u>
1-Th	17 ± 2	20 ± 10	20 ± 2
1-U	< 1	< 1	< 1
1-Np	5 ± 4	10 ± 8	9 ± 3
1-Pu	200 ± 5	189 ± 15	189 ± 5
2-Th	19 ± 2	21 ± 5	19 ± 2
2-U	70 ± 5	62 ± 2	64 ± 3
2-Np	102 ± 6	93 ± 12	93 ± 5
2-Pu	710 ± 15	694 ± 100	704 ± 8

TABLE 5: Summary of Analytical Results. All results are d/m/L.

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## APPENDIX A—ALPHA SPECTROMETRY

Alpha spectrometry is the technique used to determine the energy of alpha particles which are emitted from certain radioactive isotopes. It is useful in confirming anomalies which might be discovered during gamma ray surveys, and has been used to monitor different processes used in the uranium and thorium fuel cycles. In the future, it will be a major tool for the environmental monitoring of nuclear power stations, research laboratories, and waste disposal sites. This Appendix will discuss some of the important details and theoretical aspects of this important technique.

Alpha Decay Theory (59,60)

Alpha decay is a phenomenon which is characteristic of the heavier radioactive elements. Only a few nuclei lighter than lead have been observed to decay by this mechanism. While emission of protons, neutrons and deuterons are energetically possible, ground state nuclei of the heavy atoms tend only to emit helium nuclei and electrons. One reason is the strong binding energy of the alpha particle, approximately 28 MeV. Another is the exergonic mass relationship between the parent nucleus and the alpha-daughter pair. Equation 1 gives this energy relationship in terms of the binding energy (BE) and the energy required to remove two protons ( $E_p$ ) and two neutrons ( $E_n$ ) from the nucleus. E is generally between 2 MeV and 8 MeV.

$$E = BE - 2E_n - 2E_p \quad (1)$$

One detail which complicates this picture is the energy barrier, or activation energy of the alpha decay. Figure 15 shows the alpha potential curve showing there is, on the average, a 25 MeV energy barrier which must be overcome for the alpha to escape the nucleus. Since the emitted particle has about 6 MeV of kinetic energy, by classical mechanics the alpha particle would never be able to cross this barrier. However, calculations using the Schrodinger Equation show there is a finite, very small probability that the particle can exist outside of the potential well. In other words, there is a finite probability that the alpha can "tunnel" through the barrier energy and escape the nucleus. This is called the Tunnel Effect.

The small probability predicted using the Schrodinger Equation suggests that the alpha decay (or any radioactive decay, for that matter) is amenable to a Poisson statistical treatment. The Poisson has four assumptions: 1) there are  $n$  independent objects (atoms);  $n$  need not be known, only very large, 2) there is only one possible outcome of interest (alpha decay), 3) that there is a constant probability of the outcome occurring and the probability is small and 4) a time frame can be selected such that the probability of two simultaneous events is negligible. The following equations can be derived from the Poisson, and have been shown to be applicable to radioactive decay:

$$N = N_0 e^{-\lambda t} \quad (2)$$

Where  $N$  = number of atoms at time  $t$   
 $N_0$  = number of atoms at start  
 $\lambda$  = probability of radioactive decay (Poisson Parameter)

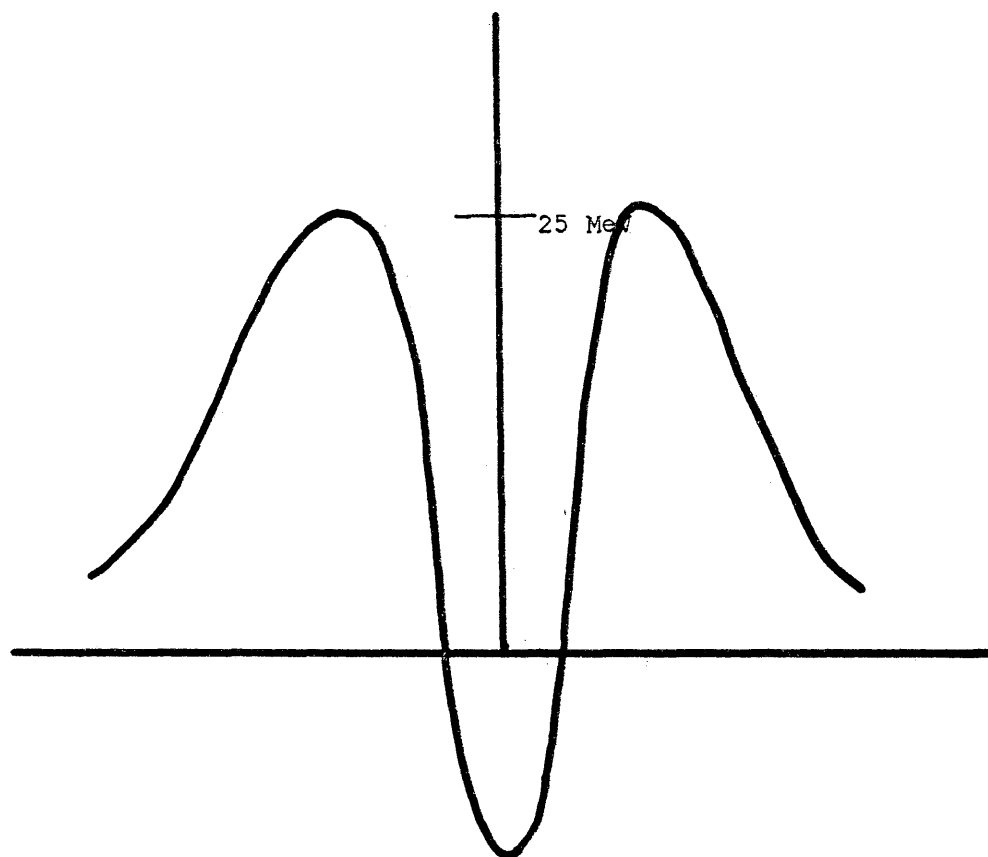


FIGURE 15: Alpha Potential Well--potential energy vs distance from center of nucleus

$$\frac{dN}{dt} = N \lambda \quad (3)$$

Where N = number of atoms

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \quad (4)$$

Where  $t_{\frac{1}{2}}$  is the time required for one half the original atoms to decay (half-life)

$$S = \frac{6.023(10^{23}) \lambda}{M} \quad (5)$$

Where S = specific activity--the decay rate of one gram of pure isotope

M = atomic mass

The energy spectra of alpha decay processes have some interesting and very useful characteristics. The spectra consist of sharply defined lines which correspond to the decay of the parent nucleus to the various energy levels of the daughter nucleus. These decay energies are unique for a given atom, and if there is some method of determining the alpha escape energies, the precise isotope from which the alpha came can be determined. This is not a trivial task, since in order to conserve momentum, the daughter atom must recoil from the alpha, and consequently not all of the escape energy is carried by the alpha particle. This relationship is given by:

$$E_t = E_n + E_a = E_a \left( \frac{M_r + M_a}{M_r} \right) \quad (6)$$

Where  $E_t$  is the total decay energy

$E_n$  is the energy carried by the recoil atom

$E_a$  is the energy carried by the alpha particle

$M_r$  is the mass of the recoil atom

$M_a$  is the mass of the alpha particle

Generally, the energy carried by the recoil atom is quite small. Using

$M_r = 228$ ,  $E_a = 4$  MeV, the  $E_n = 0.07$  MeV.

Interaction of Alpha Particles with Matter (60)

Charged particles interact with matter principally by interactions with atomic electrons. While interactions with nuclei are possible, the larger volume occupied by electrons increases the probability of electronic interactions which diminishes the probability of interactions with the much smaller nucleus. The path of heavy, charged particles through matter is essentially in a straight line. The mass of an alpha particle is much greater than the mass of an electron, and physics tells us that the electron is going to change direction before the alpha. With each collision with an electron, part of the alpha's energy is transferred to the electron, increasing its kinetic energy. If the amount of energy transferred is greater than the ionization potential for that electron, it is knocked from the atom creating a free electron and a positively charged ion. This process is continued until all of the energy of the alpha particle has been transferred to ionizing atoms and exciting electrons to higher energy states within the atoms. The net result is a path of electrons and ions along the trajectory of the alpha particle through the material. The amount of energy transferred in each collision is inversely proportional to the remaining energy of the alpha. This is shown mathematically by:

$$\frac{dE}{dx} \propto \frac{Mz^2}{E} \quad (7)$$

Where M is the alpha particle mass  
 E is the remaining alpha energy  
 z is the atomic charge (+2)



Because of Equation 7, alpha particles of a given energy have a specific range through matter. This range is approximately  $10 \text{ mg/cm}^2$  for an 8 MeV alpha. Assuming silicon has a density of  $2.3 \text{ g/cm}^3$ , it is easy to show that the maximum range of an alpha particle in silicon is approximately 50  $\mu\text{m}$ .

#### Surface Barrier Detector Theory (59-61)

As mentioned in the previous section, whenever a charged particle passes through matter, a path of free electron-ion pairs is created. For pure silicon, these pairs are created at the rate of 3.6 eV per pair. This production rate is independent of the particle energy and type, provided the sensitive depth is sufficient to totally absorb the particle's energy (greater than 50  $\mu\text{m}$  for alpha particles in silicon) and that the electric field in the sensitive region is sufficient to separate the charge carriers before they can recombine.

The silicon detector is basically a large area diode consisting of a thin p-type layer on a high purity n-type silicon wafer. Electrical contact is made through an evaporated gold contact on the p-type layer and a non-rectifying metal contact to the n-type layer. In most cases, the gold contact is the negative ground, while the non-rectifying contact has a positive applied bias.

Figure 16 is an illustration of a typical silicon surface barrier detector.  $D$  is the effective diameter of the active area,  $W$  is the sensitive depth in  $\mu\text{m}$ , and  $L$  is the total thickness of the silicon wafer. The sensitive depth is a function of the applied bias across the wafer. The sensitive depth is a function of the applied bias across the wafer. Charge carriers generated within  $W$  are separated

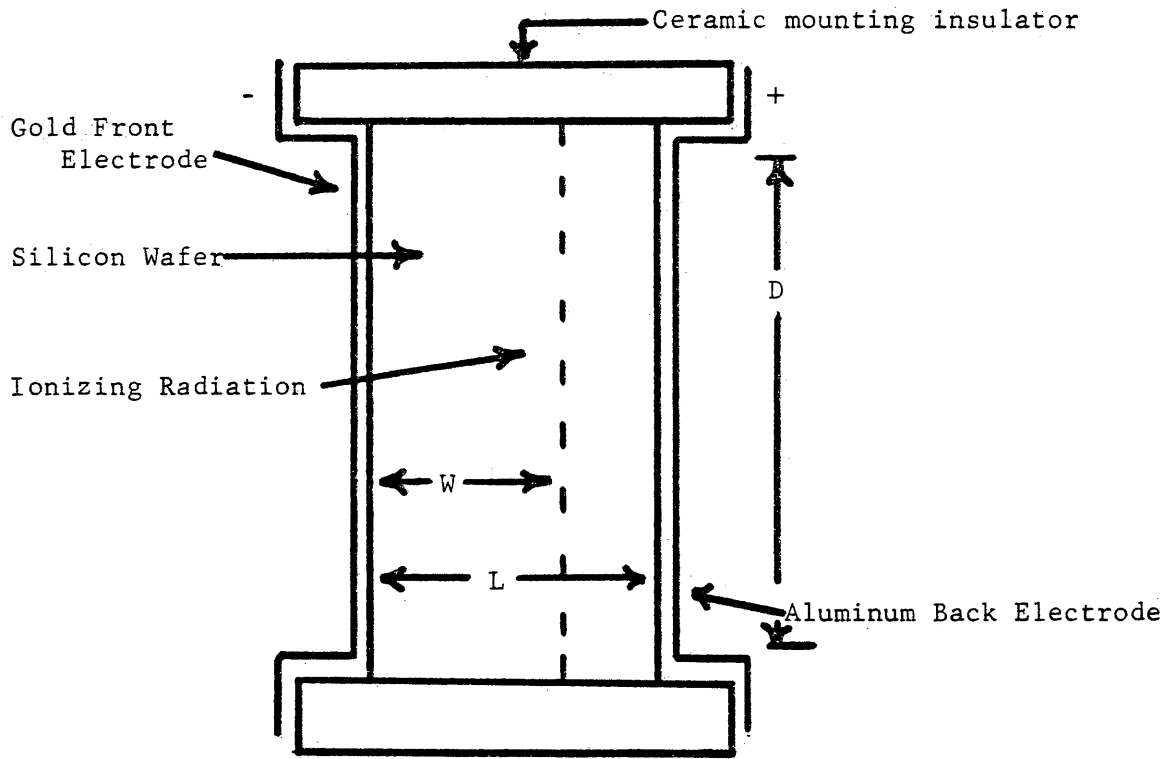


FIGURE 16: Surface Barrier Detector

by the electric field and the resulting net current is the basic information which the detector generates. The sensitive depth can be calculated by:

$$W = 0.5(P_n V_b)^{\frac{1}{2}} \quad (8)$$

Where  $P_n$  is the room temperature n-type resistivity.  
 $V_b$  is the bias voltage

The overall capacitance of the detector is given by:

$$C_d = 2.1(10^4)(A)(P_n V_b)^{-\frac{1}{2}} \quad (9)$$

Where  $C_d$  is the device capacitance in pF  
 $A$  is the diode area in  $\text{cm}^2$

For the overall circuit diagram for the detector and first preamplifier stage, see Figure 17.

The surface barrier detector has numerous advantages over other types of alpha detector systems: 1) five to ten times as many free charge carriers are created compared to gas filled systems, 2) because the electrons and positive ions have large mobilities and short collection distances, there are very short collection (or dead) times, on the order of 5 nsec., 3) because of the surface p-type layer, there is very low recombination of the free charge carriers, 4) gas purity and the associated time stability problems are absent, 5) the detectors are smaller and more compact than most other types and 6) the control of the sensitive depth, area and geometry are much easier.

There are some unique disadvantages, too. The signal generated in the detector is quite small, and therefore very sophisticated amplification electronics are needed. Also, noise due to leakage currents can be quite high.

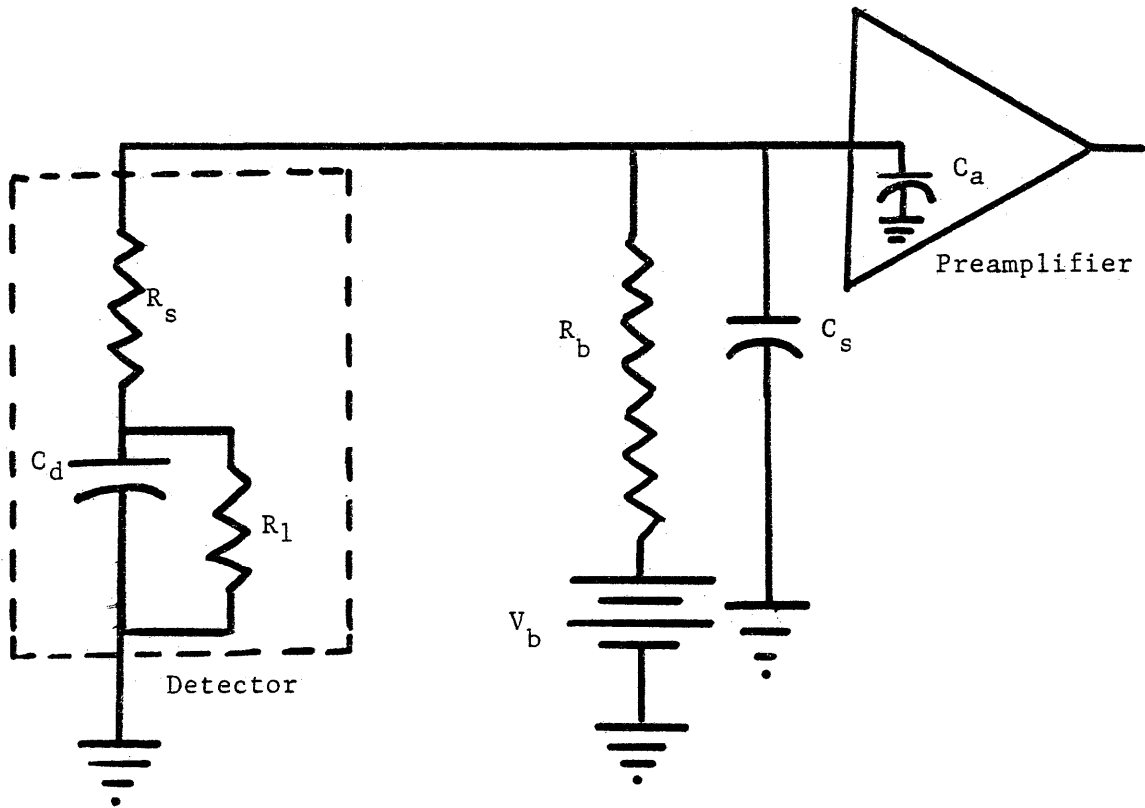


FIGURE 17: Surface Barrier Detector Circuit

Performance Parameters (61)

Many factors affect the overall performance of surface barrier detectors. The sensitive area, sensitive depth, electric field intensity, reverse leakage current, dead layer thickness, and energy resolution are the most important factors. In this section, each parameter and its importance is discussed.

The sensitive area of the detector determines the geometry of the detector-sample system. It therefore controls the ultimate count rate achievable. It also affects the amplifier noise which affects the overall system noise. The smaller the sensitive area, the smaller the system noise and the greater the resolution achievable in the system. The best resolution for alpha particle energies appears at present to be about 13 keV. If higher count rates are needed, larger detectors are needed, but this results in more noise, and less resolution. There is always a trade-off between resolution and count rate when using surface barrier detectors.

The sensitive depth must be sufficient to stop the incident radiation. Otherwise, the linearity of response does not hold. However, if the sensitive depth is too great, the sensitive volume becomes large which increases the detector noise. This, once again, decreases resolution. It is useful to calculate what depth is needed using the range given for Equation 7, the voltage needed to generate the depth as given in Equation 8, and to use a bias at most slightly greater than that calculated. This will insure complete energy collection while keeping noise to a minimum.

As can be seen in the last paragraph, the electric field intensity is a function of the needed sensitive depth. Another problem to be considered is that solid state diodes can have a cascade breakdown if the voltage is too high. This cascade breakdown sets an upper limit on the sensitive depth which can be achieved.

The reverse leakage current is the current which bleeds across the diode due to its semiconducting properties. The net result is a voltage drop across the diode. What this basically means is that the voltage across the sensitive depth is not as high as the voltage drop across the entire detector circuit. This difference must be compensated for in the applied bias to achieve the desired sensitive depth.

The dead layer thickness is defined as the thickness of any unsensitive layer which the particle must penetrate before entering the sensitive depth. Because some of the particle's energy is lost while penetrating this region, and this energy loss is not necessarily constant, the dead layer thickness affects the overall sensitivity and resolution of the detector. It also affects the linearity of response since, by Equation 7, lower energy particles would lose more energy, proportionately, going through the dead layer than would higher energy particles. In most detectors, the dead layer thickness roughly corresponds to the evaporated gold electrode thickness.

Finally, the ultimate energy resolution is a function of system noise, statistical effects, imperfect charge collection and variation of the energy lost in the dead layer. Noise and the dead layer effects

have been discussed previously. The statistical effects are due to the Heisenberg uncertainties with short-lived isotopes. In fact, one method of determining very short half-lives is to measure the band broadening of decay spectra. Imperfect charge collection affects resolution because not all charge carriers generated as the particle loses energy are registered in the final pulse from the detector. As mentioned before, the ultimate resolution for alpha particles at the present time is approximately 13 keV.

### Alpha Spectrometry

Alpha spectrometry is an analytical technique used to determine the quantity of a given alpha emitting radioisotope in a sample. One property of alpha decay processes is that the energy of the emitted alpha particle is characteristic of the nucleus from which it originated. Assuming the energy difference of two different isotopes' alpha particles is greater than the alpha resolution of 13 keV, the quantity of the two individual isotopes can be determined from a single sample disc. Otherwise, some chemical separation is needed for spectrally unresolved peaks. Sample preparation in alpha spectrometry involves separation techniques such as ion exchange, solvent extraction, carrier precipitation and electrodeposition. After the elements of interest are separated from the sample mixture, they are deposited on discs which are placed in close proximity to the surface barrier detector. The air around the sample and detector is evacuated to prevent unwanted collisions of the alpha particles with air molecules.

Bias is applied to the detector and the signals from the detector are processed and sorted according to the pulse height. This is done with a pulse height analyzer.

The pulse height analyzer is capable of determining pulses of different voltages. A block diagram of a typical system is shown in Figure 18. The signal from the detector is a very small current. This current is translated into a voltage in the preamplifier. This voltage peak is increased by the gain amplifier. Any amplified pulse below a certain voltage is rejected using a pulse discriminator. The pulses not rejected by the discriminator are converted from an analog signal (voltage) to a digital signal using an analog-digital converter (ADC). This digital signal is then delivered to a microprocessor which sorts the digital data into memory. The data thus stored can be displayed on a cathode ray tube or printed out on a hard copy printer. By integrating the number of counts under a given peak, the total number of alpha particles with energy corresponding to that peak can be determined.

### Conclusions

Surface barrier detectors can be used in association with sophisticated electronic processing equipment to determine the energy of alpha particles being emitted from a prepared sample. Since each alpha emitting radionuclide emits alpha particles at characteristic energies, spectra of the alpha energies can be used to determine the amount of a given radionuclide in the prepared sample. Using chemical



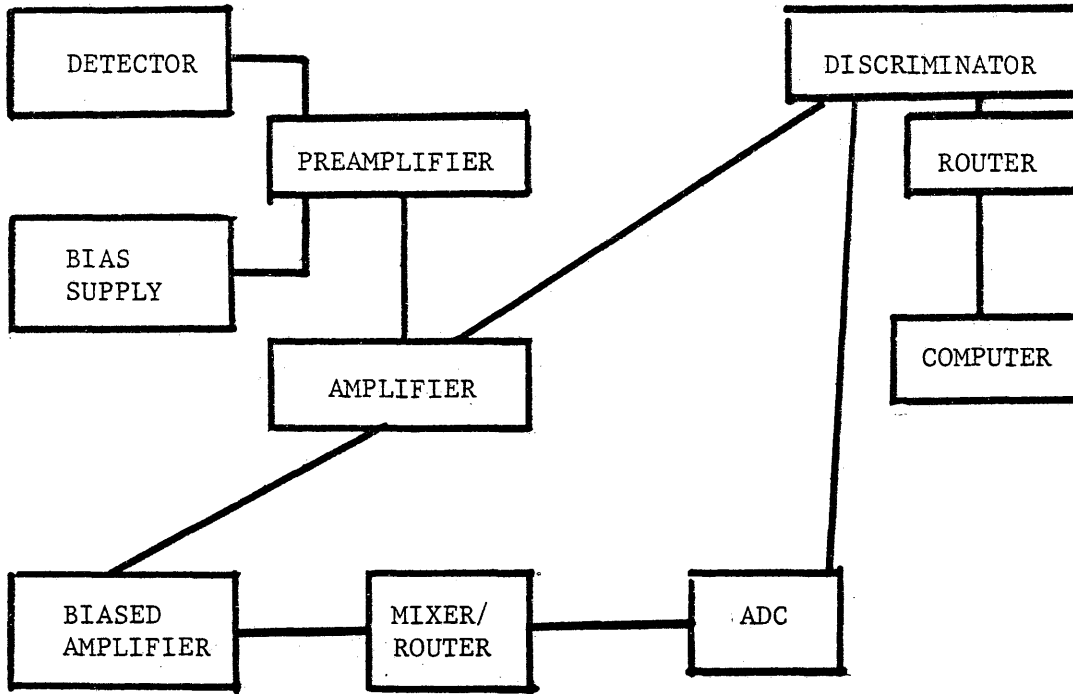


FIGURE 18: Typical alpha spectrometer block diagram

techniques, it is sometimes possible to remove interfering radionuclides from the prepared samples allowing quantitative determination of how much of a particular radionuclide is in the sample.

## APPENDIX B—PARAMETERS FOR ANALYSIS OF UNKNOWNNS

The samples which were used as unknowns in this study were collected from the Maxey Flats Nuclear Waste site in eastern Kentucky. The method of collection is described elsewhere (63). These samples were selected because they represented a worst case for groundwaters requiring analysis for the actinides. There are high levels of both inorganic and organic salts in the waters. Table 6 give the major constituents in these waters. Neptunium (V) in chloride solution was added to unknown 2 to simulate a high neptunium groundwater.

The count times used for these samples was sufficiently long to reduce the counting error to less than 1%. A typical count period of 1000 minutes would allow a detection limit of approximately 0.5 d/m/L. Sample volumes were 10 mL.

TABLE 6: Major Constituents of unknown samples

<u>COMPONENT</u>	<u>UNKNOWN 1</u>	<u>UNKNOWN 2</u>
TDS	7670 mg/L	2970 mg/L
Na <sup>+</sup>	2180 mg/L	1420 mg/L
Cl <sup>-</sup>	4370 mg/L	1010 mg/L
PO <sub>4</sub> <sup>-3</sup>	0.6 mg/L	0.1 mg/L
F <sup>-</sup>	4.6 mg/L	1.4 mg/L
DOC	470 mg/L	325 mg/L

## APPENDIX C--STATISTICAL TERMS

The pooled standard deviation is calculated from the following equation:

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \dots + (n_r - 1)s_r^2}{(n_1 + n_2 + \dots + n_r - r)}$$

where  $n_i$  is the number of observations at  $i$ ,  $s_i^2$  is the variance of the observations at  $i$ , and  $r$  is the number of different observation points where multiple observations were taken.

The confidence interval plots are calculated from the following equation:

$$S_{\hat{Y}} = S_{X|Y} \left( \frac{1}{n} + (X_0 - \bar{X})^2 / (n-1) s_X^2 \right)^{\frac{1}{2}}$$

where:  $S_{X|Y}^2 = \frac{1}{(n-2)} \sum_i^n (Y_i - \hat{Y}_i)^2$ ,  $\hat{Y}_i$  is the regression estimate of  $Y_i$ ,  $Y_i$  is the actual observed  $Y$  value,  $n$  is the number of observations,  $X_0$  is the  $X$  value of interest,  $\bar{X}$  is the mean value of  $X$  and  $s_X^2$  is the variance of the  $X$  values. It is interesting to note that if  $X_0 = \bar{X}$ , the confidence interval is the most narrow. As  $X_0$  gets further and further away from  $\bar{X}$ , the confidence interval diverges.