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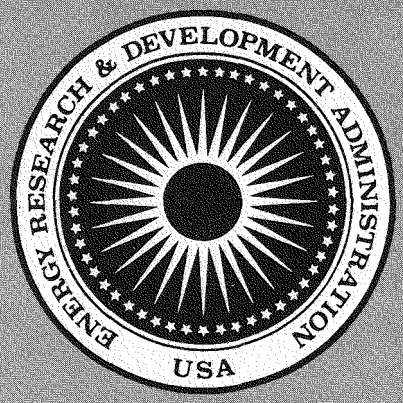

HASL-307

DETERMINATION OF ENVIRONMENTAL LEVELS OF $^{239,240}Pu$, ^{241}Am, ^{137}Cs, AND ^{90}Sr IN LARGE VOLUME SEA WATER SAMPLES

By
D. C. Sutton
G. Calderon
W. Rosa

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Energy Research and Development Administration
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DETERMINATION OF ENVIRONMENTAL LEVELS OF Pu-239,240, Am-241, Cs-137 AND Sr-90 IN LARGE VOLUME SEA WATER SAMPLES

Doris C. Sutton
Gustavo Calderon
William Rosa

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Health and Safety Laboratory
U. S. Energy Research and Development Administration
New York, New York 10014

ABSTRACT

A method is reported for the determination of environmental levels of Pu-239,240 and Am-241 in ~60 liter size samples of sea water. Cesium-137 and Sr-90 were also separated and determined from the same samples. The samples were collected at the sea surface and at various depths in the oceans through the facilities of the Woods Hole Oceanographic Institution.

Plutonium and americium were separated from the sea water by iron hydroxide scavenging then treated with a mixture of nitric, hydrochloric, and perchloric acids to destroy organic material and to achieve equilibrium between added tracers and the environmental transuranics. A series of anion exchange separations were used to remove interferences and purify plutonium and americium then each was electroplated on platinum discs and measured by solid state alpha particle spectrometry. The overall chemical yields averaged 62 ± 9 and 69 ± 14 percent for Pu-236, and Am-243 tracers, respectively.

Following the iron hydroxide scavenge of the transuranics, cesium was removed from the acidified sea water matrix by adsorption onto ammonium phosphomolybdate. Cesium carrier and Cs-137 isolation was effected by ion exchange and precipitations were made using chloroplatinic acid. The samples were weighed to determine overall chemical yield then beta counted. Cesium recoveries averaged 75 ± 5 percent.

After cesium was removed from the sea water matrix, the samples were neutralized with sodium hydroxide and ammonium carbonate was added to precipitate Sr-85 tracer and the mixed alkaline earth carbonates. Strontium was separated as the nitrate and scavenged by chromate and hydroxide precipitations. Yttrium-90 was allowed to build-up for two weeks, then milked and precipitated as the oxalate, weighed, and beta counted. The overall chemical yields of Sr-85 tracer averaged 84 ± 16 percent. The recovery of the yttrium oxalate precipitates averaged 96 ± 3 percent.

Analytical problems encountered during preliminary investigations of the sea water analysis method development on large volume samples are discussed; interlaboratory comparison results are given for plutonium, cesium, and strontium measurements; the investigations required to include americium in the analytical scheme are briefly summarized; the results of analysis are

tabulated for Pu-239,240, Am-241, Cs-137 and Sr-90 measurements of twenty seven large volume samples which included surface waters, mid-depth profiles, quality controls, and blanks; the environmental concentrations for 18 open-ocean samples ranged from 0.04 - 0.48, ≤0.004 - 0.07, 5 - 84, and 3 - 50 dpm per 100 liters of sea water for Pu-239,240, Am-241, Cs-137, and Sr-90, respectively; the analytical method is outlined.

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INTRODUCTION

The measurement of fallout and environmental levels of the transuranic elements in sea water samples contributes a small part to a better understanding of these elements in the marine environment. Since 1964, only a few investigators have reported measurements of the fallout levels of plutonium in sea water samples collected from various locations in the world's oceans. Reported measurements of americium levels in the oceans are very sparse. This is due in part to handling the size and volume of sample necessary to detect the extremely small amounts of the transuranics in sea water, the analytical difficulty of isolating these elements from a complex matrix, and the ready availability of adequate and reliable associated instrumentation for measuring quite low levels of alpha radioactivity. Many measurements are required before the levels of the transuranics are well known and before realistic predictions can be made about the marine environment in evaluating any potential hazard and its relationship to man. To support this analytical effort, the Health and Safety Laboratory (HASL) has modified and extended its method for the determination of Sr-90 and Cs-137 in large volume sea water samples (Sutton and Kelly, 1968) to include the determination of Pu-239, 240 and Am-241. The work was undertaken in cooperation with the Woods Hole Oceanographic Institution and the samples were provided through the latter facility.

Pillai et al. (1964) reported the measurement of Pu-239,240 in marine organisms and from 45 liter size sea water samples. Their procedure was not given in detail but as a general description. Concentration of plutonium from their samples was achieved by co-precipitating plutonium with bismuth phosphate. Separation from most of the bismuth phosphate was accomplished by carrying plutonium on lanthanum fluoride, finally plutonium was isolated by anion exchange and electroplated on platinum. Plutonium-236 was used as the tracer and pulse height alpha spectroscopy was the means of determining the radioactivity.

Miyake and Sugimura (1968) separated plutonium from 500 liter sea water samples by co-precipitating it with 2 grams of iron as hydroxide. The organic material was decomposed by perchloric acid digestion. The major amount of iron was separated from plutonium by iso-propyl ether extractions. Traces of iron were used to reprecipitate and carry plutonium as the hydroxide then separated from plutonium by passing the mixture dissolved in 7.5

M HNO_3 through an anion exchange resin in the nitrate form where the plutonium was absorbed and the iron was not retained. Successive washes of nitric and hydrochloric acid removed interfering ions and plutonium was eluted from the resin with dilute hydrochloric acid. Plutonium was electroplated on a stainless steel disc. Plutonium-238 was used as the yield monitor and pulse height alpha spectrometry was used to resolve the radioactive species. The overall chemical yields averaged 60 ± 10 percent. Recent work by Miyake and Sugimura (1975) using the same procedure as outlined indicate a change of their yield monitor from Pu-238 to Pu-236 and overall chemical yields ranging from 20 - 85 percent.

Detailed sequential procedures for the analysis of strontium, antimony, the rare-earths, cesium and plutonium in ~60 liter size sea water samples have been reported by Wong et al. (1970) and the determination of plutonium in sea water, sediments, and marine organisms by Wong (1971). For sea water analysis in both procedures, iron hydroxide was used as the collection agent for plutonium followed by dissolution with nitric acid. The 1971 procedure differed from the 1970 method by including a series of oxidation-reduction steps using hydrogen peroxide followed by sodium nitrite prior to plutonium purification by ion exchange. The purification process of the 1971 method employed two anion exchange resin columns, the first in the nitrate form followed with the second in the chloride form wherein the 1970 procedure purification process was accomplished with one column in the nitrate form. Both methods using ion exchange resins removed interfering ions with a series of acid washes prior to removing plutonium from the resin with a mixture of a chloride-iodide eluting agent. Finally, plutonium was electroplated on a stainless steel disc. Plutonium-236 was used as the yield monitor and pulse height alpha spectrometry was employed to resolve the radioactive species. The 1971 method gave an average plutonium recovery of 52 ± 18 percent compared to the 1970 procedure of 25 ± 14 percent.

Additional studies by Livingston et al. (1972) to improve plutonium yields in the sequential separation with strontium and cesium, used a double tracer technique (Pu-242 and Pu-236) to determine the optimum conditions for the separation of plutonium from large volume sea water samples. Their investigations included (1) factors affecting the co-precipitation of plutonium with ferrous or ferric hydroxide: the average recovery of plutonium was slightly higher with ferric hydroxide; (2) amount of iron: higher yields were found when the iron concentration was 0.5 to 1.0 grams; (3) order of hydroxide precipitation: using 0.5

to 1.0 gram of iron, the plutonium yield averaged 75 ± 13 percent when removed as the first element in the sequential separation and averaged 68 ± 6 percent when cesium was removed prior to plutonium. Their preferred order of separation from sea water when both cesium and plutonium were being determined was cesium first and plutonium second. This order of separation was based on cesium recovery which ranged from 23 to 61 percent when plutonium was removed first by iron precipitation or 56 to 90 percent cesium recovery when plutonium was removed by iron precipitation after cesium.

More recently, Bowen and co-workers (Private Communication, 1974) have suggested that the iron hydroxide step can be eliminated, thus preferring an acid strontium oxalate precipitation to carry all of the radionuclides formerly precipitated with iron hydroxide. More consistent yields were obtained as well as time saved in analysis.

Fukai et al. (1974) measured plutonium, strontium, and cesium from 90 liter size sea water samples. The analytical procedure used for plutonium was similar to that reported by Wong (1971). Plutonium-242 was used as the tracer and alpha spectrometry measurements were made on plutonium sources electrodeposited on stainless steel discs.

Murray and Kautsky (1975) measured plutonium and americium in sea water samples; plutonium was separated from 60 liter samples using a procedure similar to that described by Wong (1971). Americium measurements were made from 200 liter samples and were treated similarly to plutonium by successive hydroxide precipitations and then converted to an 8N HNO_3 medium containing plutonium, americium, and other extraneous ions. Purification of the americium fraction was accomplished by an alternate series of solvent extractions (di-2-ethyl hexyl phosphoric acid, HDEHP) and ion exchange (cation and anion) separations. Plutonium-242 and Am-243 were used as the yield monitors, the purified fractions were electroplated on stainless steel discs, and these were measured by alpha spectrometry.

This report is concerned with some of the analytical problems we encountered during the course of modifying the HASL Sr-90 and Cs-137 method to accommodate plutonium and finally americium for large volume sea water samples. Herein are found the results of analysis of preliminary investigations of the sequential separation of plutonium, cesium and strontium; interlaboratory comparison results of plutonium, cesium and strontium; preliminary investi-

gations with americium in the analytical scheme; the results of a sequential analysis of Pu-239,240, Am-241, Cs-137 and Sr-90; a discussion of some analytical problems; and an outline of the detailed procedure currently in use at HASL.

The two foremost considerations of the method development was to accomplish acceptable overall chemical yields for each radionuclide and to achieve equilibrium between environmental species and added tracers. We selected certain trends from the double tracer study by Livingston et al. (1972) to further investigate. From their work we chose (1) the sequential order of separation which gave the highest yield of plutonium tracer, that is, plutonium, cesium, and strontium; (2) 1.5 grams of iron as carrier for plutonium, and ammonium hydroxide as the precipitant; and (3) the use of hydroxylamine hydrochloride as reducing agent for iron and plutonium.

To 55-liter samples we added 1 gram of hydroxylamine hydrochloride per liter after the sample had been acidified and mixed, then added sufficient ammonium hydroxide to neutralize the acid and raised the pH to 8-9 to collect iron, plutonium and mixed hydroxides. The added cesium carrier was separated from an acid solution with ammonium phosphomolybdate (APM). Strontium was collected from an alkaline solution using ammonium carbonate.

The plutonium fraction was processed after iron collection by anion exchange, electroplating, and solid state alpha particle spectrometry. The cesium fraction was purified by cation exchange and precipitated and weighed as the chloroplatinate. The strontium fraction was purified by nitrate separation, chromate scavenging, stored for two weeks for Y-90 growth, then milked, and beta counted. The results obtained are given in Table 1.

TABLE 1

RECOVERY OF PLUTONIUM, CESIUM, AND STRONTIUM WITH AMMONIUM HYDROXIDE AS PRECIPITANT OF IRON CARRIER AND IN THE PRESENCE OF 1 GRAM OF HYDROXYLAMINE HYDROCHLORIDE PER LITER OF SAMPLE

Sample No.	Initial Amount of HCl Added for Sample Mixing	Percent Yield		
		Pu-236	Cs Carrier	Sr-85
1	500 ml	53	26	66
2	1000 ml	44	12	54
3	2500 ml	60	2	65

The cesium yield of 26% for sample 1 was comparable to the results of 23-60% found by Livingston et al. (1972) when plutonium was removed before cesium. Also samples 2 and 3 showed that increasing amounts of ammonium ion from the neutralization of different amounts of acid in the initial sample mixing caused decreasing cesium yields. We believe this to have occurred at the time of ion exchange of cesium onto APM, that is, the competition of cesium to replace NH_4^+ ions on the structure of APM is severely retarded as the NH_4^+ ions in solution increase. Because of the various conditions of samples received for analysis, such as, containing precipitates, or having been stored for a prolonged time, we believed it was necessary to know the effect of adding and neutralizing different amounts of acid which for some samples may be a requirement of the analysis. The strontium and plutonium yields were less affected by the variations in the amount of acid and the subsequent neutralization.

Sodium hydroxide was substituted as the precipitating reagent for iron and plutonium. The initial amount of acid for sample mixing was kept constant at 500 ml, the other conditions were the same as outlined for samples 1-3. The results obtained are given in Table 2.

TABLE 2

RECOVERY OF PLUTONIUM, CESIUM, AND STRONTIUM WITH SODIUM HYDROXIDE AS PRECIPITANT OF IRON CARRIER AND 1 GRAM OF HYDROXYLAMINE HYDROCHLORIDE PER LITER OF SAMPLE

Sample No.	Initial Amount of HCl Added for Sample Mixing	Percent Yield		
		Pu-236	Cs Carrier	Sr-85
4	500 ml	33	82	82
5	"	34	72	53
6	"	32	74	76

We concluded from the results shown in Table 2 that although the cesium and strontium yields were satisfactory, the plutonium yields were less than we considered acceptable for routine opera-

tion. Experiment 2 was repeated and varied only by increasing the amount of hydroxylamine hydrochloride from 1 to 1.5 grams per liter of sample. The results obtained are shown in Table 3.

TABLE 3

RECOVERY OF PLUTONIUM, CESIUM, AND STRONTIUM WITH SODIUM HYDROXIDE AS PRECIPITANT OF IRON CARRIER AND 1.5 GRAMS OF HYDROXYLAMINE HYDROCHLORIDE PER LITER OF SAMPLE

Sample No.	Initial Amount of HCl Added for Sample Mixing	Percent Yield		
		Pu-236	Cs Carrier	Sr-85
7	500 ml	18	54	64
8	"	29	63	70
9	"	17	67	72

Based on the experimental results shown in Table 3, it was clearly demonstrated under the conditions of the analysis that hydroxylamine hydrochloride gave adverse effects on the recovery of plutonium as well as a decrease in the cesium yield, therefore, its use was discontinued as a reagent in the sea water analysis.

Shown in Table 4 are the results of analysis using sodium hydroxide as precipitant for iron and plutonium at pH 10.0 ± 0.5 after the initial sample mixing using 500 ml of HCl. The analysis was continued for cesium and strontium as described in the first experiment, Table 1.

TABLE 4

RECOVERY OF PLUTONIUM, CESIUM, AND STRONTIUM WITH SODIUM HYDROXIDE AS THE PRECIPITANT OF IRON CARRIER

Sample No.	Initial Amount of HCl added for Sample Mixing	Percent Yield		
		Pu-236	Cs Carrier	Sr-85
10	500 ml	69	77	70
11	"	55	84	72
12	"	72	87	69
13	"	59	87	73

Samples 1-13 found in Tables 1-4 ranged in volume from 55-60 liters and were obtained from the New York Aquarium. Based on the chemical yields found for Pu-236, cesium carrier and Sr-85 for samples 10-13 shown in Table 4, HASL participated in an inter-laboratory calibration analysis with Bowen's group at the Woods Hole Oceanographic Institution (WHOI). Three sample types were analyzed in replicate. The intercomparison between the two laboratories was found to be satisfactory and the range of results are given in Table 5.

TABLE 5

INTERCOMPARISON RESULTS OF ANALYSIS OF Pu-239,240, Cs-137 AND Sr-90

Sample Identification	dpm/100 kg					
	Pu-239,240		Cs-137		Sr-90	
	HASL	WHOI	HASL	WHOI	HASL	WHOI
Woods Hole Harbor Quality Control Water '72	0.08-.19	0.05-.26	32-36	35-40	35-37	32-36
New Mexico Brine	0.04-.07	0.02	<0.2-1.0	0.3	<1	<1
Surface Water Northern Sargasso Sea	0.26±.04	0.28±.03	32±2	35±2	24±1	23±1

Investigations at HASL of methods to determine Am-241 in soil samples (Morse, 1974) aided our work considerably by our being able to adapt some of the separation and isolation techniques from the soil method to the sea water matrix. Briefly, americium and plutonium were collected from the sea water samples by iron hydroxide precipitation. Plutonium was absorbed on the nitrate form of an anion exchange resin. Americium and iron were not absorbed and were washed off the resin column prior to plutonium removal. Separation of the major amount of the 1.5 grams of iron carrier from americium was accomplished by carrying amercium on a calcium oxalate precipitate while the iron remained complexed in

solution. Americium was separated from calcium by adding 10 mg of iron and precipitating successively with ammonium hydroxide. The major portion of the 10 mg of iron was separated from americium by absorbing iron on a chloride form anion resin; americium was not absorbed and was washed from the resin. Final purification of americium was achieved by absorbing it and the traces of iron onto a thiocyanate form anion exchange resin and removing interfering ions particularly some of the lanthanides by washing with a thiocyanate solution.

Americium was eluted from the resin column with a mixture of dilute acid and thiocyanate. Iron was retained on the column. Removal of thiocyanate from americium was accomplished by evaporating and heating at a high temperature. Residual sulfur was removed by acid digestion. Americium was electroplated using the technique reported by Mitchell (1960) which was also used for plutonium electroplating. Measurements were made using pulse height alpha particle spectrometry.

Independently we determined a decontamination factor of plutonium from americium in the overall analytical scheme with large volume samples. For this measurement we used ~40 dpm of Pu-242 and ~5 dpm of Am-243 tracers. The decontamination factor averaged $\sim 1 \times 10^4$ which was comparable to that found in the soil investigations by Morse (1974).

Shown in Table 6 are the results of analysis of Pu-239,240, Am-241, Cs-137, and Sr-90 for an experimental group of open-ocean samples. The data are included here under preliminary investigations because the chemical yields were sufficient to give a measure of the levels of the two transuranics found in sea water except for americium E-1 where the yield was less than five percent and thus considered lost. The overall chemical yields for samples E1 - E9 averaged 52 ± 7, 60 ± 15, 78 ± 9 and 73 ± 12 percent for plutonium, americium, cesium and strontium, respectively.

TABLE 6

Pu-239,240, Am-241, Cs-137 AND Sr-90 MEASUREMENTS OF SEA WATER SAMPLES

HASL No.	Sample Identification	Net Wt. (lbs.)	Specific Gravity	Volume (liters)	Percent Yield			
					Pu-236	Am-243	Cs	Sr-85
E-1	South Riding Rock 5-15-70	129	1.029	56.9	55	-	78	68
E-2	South Riding Rock 3-2-69	121	1.029	53.3	49	55	77	78
E-3	Site I, 3-7-70 25° 04'N, 78° 59'W	131	1.031	57.6	57	64	81	84
E-4	Site II, 3-7-70 24° 42'N, 78° 54'W	129	1.030	56.8	54	60	89	85
E-5	Site III, 3-7-70 24° 42'N, 78° 33'W	130	1.032	57.1	56	58	91	81
E-6	Site VI, 3-7-70 25° 13'N, 78° 29'W	128	1.028	56.5	54	43	85	86
E-7	South Riding Rock 9-10-69	134	1.026	59.2	56	85	62	55
E-8	South Riding Rock 2-12-70	136	1.026	60.1	56	40	71	63
E-9	South Riding Rock 4-17-70	134	1.026	59.2	35	72	72	61

TABLE 6 (Cont'd)

HASL No.	dpm per 100 liters at collection date			
	Pu-239,240	Am-241	Cs-137	Sr-90
E-1	0.19 ± 0.04	-	26 ± 2	18 ± 2
E-2	0.23 ± 0.04	0.04 ± 0.01	34 ± 2	23 ± 2
E-3	0.09 ± 0.02	0.021 ± 0.008	49 ± 2	33 ± 3
E-4	0.06 ± 0.01	≤ 0.004	84 ± 2	50 ± 4
E-5	0.04 ± 0.01	0.006 ± 0.008	61 ± 5	44 ± 4
E-6	0.29 ± 0.04	0.05 ± 0.02	44 ± 2	34 ± 2
E-7	0.11 ± 0.02	0.026 ± 0.005	29 ± 2	22 ± 1
E-8	0.16 ± 0.02	0.033 ± 0.009	25 ± 2	19 ± 1
E-9	0.08 ± 0.03	0.035 ± 0.007	25 ± 2	19 ± 1

Equipment

High capacity scale, 500 lbs.
Hydrometer, specific gravity range of 1.000 - 1.220
Polyethylene centrifugal pump
Polyethylene cylindrical tank and cover, 30 gallon capacity, $\frac{1}{4}$" wall thickness
Polyethylene pail, 15 liter
Polyethylene bags, 38" × 54"
Tank cart
Millipore filtering funnel, base and clamp. Funnel, 300 ml capacity, base 4 cm diameter
Magnetic stirrers with Teflon-coated magnet bars
Ion exchange columns
Double vented conical gravity funnels (Fisher #10-381)
Teflon filter stick and funnel, 2.4 cm diameter
Nylon rings and discs, 1" diameter
Mylar film
pH meter
Buchner funnel, 24 cm diameter
Filtering flasks, 4 liter
100 µl pipette
Virgin platinum discs, 17.6 mm diameter × 0.005", mirror finish one side
Platinum dishes, 100 ml capacity
Electroplating cells
Electroplating apparatus
Alpha spectrometer
Beta counter
Gamma well counter

Reagents

Plutonium-236 tracer, ~10 dpm/g. Standardize for total alpha disintegrations. Measure purity on the alpha spectrometer.

Americium-243 tracer, ~10 dpm/g. Standardize for total alpha disintegrations. Measure purity on the alpha spectrometer.

Strontium-85 tracer. Dilute an aliquot of Sr-85 in a 2 oz. polyethylene bottle to yield a count rate of ~25,000 cpm on a gamma well counter.

Iron carrier, 100 mg Fe/ml. Slowly heat 100 gms of iron wire in 500 ml of HCl until reaction ceases. Carefully and slowly add 50 ml of HNO_3 while stirring. Cool and dilute to 1 liter.

Strontium carrier, 100 mg Sr/ml. Dissolve 304 gms of $SrCl_2 \cdot 6H_2O$ and dilute to 1 liter with 5% HCl.

Cesium carrier, 20 mg Cs/ml. Dissolve 25.3 gms of CsCl and dilute to 1 liter with 5% HCl.

Yttrium carrier, 20 mg Y/ml. Dissolve 86 gms of yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ in 80 ml of water, Add 1 ml of HNO_3 and transfer the solution with 40 ml of water to a 1 liter separatory funnel. Add 120 ml of saturated NH_4NO_3 then 240 ml of tributyl phosphate (TBP) to the funnel. Shake the funnel for five minutes and allow the phases to separate. Transfer the aqueous phase to a second separatory funnel and extract again with 240 ml of unused TBP. After the phases have separated, discard the aqueous phase. Combine the two TBP phases in one funnel. Add 200 ml of water and shake for five minutes. Transfer the aqueous phase to a clean separatory funnel. Repeat the water wash. Combine the aqueous phases. Discard the TBP. Add 50 ml of CCl_4 to the water solution, shake, allow the phases to separate. Discard the CCl_4 phase. Dilute aqueous phase to 1 liter.

Barium carrier, 20 mg Ba/ml. Dissolve 35.6 gms of $BaCl_2 \cdot 6H_2O$ and dilute to 1 liter with 5% HCl.

Sodium hydroxide, pellets.

Sodium hydroxide, 2.5 N. Dissolve 100 gms of NaOH and dilute to 1 liter with water.

Ammonium phosphomolybdate, ion exchange crystals.

Bio-Rex 40, (50-100 mesh) cation exchange resin.

Bio-Rad AG 1-X4, (100-200 mesh) anion exchange resin.

Ethylenediminetetrasodiumacetate solution, 50%. Dissolve 500 gms of Na_4 EDTA and dilute to 1 liter with water.

Chloroplatinic acid, 10%. Dissolve 25 gms of H_2PtCl_6 and dilute to 250 ml with water.

Ammonium acetate, 6M. Dissolve 463 gms of NH_4OAc and dilute to 1 liter with water.

Acetic acid, 6M. Dilute 345 ml of HOAc to 1 liter with water.

Sodium chromate, 0.3M. Dissolve 48.6 gms of Na_2CrO_4 and dilute to 1 liter with water.

Sodium chloride, 5%. Dissolve 50 gms of NaCl and dilute to 1 liter with water.

Ammonium carbonate, powder.

Ammonium carbonate, 5%. Dissolve 50 gms of $(NH_4)_2CO_3$ and dilute to 1 liter with water.

Ammonium thiocyanate, crystalline.

Nitrogen gas, water pumped.

Aerosol OT, 0.1% solution in water.

Saturated Oxalic acid solution.

Methyl red.

Phenolphthalein.

Sample Preparation

1. Thoroughly clean the area near the opening of the sample container to remove surface debris. Determine the gross weight of the sample, since sample volumes as received, vary greatly and containers may be partially or completely filled. Remove sufficient sample to determine its specific gravity and to allow mixing in the container without overflow, then, transfer this amount of sample to a 30 gallon polyethylene tank.

2. Add 500 ml of concentrated HCl to the original container for the 12-15 gallon sample. Mix each sample for two hours by bubbling with nitrogen gas at a rate of ~1.3 cu ft/min. Using the centrifugal pump, transfer and combine the sample in a 30 gallon tank. Add 200 ml of 1:1 HCl to the original container, seal, rinse and combine the solution with the sample. Weigh

the empty container and calculate the sample volume from the net weight and density.

3. Add the following carrier and tracer solutions: 500 mg strontium, ~25,000 cpm Sr-85 (in 2 oz. volume and gamma-well counted), 20 mg cesium, ~0.5 dpm Pu-236, ~0.5 dpm Am-243 and 1.0 g iron solution. Mix for two hours by bubbling with nitrogen gas at a rate of ~1.3 cu ft/min.

4. Add 340-350 g NaOH pellets while mixing and carefully stir the sample with the glass tube from which the nitrogen gas bubbles until the NaOH pellets are in solution. Adjust the pH of the solution to 10.0 ± 0.5 with 5 g increments of NaOH, if necessary. Make the pH test with a pH meter.

5. Wash down the sides of the polyethylene tank with 1 liter of deionized water and finally with 250 ml of 0.1% aerosol OT solution. Clamp on the tank cover and protect with a polyethylene bag. Allow the precipitate containing plutonium, americium, and mixed hydroxides to settle overnight.

6. Remove the polyethylene bag and tank cover and pump as much clear solution from the tank as possible into a second 30 gallon polyethylene tank and reserve. Transfer the remaining solution and precipitate to a 15 liter polyethylene pail with two 500 ml rinses of deionized water.

7. Using a Buchner funnel, filter the sample over 24 cm #42 Whatman paper and collect the filtrate in one or more 4 liter filter flask(s) until the filtration is complete.

8. Transfer the filtrate from the flask(s) to the second polyethylene tank. Mix the filtrate fraction by bubbling with nitrogen gas. Adjust the solution pH to 1.5 ± 0.5 with HCl using a pH meter, then add 200 ml of HCl in excess Cover with tank cover and polyethylene bag and reserve for cesium and strontium determination.

9. Transfer the hydroxide precipitate and paper to a 3 liter beaker, then place the funnel over the beaker and dissolve any hydroxide precipitate with 25 - 50 ml HCl and wash with 50 - 100 ml deionized water. Collect the solution in the beaker.

10. Rinse the sides of the original polyethylene tank with 500 ml of hot 1:1 HNO_3. Transfer the acid rinse to the 15 liter pail. Repeat and combine solution. Transfer the nitric acid wash to the 3 liter beaker and mix. Evaporate the sample on a medium temperature hot plate until the volume is about 400 ml. Note: To prevent bumping, it is preferable to keep a glass rod (~15" length, 5/16" diameter) in the beaker throughout all evaporations rather than use boiling chips or glass beads.

11. Remove from hot plate, add 500 ml HNO_3, mix and evaporate the sample on a medium temperature hot plate until the volume is about 250 ml.

12. Increase hot plate temperature to high. Add 250 ml HNO_3, cover beaker with a watch cover and evaporate to ~200 ml. Repeat four times.

13. Remove from hot plate and cool to room temperature. Add 75 ml $HClO_4$ and 250 ml HNO_3. Mix and evaporate on a high temperature hot plate to 100 ml. Repeat additions of HNO_3 and evaporations three times to ~100 ml. Cool solution and dilute sample with deionized water to ~2 liters. Adjust solution to pH 8-10 (Hydrion paper) with sodium hydroxide and allow precipitate to settle.

14. Filter by gravity over 24 cm #41 Whatman paper using a double vented conical funnel (Fisher #10-381). Discard filtrate.

15. Dissolve hydroxide precipitate with minimum 1:1 HNO_3 and collect the solution in the original 3 liter beaker. Reserve the filter paper in a clean 800 ml beaker.

16. Evaporate the solution to ~100 ml then dilute to ~2 liters with deionized water. Add NH_4OH to pH 8-9 (Hydrion paper) and allow the precipitate to settle.

17. Repeat steps 14-16.

18. After the second NH_4OH precipitation, filter by gravity over 24 cm #41 Whatman paper. Discard filtrate. Transfer the precipitate and paper to the 800 ml beaker containing the reserved filter papers from the first and second filtrations. Note: The sodium hydroxide collection in step 13 is designed to separate the hydroxides without the precipitation of insoluble perchlorates. The two ammonium hydroxide collections

are designed to separate minimal amounts of alkaline earths.

19. Add 500 ml HNO_3, mix and evaporate the sample on a medium temperature hot plate until the volume is about 150 ml.

20. Remove from hot plate. Increase hot plate temperature to high. Add 250 ml HNO_3, cover beaker with a watch cover and evaporate to ~50 - 70 ml. Repeat four times.

21. While still hot, immediately add an equivalent volume of deionized water and filter by gravity over 18.5 cm #40 Whatman paper. Police the beaker thoroughly and wash the precipitate with 1:1 HNO_3. Collect filtrate and washings in a 400 ml beaker. Cover and reserve for plutonium and americium separation.

22. Transfer the paper and precipitate to a 100 ml platinum dish and dry at 110°C. Ignite at 600°C or suitable temperature until carbon is completely removed. Cool to room temperature.

23. Add 25 ml of HNO_3 and 25 ml of HF to the platinum dish and evaporate to dryness on a medium temperature hot plate. Repeat.

24. Add 2 ml of $HClO_4$ and 25 ml of HNO_3. Evaporate to dryness. Cool. Add 10 ml of 1:1 HNO_3 to the residue, and heat on a medium temperature hot plate ~3 minutes. Cool. If the residue dissolves, transfer the solution to the sample reserved under step 21 using 1:1 HNO_3. If the residue is not in complete solution, filter by gravity over 9 cm #42 Whatman paper and combine the filtrate with the sample reserved under step 21 using 1:1 HNO_3. Reserve combined solution for plutonium and americium separation.

Plutonium and Americium Separation

1. Evaporate the 1:1 HNO_3 solution (reserved under Sample Preparation, step 24) to ~100 ml. Cool to room temperature and transfer to a 250 ml graduated cylinder and record the volume.

2. Dispense two 100 microliter aliquots to 150 ml beakers containing 25 ml of deionized water in each. Add 2-3 drops of 0.5% phenolphthalein (dissolved in 95% ethanol). Titrate the two solutions with standardized 0.1N NaOH to a phenolphthalein

end point. Calculate the average normality of the sample solution.

3. Transfer the sample from the graduate cylinder to the 400 ml beaker. Wash the cylinder with the amount of deionized water necessary to adjust the normality of the sample solution to 9N HNO_3.

4. Heat the 9N HNO_3 solution 90°C. Add 100 mg of sodium nitrite. Continue to heat until the evolution of nitrous oxide ceases. Using an ice water bath, cool the sample to room temperature.

5. With 9N HNO_3 wash about one-half of the Column I conditioned ion exchange resin (see Note 1) into the sample and stir for 5 minutes. Quantitatively transfer the sample and the resin to Column I.

6. Pass the solution through the resin bed at full flow and make certain that all resin particles adhering to the beaker or resin funnel are washed into the resin bed with 9N HNO_3. Allow the liquid to flow until the level reaches the top of the resin bed.

7. Wash the resin bed with three 25 ml portions of 9N HNO_3 and allow each to flow until the solution level reaches the top of the resin.

8. Collect and combine effluent solutions from steps 6 and 7 in a 600 ml beaker. Reserve.

9. Elute plutonium from the resin with 200 ml of 0.4N HNO_3 - 0.01N HF and collect the fraction in a 250 ml beaker. Evaporate the solution to dryness on a low temperature hot plate and reserve. Discard the resin.

10. The solution reserved in step 8 contains a small amount of plutonium and the major portion of americium. The following steps are designed to separate the small fraction of plutonium and combine it with the major plutonium fraction before proceeding with the determination of americium.

    a. Evaporate the solution from step 8 to ~75 ml then dilute to ~300 ml with deionized water. Adjust solution to pH 8 - 10 with NH_4OH and allow the precipitate to settle.

b. Filter by gravity over 24 cm #41 Whatman paper. Discard the filtrate. Transfer the precipitate and paper to the original 600 ml beaker. Add 300 ml HNO_3, mix and evaporate the sample on a medium temperature hot plate until the volume is about 100 ml.

c. Remove from the hot plate. Increase the hot plate temperature to high. Add 100 ml HNO_3, cover the beaker with a watch cover and evaporate to 50 - 100 ml. Repeat four times. Cool to room temperature and transfer to a 100 ml graduated cylinder.

d. Repeat steps 2-8 and reserve the solution for Americium determination.

e. Repeat step 9 and collect the second fraction of plutonium in the same beaker containing the residue with the major fraction of plutonium.

Plutonium Determination

1. Add 5 ml of HNO_3 to the sample from step 10 e under Plutonium and Americium separation and evaporate to dryness. Repeat.

2. Dissolve the residue with 15 ml of 9N HNO_3 and heat to ~90°C. Add 10 mg of sodium nitrite and continue heating until the evolution of nitrous oxide ceases. Using an ice water bath, cool the sample to room temperature.

3. With 9N HNO_3 wash about one-half of the conditioned resin in Column II (see Note 2) into the sample and agitate for 5 minutes. Quantitatively transfer the sample and resin to Column II.

4. Pass the solution through the resin bed at full flow and make certain that all resin particles adhering to the beaker or the resin funnel are washed into the resin bed with 9N HNO_3. Allow the liquid to flow until the level reaches the top of the resin bed.

5. Wash the resin with three 8 ml portions of 12N HCl and allow each solution to pass through until the level reaches the top of the resin bed. Wash the resin with three 10 ml por-

tions of 9N HNO_3 and allow each addition to reach the top of the resin bed. Discard the sample effluent and washings.

6. Elute plutonium with 100 ml of 0.4N HNO_3 - 0.01N HF and collect the fraction in a 150 ml beaker. Discard the resin. Evaporate the solution to dryness and convert the residue to chloride by adding 1 ml of HCl and evaporating to dryness twice.

7. Add 1 ml of HCl to the dried plutonium residue and warm gently, ~50° - 60°C. Transfer the solution with a transfer pipet to an electrolytic cell. Wash the beaker and pipet with two 1 ml portions of deionized water and transfer to the cell.

8. Add 1 drop of 0.1% methyl red indicator. Add the minimum amount of NH_4OH dropwise until the solution is yellow. Add the minimum amount of 1:5 HCl dropwise until the solution is red. Add 5 drops of 1:5 HCl in excess.

9. Dilute to 5 ml with deionized water. Electroplate at a current density of 1.2 amperes for 1 hour. Note: At HASL our cell is supported on a Lucite pedestal which is immersed in an ice water bath throughout the plating interval.

10. At the end of the electroplating interval, quench the electrolyte with 1 ml of NH_4OH. Dismantle the cell and rinse the electroplated disc with deionized water then ethanol.

11. Flame the disc over a burner to red heat. Cool. Count the disc on a standardized alpha spectrometer. Calculate the Pu-236 yield and determine the activity of the plutonium isotopes.

Americium Determination

1. Evaporate the reserved sample for Americium Determination from step 10 d under Plutonium and Americium Separation to 50 - 100 ml.

2. Dilute the solution to ~300 ml with deionized water. Add 100 mg of calcium. Using a mechanical stirrer, add 25 g oxalic acid to the solution and mix to dissolve.

3. From a separatory funnel add NH_4OH dropwise to the sample until the pH is 2.5 - 3.0.

4. Allow the precipitate to settle and the solution to cool to room temperature. Recheck the pH.

5. Filter by gravity over 18.5 cm #42 Whatman paper. Wash the precipitate and paper with 5% ammonium oxlate, pH 2.5 - 3.0 (50 g oxalic acid per liter and adjusted to pH 2.5 - 3.0 with NH_4OH).

6. Transfer the precipitate and paper to a 100 ml platinum dish, dry at 100°C, and ash at 600°C until all the carbon is removed.

7. Transfer the ash to a 400 ml beaker. Wash the platinum dish with a small amount of dionized water and transfer the washing to the beaker. Add 5-10 ml HNO_3 to the platinum dish and warm on a medium temperature hot plate then transfer the acid wash to the beaker and finally rinse the dish with deionized water and combine with the sample.

8. Dilute the solution to ~250 ml with deionized water. Add 10 g of oxalic acid and dissolve by using a mechanical stirrer.

9. Repeat steps 3-6.

10. Moisten the ash in the platinum dish by using the minimum amount of deionized water. Cover with a watch cover and carefully add HNO_3 dropwise until the carbon dioxide evolution ceases and the sample is mostly dissolved.

11. Make the solution ~20 ml of 1:1 HNO_3 and warm for a few minutes on a medium temperature hot plate. Transfer to a 90 ml centrifuge tube with deionized water. Add 5 ml of 1:1 HCl to the platinum dish, warm and combine with the solution in the centrifuge tube. Mix thoroughly. Add 10 mg of iron carrier solution.

12. Carefully adjust the solution to pH 8 - 10 with NH_4OH. Cool to room temperature. Centrifuge, decant, and discard the supernate.

13. Dissolve the hydroxide precipitate with HCl. Dilute with deionized water and repeat steps 12 and 13 until the hydroxide precipitate is free of calcium (three precipitations are

usually sufficient). Dissolve the final hydroxide precipitate with 50 ml of HCl.

14. Transfer the solution to ion exchange Column III (see Note 3) and allow it to flow at a rate not exceeding 1 ml/min. Collect the eluate in a 250 ml beaker. Wash the resin column with 3 - 25 ml portion of HCl and collect the wash solution in the same beaker. Evaporate the solution to dryness on a low temperature hot plate. Discard the resin.

15. Add 2 - 3 ml HCl to the residue. Cover with a watchcover and warm the sample on a hot plate to completely dissolve the residue. Cool to room temperature.

16. Add 30 ml of purified 4M NH_4SCN (see Note 4) and pass the sample through ion exchange resin column IV (see Note 5). Collect the waste in a 400 ml beaker. Wash the resin column with 200 ml of purified 4M NH_4SCN and collect the eluate in the 400 ml beaker. Discard sample waste and wash solutions.

17. Elute americium with 180 ml of a mixture of 0.4M NH_4SCN - 0.3M HCl (25 ml HCl + 100 ml purified 4M NH_4SCN diluted to 1 liter). Collect the americium fraction in a 250 ml beaker and evaporate to dryness on a low temperature hot plate. Discard the resin.

18. To remove ammonium salts, place the beaker on a tripod mounted on a stand and heat slowly with a cool bunsen flame. After ~$\frac{1}{2}$ hour increase the flame temperature and continue heating to remove all ammonium salts and sulfur, then heat briefly to dull red heat. This step requires ~1 to 1.5 hours.

19. Cool to room temperature. Add 25 ml HNO_3 and boil slowly for a few minutes. Cautiously add 1 ml 30% H_2O_2 and evaporate the solution to dryness.

20. Convert the residue to chloride by adding 1 ml of HCl and evaporating to dryness twice.

21. Add 1 ml of HCl to the dried americium residue and warm gently at ~50°C - 60°C. Transfer the solution with a transfer pipette to an electrolytic cell. Wash the beaker and pipette with two 1 ml portions of deionized water and transfer to the cell.

22. Add 1 drop of 0.1% methyl red indicator. Add the minimum amount of NH_4OH dropwise until the solution is yellow. Add the minimum amount of 1:5 HCl dropwise until the solution is red. Add 5 drops of 1:5 HCl in excess.

23. Dilute to 5 ml with deionized water. Electroplate at a current density of 1.2 amperes for 1 hour.

24. At the end of the electroplating interval, quench the electrolyte with 1 ml of NH_4OH. Dismantle the cell and rinse the electroplated disc with deionized water then ethanol.

25. Flame the disc over a burner to red heat. Cool. Count the disc on a standardized alpha spectrometer. Calculate the Am-243 and determine the activity of the americium isotopes.

Cesium Determination

1. Mix the solution reserved for cesium and strontium determination (Sample Preparation, step 8) by bubbling with nitrogen gas for one hour at a rate of 1.3 cu ft/min.

2. Add 10 g of ammonium phosphomolybdate and continue mixing with nitrogen gas for one hour. Cover with tank cover and protect with polyethylene bag. Allow the cesium ammonium phosphomolybdate to settle overnight.

3. Remove the polyethylene bag and tank cover, add 100 ml of 0.1% Aerosol OT solution to the sample (do not mix) and pump all of the solution except 300 - 500 ml into the first polyethylene tank (Sample Preparation, step 10) and reserve this for strontium determination.

4. Dissolve the cesium-ammonium phosphomolybdate with 500 ml of 2.5N NaOH and transfer the sample to a 3 liter beaker. Rinse the tank twice with 500 ml of water and combine the rinses with the sample.

5. Neutralize the solution with HCl while stirring and add 100 ml in excess. Add 1 g of ammonium phosphomolybdate and continue stirring for one hour. Filter the sample through a 4.7 cm glass fiber filter mounted on a Millipore filtering apparatus and alternately wash the sides of the funnel with 5% HCl and 0.1% Aerosol OT.

6. Transfer the paper and the cesium-ammonium phosphomolybdate to a 40 ml centrifuge tube. Add 5 ml of water and macerate the filter with a stirring rod. Add saturated NaOH dropwise with stirring until the yellow solid is dissolved.

7. Filter by suction to remove the filter pulp, wash with water and collect the filtrate and washing in a 150 ml beaker. Add 10 ml of 50% Na_4 EDTA solution to the sample and mix.

8. Pass the sample through the Bio-Rex 40 ion exchange column (see Note 6) at a flow rate not exceeding 1 ml per minute. Pass 200 ml of water through the column at a flow rate not exceeding 3 ml per minute. Wash the column with 900 ml of 0.12N HCl at a flow rate, not exceeding 1 ml per minute. Discard sample effluent and washings.

9. Elute cesium from the column with 200 ml of 2N HCl. Collect the eluate in a 400 ml beaker and evaporate the solution to dryness.

10. Dissolve the residue with 5 drops of HCl. Transfer the solution with water to a 40 ml centrifuge tube and dilute to 20 ml. Add 4 ml of 10% H_2PtCl_6 and stir until precipitation occurs. Place the sample in an ice water bath for two hours or in a refrigerator overnight.

11. Filter the sample with suction through a weighed 2.4 cm Whatman #42 paper. Dry the cesium chloroplatinate precipitate at 105°C for one hour. Weigh, mount on a 1 inch nylon disc, cover with mylar and nylon ring and beta count.

Strontium Determination

1. Adjust the reserved strontium solution (Cesium Determination, step 3) to pH 10.0 ± 0.5 by adding sodium hydroxide pellets and mix by bubbling nitrogen gas through the sample.

2. Add 1 kilogram of ammonium carbonate powder. Continue mixing the sample for two hours at a nitrogen gas flow rate of ~1.3 cu ft/min. Add 100 ml of 0.1% Aerosol OT. Cover with tank cover and protect with a polyethylene bag. Allow the precipitate to settle overnight.

3. Pump as much clear solution from the tank as possible. Transfer the remaining solution and precipitate with 5% ammonium carbonate to a 15 liter polyethylene pail, then filter over a 24 cm Whatman #42 filter paper on a Buchner funnel. Wash the precipitate with 1 liter of 5% ammonium carbonate solution. Discard filtrate and washing.

4. Transfer the filter paper and precipitate to a 3 liter beaker. Dissolve the precipitate by slowly adding 250 ml of 1:1 HNO_3, then add 500 ml of HNO_3. Mix thoroughly and evaporate on a medium temperature hot plate until the volume is 100-200 ml and salting out begins. Immediately add 460 ml of water.

5. Using a magnet stirrer, carefully add 1540 ml of 90% HNO_3 and continue stirring until the solution is at room temperature. Filter through a 12.5 cm glass fiber paper and discard the filtrate. Dissolve the nitrate precipitate with water and transfer the solution to a 600 ml beaker. Evaporate the solution to dryness.

6. Add 70 ml of water to the residue. With mechanical stirring add 240 ml of 90% HNO_3 and continue stirring until the solution is at room temperature. Filter through a 5.5 cm glass fiber paper and discard the filtrate.

7. Dissolve the precipitate with water and collect the solution in a 40 ml centrifuge tube. Add 20 mg of yttrium carrier and adjust the solution to pH 8 with ammonium hydroxide. Centrifuge and decant the supernate into a second centrifuge tube.

8. Dissolve the yttrium hydroxide precipitate with 5 drops of HCl, add 5 ml of water and reprecipitate yttrium with ammonium hydroxide at pH 8. Centrifuge and combine supernates. Discard the precipitate.

9. Add 1 ml of 6M acetic acid and 2 ml of 6M ammonium acetate. Adjust the solution to pH 5.5 with HCl or NH_4OH. Heat the sample in a hot water bath at 90°C. Add 1 ml barium carrier and 2 ml of 0.3M sodium chromate. Continue to digest the sample at 90°C until barium chromate is precipitated. Cool, centrifuge and decant the supernate into a clean centrifuge tube. Discard chromate precipitate.

10. Add 1 ml of barium carrier and digest at 90°C until barium chromate is precipitated. Cool, centrifuge and decant the supernate into a 2 oz. polyethylene bottle containing 1 ml of HCl and 10 mg of yttrium carrier. Discard the chromate precipitate.

11. Dilute the sample to a marked volume with water and gamma count Sr-85. Standardize to a 2 oz. polyethylene bottle by adding the amount of Sr-85 tracer equivalent to that used to spike the sample. Dilute to a marked volume and gamma count. Calculate the strontium recovery. Store the strontium solution for two weeks.

12. Transfer the sample after the two week buildup interval to a 150 ml beaker and evaporate to 15 - 20 ml. Transfer the solution to a 40 ml centrifuge tube, add ammonium hydroxide to adjust the solution to pH 8 for yttrium hydroxide precipitation. Record the hour and date.

13. Add 6 drops of 30% hydrogen peroxide and digest at 90°C until the peroxide is decomposed. Cool, centrifuge and decant the supernate into the original 2 oz. bottle. Dissolve the precipitate with HCl, add 5 ml of water and reprecipitate yttrium with ammonium hydroxide at pH 8. Centrifuge and combine supernates. Make the solution acid with HCl in the 2 oz. bottle, add 10 mg of yttrium carrier and reserve for future milkings.

14. Dissolve the yttrium hydroxide precipitate with HCl and dilute to 20 ml with water. Add 20 mg of strontium carrier and precipitate yttrium with ammonium hydroxide at pH 8. Centrifuge and discard the supernate. Repeat step 14 without adding strontium carrier.

15. Dissolve the precipitate with 4-5 drops of HCl and dilute with water to 20 ml. Add 1 ml of saturated oxalic acid and adjust the solution to pH 2.5 - 3.0 with ammonium hydroxide. Digest for 10 minutes at 90°C. Cool in a cold water bath and filter through a weighed 2.4 cm Whatman #42 filter. Discard the filtrate.

16. Dry the yttrium oxalate precipitate at 105°C for one hour. Weigh, mount and beta count on a low background counter. Record the hour and date.

17. Standardize the beta counter with an Y-90 standard which has been precipitated and mounted similar to the sample. Calculate the yttrium recovery. Correct for both strontium and yttrium yields.

Note 1

Column I Preparation. The column is made from borosilicate glass. The outside diameter is 17 mm with a reservoir at the top of the column (35 mm diameter and 77 mm long) and a glass stopcock at the lower end. The overall length of the column is 315 mm. Position a plug of glass wool at the base of the column. Add 20 ml of wet settled resin (Bio-Rad AG 1-X4, 100-200 mesh). Wash the resin with 50 ml of 0.4N HNO_3 - 0.1N HF solution. Pass 150 ml of 9N HNO_3 through the resin or a sufficient volume to remove all chloride indicated by a negative silver nitrate test.

Note 2

Column II Preparation. The column is made from borosilicate glass. The dimensions are the same as Column I except that the outside diameter is 11 mm. Prepare column II in the same way as column I, except add 5 ml of resin.

Note 3

Column III Preparation. The column is made from borosilicate glass and the dimensions are the same as used under Note 1. Position a plug of glass wool at the base of the column. Transfer with deionized water 10 ml of wet settled resin (Dowex 1-X4, 100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass two 50 ml volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug. The column is now ready for the sample solution.

Note 4

Ammonium Thiocyanate, 4M. Dissolve 304 g of NH_4SCN in deionized distilled water and dilute to one liter. For 10 samples make 4 liters of solution in a 5 liter polyethylene beaker.

Purification of 4 liters of 4M NH_4SCN. Filter 150 ml of wet settled Dowex 1 × -4 (100-200 mesh) ion exchange resin in the chloride form through #41 Whatman paper. Transfer about one-half of the resin to the 4 liter solution of 4M NH_4SCN. Mix for 1 hour using a magnetic stirrer. Remove the magnet and allow the resin to settle. Transfer the remaining clean resin to a second 5 liter polyethylene beaker and decant the 4M NH_4SCN into the second beaker. Mix for one hour using a magnetic stirrer. Discard the first resin. Using a Buchner funnel and dry flask, filter the solution through #40 Whatman paper and store in a dry polyethylene bottle. Discard the resin.

0.4M NH_4SCN - 0.3M HCl Mixture. Dilute 100 ml of purified 4M NH_4SCN to 500 ml with deionized distilled water then add 25 ml HCl and dilute to 1 liter. Make 2 liters of solution for 10 samples.

Note 5

Column IV Preparation. The column is made from borosilicate glass and the dimensions are the same as used under Note 1. Position a plug of glass wool at the base of the column. Transfer with deionized distilled water, 15 ml of wet settled resin (Dowex 1-X4-100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stop-cock open allow the water level to reach the top of the upper plug. Pass 100 ml of purified 4M NH_4SCN through the resin bed in two 50 ml portions allowing the level of each to reach the top of the upper glass wool plug. The column is now ready for the sample solution.

Note 6

Column V Preparation. Transfer 500 g of Bio-Rex 40 (50-100 mesh) to a 3 liter beaker. Add 2 liters of water and stir for 30

minutes. Allow the resin to settle. Decant and discard the wash solution. Repeat the washing procedure with 2 liters of each of the following solutions: 1N NaOH, water (twice), 1N HCl, and water (twice). After the final wash, transfer the resin with water to a 1 liter polyethylene bottle for storage. The column dimensions are the same as for column I (Note 1). Fill the column with water and position a wad of glass wool at the bottom of the column with a glass rod. Transfer 15 ml of wet-settled resin to the column and allow it to settle. Place a second wad of glass wool on top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass 200 ml of 5% NaCl through the resin at a flow rate not exceeding 5 ml per minute. The column is now ready for the sample solution.

RESULTS AND DISCUSSION

Using the procedure as outlined, the results of analysis of Pu-239,240, Am-241, Cs-137 and Sr-90 are shown in Table 7. The samples include mid-depth vertical profiles from three hydrographic stations, location and collection date not identified; five quality control samples; and four large volume deionized water samples which were analyzed concurrently to determine the blank levels. The sample net weight, specific gravity and overall chemical yield are given for completeness. The results of analysis are reported as dpm per 100 liters.

For the sea water samples shown in Table 7, the chemical yields averaged 62 ± 9 and 69 ± 14 percent for Pu-236 and Am-243 tracers, respectively. The results of analysis for Pu-239,240 and Am-241 ranged from 0.10 - 0.48 and 0.005 - 0.07 dpm per 100 liters, respectively. The overall yields for the transuranics in the blank samples were comparable to the yields for the sea water samples. The levels of the blank analyses ranged from 0.003 - 0.03 and 0.001 - 0.01 dpm per 100 liters for Pu-239,240 and Am-241, respectively. Because of the variation of the blanks, the plutonium and americium values reported herein have not been corrected. The error term associated with the transuranic values is a single Poisson error due to counting.

The average chemical yields were 75 ± 5 and 86 ± 14 percent for cesium carrier and Sr-85 tracer, respectively, for the sea water samples. Cesium carrier yields were comparable for the blanks. Strontium yields for the blanks ranged from 47-59 percent; higher yields for blanks may be accomplished by reducing the volume of the initial nitrate separation. The reported Cs-137 and Sr-90 values for the sea water samples were corrected for blank. The error term associated with the Cs-137 values is a single Poisson error. The error term for the Sr-90 values is a 70% confidence interval.

Our analytical measurements of Pu-239,240 and Am-241 are briefly compared with other measurements of sea water samples collected by different investigators from various locations in the world's oceans. The Pu-239,240 and Am-241 concentrations reported in Table 6 for samples E1 - E9 range from 0.2 - 1.3 and <0.02 - 0.2 femtocuries (fCi) per liter, respectively. The Pu-239,240 and Am-241 concentrations reported in Table 7 for sea water samples range from 0.5 - 2.2 and 0.02 - 0.3 fCi per liter, respectively.

TABLE 7

Pu-239,240, Am-241, Cs-137 AND Sr-90 MEASUREMENTS OF MID-DEPTH PROFILES, QUALITY CONTROL SEA WATERS AND BLANK SAMPLES

HASL No.	Sample Identification	Net Wt. (lbs.)	Specific Gravity	Volume (liters)	Percent Yield			
					Pu-236	Am-243	Cs	Sr-85
E-10	AII 78 1993 (100 m) (3665)	131	1.027	57.8	70	72	65	93
E-11	AII 78 1993 (300 m) (3662)	124	1.026	54.8	83	81	75	94
E-12	AII 78 1993 (700 m) (3659)	115	1.025	50.9	42	79	78	94
E-13	AII 85 (QCW) (3670)	132	1.025	58.4	56	67	72	90
E-14	IAEA AII 66 33 (QCW) (3667)	133	1.024	58.9	61	64	70	95
E-15	AII 78 2005 (100 m) (3653)	126	1.024	55.8	58	67	71	95
E-16	AII 78 2005 (300 m) (3660)	129	1.024	57.1	62	73	76	98
E-17	IAEA AII 6635 (QCW) (3669)	121	1.025	53.5	64	62	81	93
E-19	Deionized water blank	-	-	60.0	74	78	81	59

TABLE 7 (Cont'd)

HASL No.	Sample Identification	Net Wt. (lbs.)	Specific Gravity	Volume (liters)	Percent Yield			
					Pu-236	Am-243	Cs	Sr-85
E-20	Deionized water blank	-	-	60.0	77	52	83	58
E-21	AII 78 1919 Surface (3664)	120	1.028	52.9	57	63	77	73
E-22	AII 78 1919 (140 m) (3668)	129	1.027	57.0	63	29	79	87
E-23	AII 78 1919 (200 m) (3657)	126	1.026	55.7	70	75	70	48
E-24	AII 78 1919 (400 m) (3652)	127	1.024	56.2	62	86	74	55
E-25	AII 85 (QCW) (3654)	133	1.026	58.8	53	66	77	80
E-26	IAEA (QCW) (3661)	133	1.025	58.8	67	84	79	88
E-27	Deionized water blank	-	-	60.0	55	88	77	48
E-28	Deionized water blank	-	-	60.0	51	70	65	47

TABLE 7 (Cont'd)

HASL No.	dpm per 100 liters			
	Pu-239,240	Am-241	Cs-137	Sr-90
E-10	0.24 ± 0.03	0.03 ± 0.01	33 ± 2	22 ± 1
E-11	0.44 ± 0.04	0.06 ± 0.01	37 ± 2	23 ± 2
E-12	0.14 ± 0.04	0.07 ± 0.02	4.7 ± 0.6	2.9 ± 0.6
E-13	0.15 ± 0.02	0.01 ± 0.007	26 ± 2	15 ± 1
E-14	0.19 ± 0.03	0.027 ± 0.007	32 ± 2	21 ± 3
E-15	0.18 ± 0.02	0.013 ± 0.005	24 ± 2	15 ± 1
E-16	0.48 ± 0.05	0.06 ± 0.01	29 ± 2	20 ± 3
E-17	0.14 ± 0.02	0.010 ± 0.006	30 ± 4	22 ± 2
E-19	0.003 ± 0.003	<0.01	0.5 ± 0.2	0.8 ± 0.2

TABLE 7 (Cont'd)

HASL No.	dpm per 100 liters			
	Pu-239,240	Am-241	Cs-137	Sr-90
E-20	0.017 ± 0.007	0.001 ± 0.004	0.3 ± 0.2	0.8 ± 0.1
E-21	0.10 ± 0.02	0.01 ± 0.01	17 ± 2	13 ± 1
E-22	0.23 ± 0.03	0.012 ± 0.008	33 ± 2	23 ± 2
E-23	0.27 ± 0.03	0.06 ± 0.01	34 ± 2	21 ± 2
E-24	0.35 ± 0.04	0.06 ± 0.01	30 ± 2	21 ± 2
E-25	0.15 ± 0.03	0.005 ± 0.004	24 ± 2	15 ± 1
E-26	0.16 ± 0.03	0.03 ± 0.01	29 ± 2	20 ± 2
E-27	0.03 ± 0.01	0.012 ± 0.004	0.2 ± 0.2	1.1 ± 0.3
E-28	<0.005	0.012 ± 0.004	0.3 ± 0.2	1.5 ± 1.1

Miyake and Sugimura (1975) recently summarized the Pu-239,240 analytical results of sea water measurements reported by several investigators: Pillai et al. (1964); Miyake and Sugimura (1968); Bowen et al. (1971); and Noshkin et al. (1974). The summary comprised a total of 60 samples. The Pu-239,240 concentrations of surface sea water samples collected in 1964 by Pillai et al. (1964) from the Scripps Pier, La Jolla, California and from selected stations in the eastern North Pacific ranged from 0.3 - 0.5 and 2.0 - 3.0 fCi per liter, respectively. The Pu-239,240 concentrations of surface samples collected in 1967 by Miyake and Sugimura (1968) from selected stations in the western North Pacific Ocean ranged from 0.1 - 1.4 fCi per liter, and 0.2 - 0.3 fCi per liter at 1000 - 3000 meters. The Pu-239,240 concentrations of surface sea water samples reported by Bowen et al. (1971) from selected stations in the North Atlantic Ocean during 1963, 1964, 1967, 1968 and 1969 ranged from 0.3 - 1.8 fCi per liter; the Pu-239,240 concentrations of samples collected from 300 - 700 meters in 1968-1969 from selected stations in the North Atlantic ranged from 0.4 - 3.0 fCi per liter, and 0.1 - 0.4 fCi per liter at 1000 - 3000 meters; samples collected from 0 - 100 meters during 1968 from selected stations in the South Atlantic ranged from 0.3 - 0.5 fCi Pu-239, 240 per liter. The Pu-239,240 concentrations of surface sea water samples reported by Noshkin et al. (1974) from selected stations in the eastern North Pacific during 1972 ranged from 0.3 - 1.5 fCi per liter.

Miyake and Sugimura (1975) also reported the Pu-239,240 concentrations found in 48 North Pacific and South Pacific Ocean water samples collected during 1968 to 1973; the plutonium content for surface samples ranged from 0.22 - 0.94 and 0.13 - 0.34 fCi per liter, respectively. The plutonium content in Pacific deep waters (1000 - 3000 meters) collected from selected north and south stations ranged from 0.13 - 0.38 fCi Pu-239,240 per liter, and the Pu-239,240 concentrations found for surface samples collected from the Japan Sea ranged from 0.18 - 1.26 fCi per liter.

Fukai et al. (1974) measured the Pu-239,240 concentrations in Mediterranean Sea water. The plutonium content of water samples collected (collection date not given) from the Liguarian Sea ranged from 0.9 - 2.7 fCi per kilogram at a depth of 5 meters; 2.6 - 8.5 fCi per kilogram at a depth of 50 meters; and 0.5 - 1.6 and 0.7 - 2.4 fCi Pu-239,240 per kilogram at depths of 500 and 2000 meters, respectively.

Murray and Kautsky (1975) have recently reported plutonium and americium measurements of samples from selected stations in

the North Sea and the English Channel. They indicate that some of their measurements reflect waste discharges from nuclear fuel reprocessing operations. The concentrations of Pu-239,240 and Am-241 found in surface waters collected in 1975 from selected stations in the English Channel ranged from 1.6 - 10.6 and 0.09 - 1.6 fCi per liter, respectively: the concentrations of Pu-239,240 and Am-241 found in surface water collected in 1975 from selected stations in the North Sea ranged from 0.7 - 4.9 and 0.12 - 0.14 fCi per liter, respectively.

As indicated throughout, this report is concerned primarily with the analytical measurements of sea water samples; the oceanographic implications of the measurements are not within the scope of this paper and this will be reported independently elsewhere. However, we believe a discussion of pertinent procedural problems beyond the preliminary investigations should be useful to others whether or not plutonium and americium are determined alone or in sequence with cesium and strontium.

Sample Preparation

Intercomparison analyses cited by Bowen (1974) showed that plutonium was not absorbed onto the walls of the polyethylene sample collecting containers. This was determined by measuring samples soon after collection and an independent measurement some 18 months later. Samples for measurement that we have received are most often clear in general appearance, and seem to be free of particulates. There have been occasions where the samples are turbid; contain floating particulates, sand deposits, surface oil films, settled heavy crude oil, and barrel filings. Each of these situations required some variation in the initial approach of sample preparation. In all cases, we made an effort to analyze the sample as received within practicable limits. Where the sample was turbid, or contained floating particulates throughout, or displayed a surface oil film, no change was made in the sample preparation procedure. Where sand deposits or barrel filings were found, these were removed by filtering and given a minimal acid wash then the washings combined with the sample. Heavy crude oil was extracted with chloroform and the chloroform was washed several times with hydrochloric acid then the acid combined with the sample. For all samples, it is recommended that after most of the sample has been transferred by pumping from the original container to the 30 gallon tank, the acid rinse of the container be transferred to a 15 liter polyethylene pail before combining with the main sample to determine if a variation is required in the procedure.

During the course of the preliminary investigations, we began reducing the amounts of some of the added tracers and carriers in the method. We reduced the amount of iron carrier from 1.5 to 1 gram which is presently in use in the procedure. The amounts of Pu-236 and Am-243 tracers were reduced from a known weight of ~2 dpm to ~0.5 dpm. The latter level of tracers for the transuranics was sufficient and was found to be satisfactory and compatible with practical counting intervals of measuring the fallout levels of plutonium and americium.

Because of the complexity of the chemistry of plutonium in its many valency states we continue to believe that the transuranics should be removed first as hydroxides from the sea water matrix. Recent investigators giving very comprehensive details concerning the chemical and physical states of plutonium in aqueous systems (Coleman, 1965; Milyukova et al., 1969; Matlack 1974; and Schell and Watters, 1975) emphasize plutonium existence in several valency states and the tendency of each towards hydrolysis, polymerization, complex formation, disproportionation, and oxidation and reduction depending on the treatment in solution. Milyukova et al. (1969) summarize the effect of the co-precipitation of trace amounts of plutonium in the three main valency states, Pu III, Pu IV, and Pu VI, with various carriers. When compared to other carriers such as phosphates, fluoride, sulfates, arsonates, oxalates, and iodates, only hydroxides quantitatively co-precipitate plutonium in the three main valency states.

Since the plutonium yields we found were consistently below 70 percent, we made a second hydroxide collection of the samples during the determination of the decontamination factor of plutonium from americium. We had used ~40 dpm of Pu-242 tracer and a second iron hydroxide collection was made to determine the loss in the first collection from the large volume sample; we found less than one percent of the tracer remaining after the first hydroxide collection. This amount perhaps was due to finely suspended particles of hydroxide which had not settled out of solution when the first filtrate was removed by pumping.

Equilibration of Tracers, Carriers and Sample Radionuclides

The initial acid mixing of the sample after adding carriers and tracers was adequate for the equilibration of cesium and strontium. We experienced various degrees of difficulty in destroying organic material associated with the hydroxide collection of the transuranics in order to be certain of equilibrium.

The samples collected from the New York Aquarium required much less treatment with strong mixed acids than those collected from the open ocean. We have attributed this to the necessity of decomposing small but variable amounts of petroleum hydrocarbons of which possibly all open-ocean samples presently contain. Where careful analyses were carried out at the organic removal step, the length of time and amount of acid differed from sample to sample thus requiring special attention for each. The importance of attempting to render the iron-plutonium-americium fraction free of organic material before proceeding to the ion exchange absorption of plutonium cannot be overemphasized.

Ion Exchange Separations

The separation of cesium by batch adsorption onto ammonium phosphomolybdate (APM) was discussed under preliminary investigations. At HASL other laboratory operations requiring the use of ammonium reagents are not performed in the same area during the analysis of cesium, such as, continuing the procedure by the precipitation of strontium where it is necessary to weigh large amounts of ammonium carbonate, or where reprecipitations or iron carrier in the plutonium procedure maybe required with ammonium hydroxide. Also, we dry for 24 hours at 105°C the APM; the dried ion exchanger permits better handling during weighing. Both ion exchange operations for cesium, i.e., APM and Bio-Rex 40, as outlined in the method are without problems.

Our experience with the nitrate anion separation of plutonium was the least reliable of all the operations involving the determination of plutonium. We used sodium nitrite to effect a Pu (IV) valency state prior to nitrate anion exchange. This was based on the oxidation of Pu III to Pu IV by nitrite treatment which also causes the reduction of Pu VI to Pu IV. Under these conditions we found when the sample and the ion exchanger (Dowex 1X-4, 100-200 mesh) were prepared in corresponding concentrations of 7,8, and 9N HNO_3 a recovery of 50-55 percent plutonium was obtained. When the 7, 8 and 9N HNO_3 effluent wash solutions containing the iron and americium were evaporated, diluted, and reprecipitated with ammonium hydroxide and again converted to the previous acid concentrations for sample and freshly prepared resin, a recovery of 25-30 percent of plutonium was found. As a result of these findings, we include in the method two ion exchange passes for plutonium prior to reserving the sample for americium analysis. The two eluted fractions of plutonium are combined for final purification from traces of iron, thorium, and uranium. Although

we use 9N HNO_3 in our method and this concentration is achieved by titrating a 100 microliter aliquot of the sample then making the necessary adjustment, we did not find it superior to 7 or 8N HNO_3 in the ion exchange separation.

The ion exchange separations related to americium purification are without problems. The ion exchange batch extraction for the purification of the ammonium thiocyanate reagent eliminates traces of iron. Also, the reagent purification tends to remove some impurities which may affect the quality of the electroplated source of americium.

Electrodeposition

The resolution by alpha particle spectrometry of the radioactive species of plutonium and americium from their respective electroplated sources is best accomplished when the source is free of mass. Particular care is required in keeping as clean as possible the operations of final purification and electrodeposition. We observed very carefully the final residue of the plutonium and americium fractions just prior to electrodeposition to determine whether or not the isolation was satisfactory for producing a relatively mass free source. For some samples repeating the final purification was necessary. Toward the end of this work we used high purity acids in the final steps. Improvement in the quality of the electrodeposited source was observed, but we cannot say with certainty that this was due to the use of high purity acids or that our own techniques in the preparation of the sources were of higher quality.

Counting

At HASL updating of the alpha spectrometry systems is now under way because of the increased program demand of the measurement of the transuranics in a variety of materials. We are now beginnning to have come into operation highly stable electronic alpha spectrometry systems. During the work reported here we did not have available to the sea water program alpha spectrometry systems in continuous operation with long term stability over prolonged counting intervals, therefore, repeated counting was necessary quite often to achieve average values of our measurements. This of course made to some degree an inefficient operation. Because of this the Pu-239,240 values reported here are average

values obtained by measurements at HASL and independent assays of the electrodeposited sources at Woods Hole. For all samples the Am-243 tracer yields were determined at HASL and the electrodeposited sources were counted again at Woods Hole to obtain the Am-241 values reported here.

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