

DETERMINATION OF FISSION-PRODUCTS AND ACTINIDES IN THE BLACK SEA FOLLOWING THE CHERNOBYL ACCIDENT

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Radiochemical procedures are discussed for the isolation and determination of a suite of radionuclides in samples from the Black Sea following their input from the Chernobyl reactor accident. The samples analyzed include discrete water samples and both suspended and dissolved phases collected by in-situ chemisorption techniques. The radiochemical scheme permits the separation and analysis of ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{144}Ce , ^{147}Pm , ^{106}Ru , ^{239}Pu , ^{240}Pu , and in some instances ^{242}Cm , ^{238}Pu , and ^{241}Am . The detection techniques employed include various instrumental gamma spectrometric methods, low-level beta counting, alpha spectrometry, and mass spectrometry.

The method's developments are described and data are presented on some representative samples from the Black Sea. The sensitivity of the analysis for the various nuclides and sample types is summarized and questions of radiochemical interferences are addressed.

INTRODUCTION

A wide variety of man-made radioactive elements have been introduced into the environment as a consequence of the development of atomic power and nuclear weapons technology. These radiotracer releases have been studied for a number of reasons. In oceanography, for example, considerable effort has been spent studying the distribution and fate of fallout radionuclides from atmospheric nuclear weapons testing programs and from radioactive discharges from nuclear fuel reprocessing plants. Such tracer studies can provide information on the mixing rates of oceanic water masses, biological uptake rates of trace elements, vertical scavenging and removal processes, dating of samples, geochemical cycling of trace elements, and other processes.

The Chernobyl nuclear power station accident in April of 1986 created a new source of fallout radioisotopes to the environment and, immediately following the Chernobyl accident, considerable effort was spent determining the activities of a wide variety of Chernobyl fallout radionuclides in the environment (4, 5, 6, and many others). The highest activities were generally associated with isotopes

having the shortest half-lives and direct gamma counting of samples was the most common analytical technique used. Due to the nature of the Chernobyl releases and the prevailing wind and precipitation patterns at that time, the Black, Baltic, and North Seas received the highest Chernobyl fallout activities of any salt water basins.

We report here our analytical procedures which were developed for measuring the Chernobyl fallout radioactivity in the Black Sea. We have focused only upon those radiotracers which were released in relatively large quantities and whose half-lives are close to a year or more. This enables us to follow their distribution and fate during a time span of two or more years following the accident. The Chernobyl radiotracers of interest to us include ^{137}Cs , ^{134}Cs , ^{144}Ce , ^{147}Pm , ^{106}Ru , and ^{90}Sr which have half-lives of 30.17, 2.07, 0.78, 2.62, 1.02, and 29.0 years, respectively. We have also measured the long-lived actinides $^{239,240}\text{Pu}$, ^{238}Pu , ^{241}Am , and ^{242}Cm . Of these isotopes, ^{137}Cs , ^{134}Cs , ^{144}Ce , and ^{106}Ru could initially be measured by direct, non-destructive gamma-counting techniques. We were later forced to develop a more sensitive analytical procedure due to a reduction in the tracer signals over time as a result of radioactive decay, water mixing processes, and vertical scavenging and removal. This procedure, described here, involves the radiochemical separation and purification of all the fission products and actinides of interest, followed by their detection by more sensitive beta or alpha-counting techniques.

SAMPLING STRATEGY

The main focus of this paper will be a detailed description of our procedure for the separation, purification, and detection of the Chernobyl tracers in seawater samples. Where possible, reference will be made to existing procedures which have been used in these labs in previous marine radionuclide studies. Most samples analyzed by this procedure ranged from 10-20 liters and were collected by standard wire-mounted Niskin bottle samplers. Such discrete water samples were not treated on board ship, but were returned to Woods Hole for the analyses described here.

In a later section of the paper we will briefly describe, for the sake of comparison, our procedures and results with larger volume samples (100-1000 liters) which were collected by a previously developed pumping system and in-situ chemisorption techniques (7, 10, 11). Large volume samples were needed to measure the radiotracer distribution between the filterable particulate and dissolved phases and to measure the extremely low activities of ^{241}Am , ^{242}Cm , and ^{238}Pu in the Black Sea.

ANALYSIS OF 10-20 LITER SEAWATER SAMPLES

The following analytical scheme has been used for low-level radionuclide analysis on 10 to 20 liters of seawater. It permits the separation and measurement of ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{106}Ru , ^{239}Pu , ^{240}Pu , ^{147}Pm , and ^{144}Ce . The entire procedure is outlined in the flow chart in Figure 1. The sample is first acidified with 3M HCl to pH 1.5 in its original storage container (10 or 20 liter plastic cubitainer). Carriers and tracers are added (10 mg Cs, 2 g Sr, 20 mg Ru, 0.1 mg Nd, 10 mg Ce, 25

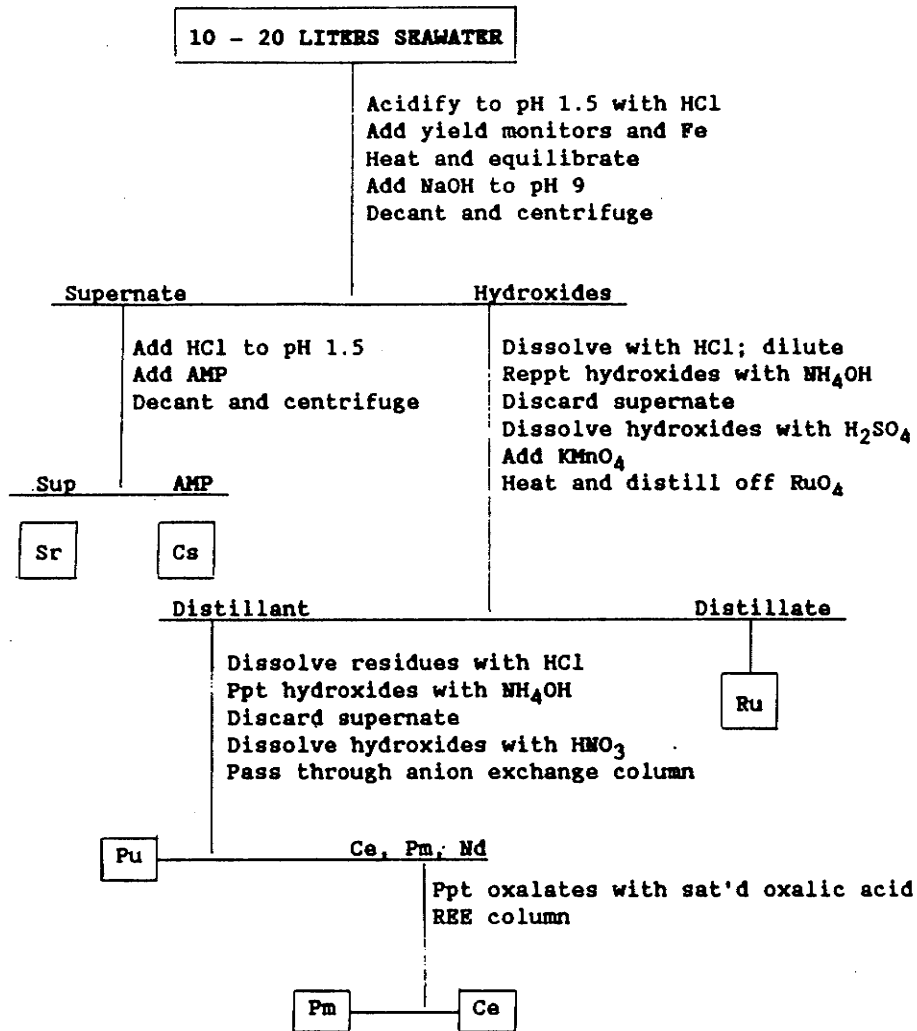


Figure 1. Flow chart of radionuclide separation scheme

mg Fe, and 0.05 mBq ^{242}Pu for mass spectrometric Pu analysis), and the sample is heated at 60°C for at least 48 hours to allow for tracer equilibration. The hydroxides (containing Ru, Nd, Ce, Pm, and Pu) are precipitated at pH 9 with 10M NaOH. We have found that it is important to use NaOH rather than NH_4OH to optimize Cs recovery when co-precipitating Cs with ammonium molybdophosphate (AMP) in subsequent steps. The hydroxides are allowed to settle and the supernate, containing Cs and Sr, is decanted. Cesium is then concentrated with AMP, purified, and mounted for counting as a Cs-chloroplatinate precipitate (18); Sr is precipitated as an oxalate and processed according to published procedures (18). The hydroxides are dissolved with 6M HCl, diluted with deionized water ($\text{DI H}_2\text{O}$), and reprecipitated with NH_4OH , centrifuged and dissolved in 25 ml of 9M H_2SO_4 . This is transferred to a distillation flask for the separation of Ru from Pu and the rare earth elements.

A. Ruthenium Analysis

The Ru procedure we developed is based upon procedures described by Wyatt and Rickard (19) and Volchok and Deplanque (16). Ruthenium is initially separated from Pu and the rare earth elements by its selective distillation as the highly volatile ruthenium tetroxide (RuO_4).

The distillation flask used has an air inlet as well as a vapor outlet which extends into a 60-ml centrifuge tube containing 30 ml of 6M NaOH placed in an ice bath. One gram of KMnO_4 is added to the sample in the flask to oxidize the Ru to RuO_4 . Air is gently bubbled through the sample while heating to 90°C for 30 minutes. Under these conditions, the RuO_4 is distilled into the NaOH solution. The distillate is allowed to cool, another gram of KMnO_4 is added, and the distillation process is repeated to assure complete distillation of Ru.

The RuO_4 is reduced to ruthenium dioxide (RuO_2) by the addition of 1 ml of ethanol to the distillate and heating in a boiling water bath until black RuO_2 forms. The sample is centrifuged, and the supernate, if clear and colorless, is discarded. If a blue-green supernate is present, indicating incomplete precipitation of the RuO_2 , the solution must be neutralized with HCl and 1 ml 6M NaOH is added. The heating with ethanol is repeated and the sample is centrifuged. The RuO_2 precipitate is dissolved in 2 ml of concentrated HCl and diluted to 20 ml with DI H_2O .

Powdered magnesium metal is added in small increments to the dissolved RuO_2 to reduce it to black Ru metal. This is done in a hot water bath until the Ru metal precipitates and the solution becomes clear and colorless. Concentrated HCl is added dropwise to dissolve any excess Mg metal. The sample is cooled and centrifuged. The Ru is washed with boiling DI H_2O and filtered onto a tared 25 mm diameter Millipore type HA 0.45 μm filter, rinsed with DI H_2O followed by ethanol. After drying at 60°C , the sample is weighed and a yield is computed. Typical chemical recoveries for Ru ranged from 50-70%. The precipitate of metallic Ru contains a small amount of oxide (19), therefore standardization of the Ru carrier is made under the same conditions.

The Ru carrier solution contains ruthenium (III) chloride trihydrate, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, dissolved in 0.1M HCl and diluted to yield a 20 mg Ru/g solution. Six weighed aliquots of the carrier, containing 2-25 mg Ru, are transferred to Erlenmeyer flasks, diluted with 25 ml DI H_2O , and acidified with 2 ml 12M HCl. Powdered Mg (0.4 g) is added in small increments, shaking after each addition. The samples are boiled gently until the Ru coagulates and the supernates are clear and colorless. An additional 10 ml of 12M HCl is added slowly to dissolve any excess Mg. The samples are boiled gently for two minutes, allowed to cool, and filtered onto tared 25 mm diameter Millipore type HA 0.45 μm filters; each being washed three times with 5 ml of hot DI H_2O , followed by ethanol. The filters are dried at 60°C for ~30 minutes and weighed. The weight of the filtered Ru was consistently 5% greater than the calculated Ru content of the RuCl_3 carrier solution due to the contribution of Ru-oxides (19).

The Ru filters are mounted for counting on a lucite card and covered with a film of Mylar (0.9 mg/cm^2). A 45 mg/cm^2 foil is placed over the samples to effectively absorb any 0.3 MeV or under beta emitting interference. The determination of ^{106}Ru activity in the sample is made by low-level beta counting (12) of the 3.5 MeV ^{106}Rh daughter. The ^{106}Ru beta emission is very weak, 39 keV, and does not contribute to the count rate. Six standards were prepared to establish the detector counting

efficiency for ^{106}Ru . Each standard contained 3.8 Bq of ^{106}Ru (Amersham ^{106}Ru standardized solution) and 2, 5, 10, 15, 20, or 25 mg of stable Ru, a range spanning sample radiochemical recoveries. The counting standards were prepared in a manner similar to the carrier standards. The efficiency of ^{106}Ru detection was 0.434 ± 0.010 over the above range of carrier weights.

B. Plutonium Analysis

After the Ru separation, the distillate containing residues of KMnO_4 is dissolved in 3M HCl and the solution is cleared with 30% H_2O_2 . The hydroxides, containing Pu and the rare earth elements, are precipitated at pH 9 with concentrated NH_4OH . The precipitate is dissolved in 100 ml of 8M HNO_3 . Plutonium is oxidized to the quadrivalent state with 1.0 g NaNO_2 and adsorbed onto an anion exchange resin column (25 ml volume containing BioRad AG 1 X 8 resin, 50-100 mesh). The rare earth elements pass through the column in the initial HNO_3 solution and subsequent 300 ml 8M HNO_3 wash (a minor amount, ~10% of Ce remains on the column) and are held for further purification. The column is washed with 150 ml of 12M HCl, and Pu is eluted from the column with 100 ml of 12M HCl containing 5 ml of 1M NH_4I . The eluate is dried and held for further purification prior to analysis of ^{239}Pu and ^{240}Pu by mass spectrometry (2).

C. Rare Earth Elements Analyses

The purification of the rare earth element fraction is based upon the separation of ^{147}Pm from ^{144}Ce by ion exchange and the use of stable Nd and Ce as yield monitors for ^{147}Pm and ^{144}Ce , respectively. The procedures are adapted from Shirey et al. (14).

The rare earth element eluate from the Pu column is evaporated to 25 ml and diluted to 400 ml with DI H_2O . The stable Ce carrier permits the co-precipitation of rare earth oxalates in an excess of oxalic acid (15). The oxalate precipitate (containing Ce, Nd, and Pm) is dissolved in 16M HNO_3 , evaporated to dryness and resolubilized in a minimum volume (0.5-1.0 ml) of 0.2M 2-methylactic acid (2-hydroxy-isobutyric acid) at pH 4.6. The solution is loaded onto a column (2 mm I.D., 35 cm length) containing 1 ml of BioRad AG 50W x 4, <400 mesh resin. A positive pressure of 0.4 atmospheres is applied to the column via tank nitrogen. An optical sensor (Model 9100, Accura Flow Products Co.) is attached to a counter (CUB-2000, Empire Electric Co.) to monitor the number of drops eluted from the column (approximately one drop per minute; 1 drop ~ 0.05 ml).

After the sample solution has been loaded onto the resin, approximately 10 ml of 0.2M 2-methylactic acid (pH 4.6) is added to the reservoir above the resin. The first 2 ml eluted are discarded as they contain the heavy rare earth elements. Promethium is eluted from the column in the next 4.25 ml fraction (drops 40-125). Iron carrier (1 mg Fe as FeCl_3) is added to the Pm fraction and Pm is quantitatively co-precipitated with $\text{Fe}(\text{OH})_3$ at pH 9 with 14M NH_4OH . The precipitate is carefully collected onto a 25 mm Millipore type HA 0.45 μm filter and dried at 60°C. The filter is mounted on a lucite card, covered with Mylar film (0.9 mg/cm^2), and ^{147}Pm (225 keV) is counted via low-level beta detection (12).

Three standards were prepared to establish the detector counting efficiency for the ^{147}Pm samples. Each standard contained 10 Bq ^{147}Pm (Amersham ^{147}Pm standardized solution) in 2 ml of 0.2M

2-methylactic acid at pH 4.6. The standards were precipitated and mounted in a manner similar to the samples. The efficiency of detection was 0.158 ± 0.005 .

The Nd eluate is collected in the next 2.5 ml fraction (drops 126-175) for the determination of the chemical yield of ^{147}Pm . An aliquot of approximately 10% (by weight) of the Nd eluate is used in the yield titration. Eriochrome Black T (0.25 ml) is added as a pH-sensitive colorimetric indicator of the presence of the rare earth elements (pink). The pH of the aliquot is adjusted to 7.0 with 0.1M triethenolamine (TEA). The amount of Nd present in the aliquot is determined colorimetrically by titration from pink to a blue endpoint with 10^{-4}M EDTA. The Nd carrier solution contains pure neodymium oxide, Nd_2O_3 (from Alfa Division Ventron), dissolved in 1M HNO_3 , and diluted to yield a calibrated 100 μg Nd/g solution. Typical chemical recoveries for ^{147}Pm ranged from 30-75%.

The eluting acid is changed to 2.5M HNO_3 and the first 0.5 ml of the eluate is discarded. Cerium is eluted in the next 4.5 ml (90 drops). An aliquot of approximately 5% (by weight) of the Ce eluate is used for the determination of the chemical yield of ^{144}Ce . Eriochrome Black T (0.25 ml) is added, the pH is adjusted to 7.0 with 1M TEA, and the solution is titrated to a blue endpoint with 10^{-3}M EDTA, in a manner similar to the Nd determination. Typical chemical recoveries for ^{144}Ce ranged from 30-70%. Iron carrier (1 mg Fe) is added to the Ce fraction to be counted, and the Ce is quantitatively coprecipitated with $\text{Fe}(\text{OH})_3$, filtered and mounted identically to ^{147}Pm . The combined ^{144}Ce (320 keV) and ^{144}Pr (3.0 MeV) daughter signals are counted via low-level beta detection (12).

An alternative mounting technique was tested in which the Ce fraction was directly evaporated onto a lipped stainless steel planchette. With the evaporated samples, however, we found an inevitable uptake of moisture by the sample residue, which resulted in variable counting efficiencies if samples were stored for any length of time before counting. The samples mounted as $\text{Fe}(\text{OH})_3$ precipitates did not encounter this problem.

The Ce carrier solution contains Ce(III) chloride heptahydrate, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, dissolved in 0.01M HNO_3 and diluted to yield 10 mg Ce/g solution. In order to standardize the Ce carrier, three weighed aliquots of the carrier were transferred to 2-liter beakers, diluted to 500 ml with DI H_2O , and the oxalates precipitated at pH 1.0 with saturated oxalic acid. The cerium oxalates were filtered through tared 7-cm diameter Whatman #42 filter papers, washed with DI H_2O , and dried in a vacuum desiccator for five minutes. The cerium oxalates were placed in tared ceramic crucibles and heated at 800°C for 30 minutes. The resulting cerium dioxide, CeO_2 , was weighed to establish the concentration of Ce in the carrier solution (15).

Eight counting standards were prepared to establish the detector counting efficiency for ^{144}Ce . The eight standards consisted of two replicates containing 0, 3, 7, or 10 mg of stable Ce, in addition to 2.8 Bq of ^{144}Ce (Amersham ^{144}Ce standardized solution) in a 2.5M HNO_3 matrix. The counting standards were precipitated and mounted exactly as the samples had been. The efficiency of detection was 0.602 ± 0.027 , with no significant difference between standards containing no stable Ce and those containing up to 10 mg of stable Ce.

LARGE VOLUME CHEMISORPTION SAMPLES

Large volume seawater samples can be collected by chemisorption techniques as an alternative to discrete water sampling of surface waters. Seawater is pumped (Flotec flexible impeller pump) at 5-8 liters/minute from 0.5 m beneath the surface water, through five in-line cartridges which serve as radionuclide collectors. The first cartridge serves as a pre-filter and consists of a wound 0.5 μm nominal pore-sized polypropylene filter (CUNO Microwynd DPPPZ) which collects the particulate radionuclides. Following this pre-filter are two MnO_2 -coated wound cotton cartridges (11) which are used to extract dissolved actinides - and in this study Ru and Ce - from seawater. The collection efficiency for the dissolved radionuclides is determined by the difference in activity between the first and second MnO_2 cartridges as described in Mann et al. (11) and Livingston and Cochran (7).

Following the MnO_2 cartridges are two cupric ferrocyanide-based ($\text{CuFe}(\text{CN})_6$) Cs adsorber cartridges. Dissolved Cs, which passes through the first three cartridges, is efficiently collected on these cartridges (see Mann and Casso (10) for discussion of a similar technique). The Cs collection efficiency is determined in the same way as for the MnO_2 cartridge pair. We have included in Appendix A a description of our $\text{CuFe}(\text{CN})_6$ cartridge preparation procedure.

For the analyses of the pre-filters, one of two procedures was used. In both cases the pre-filter is placed in a 2-liter beaker with a foil cover and ashed at 400°C for 24 hours (see following section for a discussion of potential losses during the ashing period). In the simplest case, the ash is transferred to a 6.5 cm diameter plastic jar and counted directly on a Ge(Li) detector for particulate ^{106}Ru , ^{144}Ce , ^{137}Cs , and ^{134}Cs . This procedure was successful for those samples containing Chernobyl tracers with relatively high activities in the particulate phases.

For particulate Pu, Am, and Cm isotopes, further radiochemical treatment is necessary. The ashed filters are digested in hot 8M HNO_3 in the presence of chemical yield monitors (10 mBq of ^{242}Pu and 20 mBq of ^{243}Am), followed by radiochemical purification, electrodeposition, and alpha counting (8, 13, 17). It would also be possible to use mass spectrometry for the analysis of particulate Pu (2).

We did not attempt to analyze the Chernobyl fission product particulates other than by instrumental gamma-counting since their activities were sufficiently high for the simpler, non-destructive gamma procedures. However, the pre-filter ash could be digested in 8M HNO_3 , and a separation scheme similar to that outlined above for the discrete water samples could be followed. This would have the advantage of substantially increasing detection limits for particulate ^{106}Ru and ^{144}Ce . Radiochemical procedures would also allow for the determination of particulate ^{147}Pm by beta counting.

The Cs activities found in Black Sea surface waters were sufficiently high that the $\text{CuFe}(\text{CN})_6$ cartridges could be placed directly on a Ge(Li) detector and counted instrumentally for ^{134}Cs and ^{137}Cs . The Ge(Li) detectors were calibrated with cartridges prepared in the lab with a known amount of ^{137}Cs and ^{134}Cs . The whole Cs cartridges required 8 to 48 hours of counting time to obtain statistics of 10% or better for the Cs activities (sample sizes ranged from 100-1000 liters and ^{137}Cs activities from 50-350 Bq/m^3). The Cs cartridges could also be ashed and either gamma counted directly or, for greater sensitivity, processed for radiochemical analysis and mounted as Cs precipitates

Table I
Comparison of ^{137}Cs , ^{106}Ru and ^{144}Ce on discrete water samples
and by chemisorption techniques

<u>Nuclide</u>	<u>Sample I.D.</u>	<u>10-Liter Samples</u>	<u>Large Volume Chemisorption Samples</u>	
		(1)	(1)	(2)
		<u>Bq/m³</u>	<u>Bq/m³</u>	<u>Collection Efficiency (%)</u>
^{137}Cs	BS86/9-15	62±2	56± 1	85.7± 1.2
	BS86/13-21	120±1	118± 3	69.6± 1.6
	BS86/13-22	120±3	119± 2	92.3± 0.5
^{106}Ru	BS86/9-10	76±5	114±32	12.2± 3.4
	BS86/13-10	79±2	27± 2	65.2± 2.8
^{144}Ce	BS86/9-13	8±2	6± 1	79.1±1.9
	BS86/13-10	17±2	15± 1	60.8±6.3

- (1) Radioactivity data are provided with a 1- σ counting uncertainty as of May 1, 1986.
 (2) Cartridge collection efficiencies \pm their associated uncertainties are calculated from 1-B/A, where B and A are the measured activities on the second and first cartridge, respectively (Livingston and Cochran, 1987).

for beta and/or gamma counting. We have found negligible losses of Cs during 24-hour ashing at 550°C. When the ashing time was increased to three days, losses of 10% or greater for Cs were found.

The MnO₂ cartridges were processed in a manner similar to the pre-filters. This involved either ashing (at 550°C) and direct gamma counting for ^{106}Ru and ^{144}Ce , or the acid digestion of the ash followed by radiochemical purification, electrodeposition, and alpha counting for Pu, Am, and Cm isotopes (8, 13, 17). As with the pre-filters, we did not attempt to process the MnO₂ ash radiochemically for the beta analysis of ^{106}Ru , ^{144}Ce , and ^{147}Pm , although this is possible.

The Ce cartridge collection efficiency was consistently high (60-80%), hence the MnO₂ chemisorption technique would be a viable alternative to discrete sampling. We found the MnO₂ cartridges to be inefficient collectors for Ru (10-60% collection efficiency), resulting in large errors associated with the ^{106}Ru determination using this collection technique. Ru losses due to ashing may also be a considerable problem with our current procedures. We have found Ru losses of 15-30% for a three-day ashing of the MnO₂ cartridges at 550°C. The losses for Ce are generally smaller, on the order of 10-20%. With a 24-hour ashing at up to 550°C, no measurable losses of either Ce or Ru were detected.

RESULTS AND DISCUSSION

 ^{137}Cs and ^{134}Cs

The concurrence of ^{137}Cs determined on discrete 10-20 liter water samples and large volume Cs adsorber samples has been good (Table 1). With the discrete water analysis technique, the combined activities of both ^{134}Cs (0.65 MeV-B) and ^{137}Cs (0.51 MeV-B) would be detected with essentially equal efficiency by beta-counting. Since both ^{134}Cs and ^{137}Cs were released from Chernobyl, gamma counting techniques are needed to detect directly the activity of each Cs isotope. The $^{134}\text{Cs}/^{137}\text{Cs}$ ratio can be easily obtained if large volume Cs cartridge samples are available. In order to separate the two Cs isotope beta signals in the 10-liter samples, we either: a) gamma counted the Cs-chloroplatinate precipitate (this only is feasible for samples with the highest activities), or b) used the cartridge $^{134}\text{Cs}/^{137}\text{Cs}$ ratio from the same station and depth to separate the combined beta-counting $^{134,137}\text{Cs}$ values. The sample ^{134}Cs and ^{137}Cs activities can also be calculated from the total $^{134,137}\text{Cs}$ beta-counting results by using a fallout Chernobyl $^{134}\text{Cs}/^{137}\text{Cs}$ ratio and a pre-Chernobyl ^{137}Cs activity. In the Black Sea we calculated a $^{134}\text{Cs}/^{137}\text{Cs}$ ratio of 0.53 ± 0.01 ($n=28$) for fresh Chernobyl fallout from observed surface water data (after correction for pre-Chernobyl ^{137}Cs). Pre-Chernobyl ^{137}Cs activities can be obtained from ^{137}Cs determinations in ^{134}Cs -free subsurface waters (9).

Some typical concentrations of surface water ^{134}Cs and ^{137}Cs in the Black Sea are provided in Table 2. Note that the ^{137}Cs activities are quite high (up to 360 Bq/m^3) relative to pre-existing ^{137}Cs levels ($10\text{-}15 \text{ Bq/m}^3$). The ^{134}Cs activities are roughly half the corresponding ^{137}Cs activities (decay corrected to May 1, 1986).

 ^{90}Sr

Strontium-90 is not discussed in detail above, since the radiochemical procedures used in its analysis are well documented (18). In Table 2 we show for comparison to the other isotopes, the ^{90}Sr activities we have found in the Black Sea surface waters. This data represents the combined activity of ^{90}Sr from the Chernobyl source and pre-existing ^{90}Sr from nuclear weapons testing fallout.

 ^{106}Ru

Both discrete water samples analyzed by beta-counting techniques and large volume MnO_2 cartridges analyzed by gamma-counting are not always consistent for ^{106}Ru (Table 1). In practice, the MnO_2 cartridge collection efficiencies for ^{106}Ru are low and variable (10-60%), and the gamma-counting efficiencies for ^{106}Ru are low. The combined effects of poor collection efficiency and the potential for Ru loss during ashing have led us to view cautiously any ^{106}Ru cartridge data. Better sensitivity for ^{106}Ru detection is obtained by using the discrete water sample procedure followed by beta-counting, rather than any gamma-based chemisorption technique (Table 3).

Since the separation chemistry for Ru involves the distillation of RuO_4 , it appears that the above outlined procedures would be quite selective for Ru. An exception might be samples containing large amounts of ^{99}Tc . However we have found that TcO_4 does not distill over with RuO_4 under the

Table 2
Activities of radionuclides in Black Sea surface waters - 1986

	Bq/m ³ (a)					mBq/m ³ (b)				
	¹³⁷ Cs	¹³⁴ Cs	⁹⁰ Sr	¹⁰⁶ Ru	¹⁴⁴ Ce	¹⁴⁷ Pm	^{239,240} Pu	²³⁸ Pu	²⁴¹ Am	²⁴² Cm
June:										
Station 13	52±2	21±1	18±1	18±1	8±2	11±1	10±2	0.9±0.3	1±5	10±3
September:										
Station 10	231±2	119±2	46±2	75±1	17±2	12±1	9±1	2.2±0.4	2±1	26±2
Data Range (c)										
Minimum	52	21	18	17	2	5	7	0.9	1.0	0.4
Maximum	360	183	50	79	28	20	17	3.9	2.1	34

(a) = Data reported as Bq/m³ and decay corrected to May 1, 1986. Values were obtained from 10-liter discrete water samples and represent total activities with a 1 σ counting uncertainty.

(b) = Transuranic data reported as mBq/m³ (=10⁻³Bq/m³). Values were obtained via chemisorption cartridge technique as described in text. Total activities reported with a 1 σ counting uncertainty.

(c) = The data range represents the minimum and maximum total activities found in 1986 southern Black Sea samples (decay corrected to May 1, 1986). Some of the data can be found in Livingston et al., 1988.

Table 3
Sensitivity for determination of radionuclides by various techniques

	¹³⁷ Cs			¹³⁴ Cs		
	Beta (4)	Gamma (5)	Gamma (6)	Beta (4)	Gamma (5)	Gamma (6)
mBq (1)	3.0	30.6	561	3.0	40.1	539
Bkg cpm (2)	0.300	0.283	0.283	0.300	0.196	0.196
Det eff (3)	0.330	0.031	0.0017	0.330	0.0201	0.0015

	¹⁰⁶ Ru		¹⁴⁴ Ce		¹⁴⁷ Pm
	Beta (4)	Gamma (7)	Beta (4)	Gamma (7)	Beta (4)
mBq (1)	2.3	397	1.7	240	6.3
Bkg cpm (2)	0.300	0.183	0.300	1.165	0.300
Det eff (3)	0.434	0.002	0.602	0.008	0.158

	²³⁸ Pu	^{239,240} Pu		²⁴¹ Am	²⁴² Cm
	Alpha (8)	Alpha (8)	m.s. (9)	Alpha (8)	Alpha (8)
mBq (1)	0.13	0.14	0.01	0.13	0.10
Bkg cpmx10 ³ (2)	0.50	0.70		0.50	0.13
Det eff (3)	0.294	0.294		0.294	0.294

- 1= mBq (=10⁻³Bq) per sample required to achieve a 25% 1 σ counting uncertainty by β or γ counting for 3000 min or α counting for 7 days.
- 2= The detector background for β and α counting; the detector background in the region of interest for γ counting.
- 3= Detection efficiency includes the detector efficiency for the nuclide in a particular geometry multiplied by its branching ratio.
- 4= β counting as described in text.
- 5= γ counting a Cs₂PtCl₆ precipitate on a Ge(Li) detector.
- 6= γ counting a whole Cs cartridge on a Ge(Li) detector.
- 7= γ counting an ashed MnO₂ cartridge on a Ge(Li) detector.
- 8= α counting on a Si-surface barrier detector.
- 9= Analyzing by mass spectrometry (Buesseler and Halverson, 1987).

relatively low temperature conditions described. We have measured ¹⁰⁶Ru sample activities down to the 0.3 mBq level and have no procedural blank.

In Table 2, some typical ¹⁰⁶Ru activities from Black Sea surface waters are reported. We have found ¹⁰⁶Ru activities up to 79 Bq/m³ in Black Sea surface waters. Preliminary ¹⁰⁶Ru data is discussed by Livingston et al. (9) and suggests the removal of ¹⁰⁶Ru from surface waters and its release from sinking particles at depth. Present studies of Chernobyl ¹⁰⁶Ru, due to its short half-life and rapid removal, must, therefore, rely on the more sensitive beta-counting procedures.

^{144}Ce

The activities of ^{144}Ce from 10-liter samples and ashed cartridge samples are consistent within the calculated error (Table 1). Concurrence is greatest when the chemical recoveries and activities are high. The sensitivity of ^{144}Ce measurement via low-level beta detection is two orders of magnitude higher than ^{144}Ce measurement via gamma detection (Table 3). The poor detection efficiency and high background of the Ge(Li) detectors emphasizes the advantage of measuring ^{144}Ce via beta techniques, particularly as the signal disperses through the water column and Ce is removed from surface waters by particle scavenging.

As with any beta counting technique, it is important to be certain that the sample to be counted is free of any other beta emitting interferences. The concurrence at the higher activity levels between the gamma and beta techniques (Table 1) does not address this blank issue directly. The radiochemical purity of ^{144}Ce from our separation scheme was verified by processing a seawater blank (North Atlantic Ocean 47°45'N, 35°45'W, 4200 m collected in 1974) to check for interferences with the low-level beta detection of ^{144}Ce caused by the naturally occurring ^{212}Pb , ^{214}Pb , and ^{227}Ac daughters. The blank was found to contain no activity beyond background level. Additionally, several ^{144}Ce samples were recounted over a one-month period to check for changes in the sample count rate. The recounted samples showed no evidence of ingrowth or decay of other potential beta emitters.

Typical ^{144}Ce activities and the range of activities in the Black Sea surface waters are listed in Table 2. We have found ^{144}Ce activities up to 28 Bq/m³ in the Black Sea. As with the other particle reactive tracers, the affinity for particle surfaces and hence rapid removal onto large, rapidly sinking particles is the major contributing factor for the distribution of ^{144}Ce in the oceans (3). By 1987, the surface water signal of Chernobyl ^{144}Ce had become too low to detect by simple chemisorption and gamma techniques.

 ^{147}Pm

Due to the poor detection efficiency of the low energy ^{147}Pm beta emission, the sensitivity of ^{147}Pm analysis via low-level beta detection is not as high as that for ^{144}Ce (Table 3). Promethium-147 cannot be measured via the gamma techniques used on the large volume cartridge samples; however, it is possible to consider digesting the ashed MnO₂ cartridges or pre-filters and following a separation scheme similar to that outlined previously for Pm in discrete samples.

As with ^{144}Ce , the ^{147}Pm signal was monitored for beta interferences by processing a seawater blank as a sample. The radiochemical purity of the ^{147}Pm samples was established when there was no evidence of blank activity.

Typical ^{147}Pm activities and the range of activities in Black Sea surface waters are listed in Table 2. The variability in the $^{147}\text{Pm}/^{144}\text{Ce}$ ratio is likely to be a function of the differential scavenging of Pm vs. Ce in the oceans.

Transuranics

The concentrations of $^{239,240}\text{Pu}$, ^{238}Pu , ^{241}Am , and ^{242}Cm found in surface water at two stations occupied in 1986, together with the observed ranges of surface activities, are shown in Table 2. These

values were obtained by the large volume chemisorption technique described above and represent the sum of the measured concentrations in the dissolved and particulate phases (8).

It is important to note the finding of transuranics of Chernobyl origin. This derives from the sharply elevated $^{238}\text{Pu}/^{239}\text{Pu}$, ^{240}Pu ratios and the presence of ^{242}Cm - both are characteristics of fallout from the Chernobyl accident (1). Using mass spectrometric techniques on the 10-liter samples, ^{240}Pu and ^{239}Pu have also been detected. Elevated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (up to 0.50) over the global fallout average (≈ 0.18) indicate the presence of reactor-derived Chernobyl plutonium in this basin.

*

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APPENDIX A

PROCEDURE FOR CS CARTRIDGE PREPARATION

Reagents

1. Weigh out 5.0 g $\text{Cu}(\text{NO}_3)_2$ (store dry $\text{Cu}(\text{NO}_3)_2$ in a dessicator).
2. Weigh out 5.0 g $\text{K}_4\text{Fe}(\text{CN})_6$.
3. Six liters of DI H_2O is needed per cartridge.
4. The cartridge used for impregnation is a CUNO Microwynd DCCPY wound cotton fiber filter with a 1 μm nominal pore size.

Procedures

1. Dissolve the $\text{K}_4\text{Fe}(\text{CN})_6$ in 1 liter DI H_2O .
2. Pour 5 liters DI H_2O into a large plastic container; add 5 g $\text{Cu}(\text{NO}_3)_2$.
3. Stir the $\text{Cu}(\text{NO}_3)_2$ solution vigorously on a stir plate until dissolved.
4. Place a new cartridge in the cartridge housing.

5. Pour $K_4Fe(CN)_6$ solution into the filter's center core to saturate the entire cartridge with the solution.
6. Attach cartridge housing to a pump (Flotec #F360 impeller pump) with inlet and outlet hoses in the $Cu(NO_3)_2$ solution.
7. Turn on pump - full speed at first, slowing down to 1-2 liters/min. Note starting time.
8. Pump for 30 minutes or until the solution is clear, or nearly so.
9. Remove the hose leading into the cartridge from the solution and continue pumping so that the housing partially empties.
10. Take the cartridge out of the housing and allow to drain.
11. Dry cartridge in oven at $80^\circ C$ for 48 hours; place the dry (and cool) cartridge in a sealed plastic bag.

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