7 Radioactive Elements

7.1
Naturally Occurring Cations

7.1.1
Actinium

Lin [1] used coprecipitation with lead sulfate to separate ^{237}actinium from seawater. The ^{237}actinium was purified by extraction with HDEHP and determined by α-spectrometry with a Si (Au) surface barrier detector. The method has a sensitivity of 10^{-3} Ci/g of ashed sample.

7.1.2
Polonium and Lead

Skwarzek and Bojanowski [2] in a study of the accumulation of ^{210}polonium in Southern Baltic seawater showed that the mean concentration was 0.49 mBq/dm^3, of which approximately 80% was dissolved. ^{210}Polonium concentrations in phytoplankton and zooplankton were 21–61 and 21–451 mBq/g dry weight, respectively. Mean ^{210}polonium concentration factors were 5000 in phytoplankton, 18 300 in macrozooplankton, and 42 000 in mesozooplankton. The higher mean ^{210}polonium concentration in mesozooplankton from the Slupsk Trough compared with that in mesozooplankton from the Gdansk basin (214 against 55 mBq/g dry weight) might have been due to blue-green algal blooms in the Gdansk basin.

Various workers [3–7] have discussed the determination of polonium and lead in seawater.

Similar affinity of polonium and plutonium for marine surfaces implies that studies of the more easily measured polonium might be valuable in predicting some consequences of plutonium disposal in the oceans [8–11]. Rates at which plutonium and polonium deposit out of seawater onto surfaces of giant brown algae and "inert" surfaces, such as glass and cellulose, suggest that both nuclides are associated in coastal seawater with colloidal sized species having diffusivities of about 3×10^{-7} cm^2/s. The parallel behaviour possibly

represents an initial step in the incorporation of both α-radioactive heavy elements into marine food chains and/or their transport by the greater activity concentrations found on marine surfaces and in seawater, about 200 times that of plutonium.

Tsunogai and Nozaki [6] analysed Pacific Oceans surface water by consecutive coprecipitations of polonium with calcium carbonate and bismuth oxychloride after addition of lead and bismuth carriers to acidified seawater samples. After concentration, polonium was spontaneously deposited onto silver planchets. Quantitative recoveries of polonium were assumed at the extraction steps and plating step. Shannon et al. [7], who analysed surface water from the Atlantic Ocean near the tip of South Africa, extracted polonium from acidified samples as the ammonium pyrrolidine dithiocarbamate complex into methyl isobutyl ketone. They also autoplated polonium onto silver counting disks. An average efficiency of 92% was assigned to their procedure after calibration with ^{210}Po–^{210}Pb tracer experiments.

Shannon [3] determined ^{210}polonium and ^{210}lead in seawater. These two elements are extracted from seawater (at pH 2) with a solution of ammonium pyrrolidine dithiocarbamate in isobutyl methyl ketone (20 ml organic phase to 1.5 litres of sample). The two elements are back-extracted into hydrochloric acid and plated out of solution by the technique of Flynn [12] but with use of a PTFE holder in place of the Perspex one, and the α-activity deposited is measured. The solution from the plating-out process is stored for 2–4 months, then the plating-out and counting are repeated to measure the build-up of ^{210}polonium from ^{210}lead decay and hence to estimate the original ^{210}Pb activity.

Nozaki and Tsunogai [4] determined ^{210}lead and ^{210}polonium in seawater. The ^{210}lead and ^{210}polonium in a 30–50 litre sample are coprecipitated with calcium carbonate together with lead and bismuth and are then separated from calcium by precipitation as hydroxides. The precipitate is dissolved in 0.5 M hydrochloric acid, and ^{210}polonium is deposited spontaneously from this solution on to a silver disk and is determined by α-spectrometry. Chemical yields of lead and bismuth are determined in a portion of the solution from which the polonium has been deposited; hydroxides of lead and other metals are precipitated from the remainder of this solution and after a period exceeding three months, the ^{210}polonium produced by decay of ^{210}lead is determined as before. The activity of ^{210}lead is calculated from the activity of ^{210}polonium. The method was used to determine the vertical distribution of lead and ^{210}polonium activities in surface layers of the Pacific Ocean.

Cowen et al. [5] showed that polonium can be electrodeposited onto carbon rods directly from acidified seawater, stripped from the rods and auto-plated onto silver counting disks with an overall recovery of tracer of $85 \pm 4\%$ for an electrodeposition time of 16 h [13].

These workers compared two procedures for concentrating ^{210}polonium from seawater:

1. Coprecipitation upon partial precipitation of the natural calcium and magnesium with sodium hydroxide.
2. Electrodeposition of polonium directly from acidified seawater onto carbon rods.

Polonium thus concentrated was autoplated onto silver counting disks held in spinning Teflon holders.

Recoveries of ^{208}polonium tracer in the precipitation method were $77 \pm 7\%$ ($n = 8$) compared with $40 \pm 2\%$ ($n = 2$) for the electrodeposition method with 16 h plating time, $64 \pm 1\%$ ($n = 2$) in 24 h, and $85 \pm 4\%$ ($n = 2$) in 48 h.

Biggin et al. [115] have described a time efficient method for the determination of ^{210}lead, ^{210}bismuth, and ^{210}polonium activities in seawater using liquid scintillation spectrometry.

7.1.3
Radium

Orr [14] has proposed a scintillation and β–γ coincidence methods for the determination as measured by ^{220}radon emanation.

Burnett and Tai Wei-Chieh [15] used α liquid scintillation to determine radium radionuclides in seawater. The method was applied in the $7-35$ dpm $100 \, kg^{-1}$-range using 1 litre samples.

Cohen and O'Nions [16] determined femtogram quantities of radium radionuclides in seawater by thermal ionisation mass spectrometry.

Bettoli et al. [17] has described a shipboard system to measure the concentrations of ^{222}radium and ^{226}radium in sea and coastal waters.

7.1.3.1
Radium, Barium, and Radon

Perkins [18] carried out radium and radiobarium measurements in seawater by sorption and direct multidimensional gamma-ray spectrometry. The procedure described includes the removal of radium and barium from water samples on sorption beds of barium sulfate impregnated alumina ($0.5-1$ cm thick) and direct counting of these beds on a multidimensional γ-ray spectrometer. The radioisotopes can be removed at linear flow rates of sample of up to 1 m/min.

Oceanographers have developed methods to measure the ^{228}radium content of seawater, as it is a useful tracer of mixing in the ocean. These procedures are based on concentrating radium from a large volume of seawater, removing all ^{228}thorium from the sample and ageing the sample while a new generation of ^{228}thorium partially equilibrates with ^{228}radium. After storage periods of $6-12$ months, the sample is spiked with ^{230}thorium and after ion exchange and solvent exchange separations, the thorium isotopes are measured in a γ-ray spectrometer system utilising a silicon surface barrier detector.

Early work was based on concentrating the radium from the seawater sample by adding barium and coprecipitating with barium sulfate. This concentration procedure has been replaced by one involving the extraction of radium from seawater on acrylic fibre coated with manganese dioxide [19, 20] (Mn fibres). By use of this technique, volumes of 200–2000 litres may be sampled routinely.

Measurements of [226]radium are simpler than those for [228]radium and are more precise. These measurements are generally made by concentrating the radium from up to a few litres via barium sulfate precipitation followed by thick source α counting or by [222]radon extraction following dissolution of barium sulfate [21].

Oceanographers use different techniques for measuring [226]radium in seawater. Some workers store the sample in a 20 l glass bottle and extract successive generations of [222]radon [22, 23]. Others quantitatively extract the radium onto manganese fibre and measure radon directly emanating from the manganese fibre [24] or in a hydrochloric acid extract from the fibres. The [222]radon activity is then determined by α-scintillation counting. All of these techniques give high levels of reproducibility and accuracy as determined by the oceanographic consistency of the results [22, 23].

The introduction of high-resolution, high-efficiency γ-ray detectors composed of lithium-drifted germanium crystals has revolutionised γ-measurement techniques. Thus, γ-spectrometry allows the rapid measurement of relatively low-activity samples without complex analytical preparations. A technique described by Michel et al. [25] uses Ge(Li) γ-ray detectors for the simultaneous measurements of [228]radium and [226]radium in natural waters. This method simplifies the analytical procedures and reduces the labour while improving the precision, accuracy, and detection limits.

In this method the radium isotopes are preconcentrated in the field from 100 to 1000 litre water sample onto manganese impregnated acrylic fibre cartridges, leached from the fibre and coprecipitated with barium sulfate. This manganese fibre γ-ray technique is shown to be more accurate than the [228]actinium methods recommended by the Environmental Protection Agency [26] and as accurate but more rapid than the [228]thorium ingrowth procedure.

Key et al. [27] have described improved methods for the measurement of radon and radium in seawater and marine sediments using manganese dioxide impregnated fibres. The basic method that these workers used was that of Broecker [28]. Seawater samples were taken in 30 litre Niskin bottles.

7.1.3.2
Radium, Thorium, and Lead

[226]Radium, [230]thorium, and [210]lead in large volumes of seawater have been collected on manganese oxhydroxide-impregnated cartridges prior to determination by radiochemical methods [29].

   Colley and Thomas [29] determined ^{226}radium, ^{230}thorium, and ^{210}lead in large sample volumes of seawater. In situ pumps were used to collect particles on a 1 μm filter. The dissolved species were collected on manganese oxyhydroxide impregnated cartridges prior to final analysis for nuclides.

   Baskaran et al. [30] pumped seawater at 35 l/min and collected dissolved species on cartridges prior to determining radium, thorium, and lead by γ counting methods.

7.1.4
^{99}Technetium

Chen et al. [31] preconcentrated ^{99}technetium in seawater on an anion exchange column to determination in amounts down to 3 mBq/m^3.

   Ballestra et al. [32] described a radiochemical measurement for determination of ^{99}technetium in rain, river, and seawater, which involved reduction to technetium (IV), followed by iron hydroxide precipitation and oxidation to the heptavalent state. Technetium (VII) was extracted with xylene and electrodeposited in sodium hydroxide solution. The radiochemical yield was determined by gamma counting on an anticoincidence shield GM–gas flow counter. The radiochemical yield of 50 to 150 litre water samples was 20–60%.

   ^{99}Technetium has been determined in seawater by inductively coupled plasma mass spectrometry after preconcentration by coprecipitation with iron hydroxide [33].

   Keith-Roach et al. [114] has described a radiochemical separation and ICPS protocol for determining ^{99}technetium in seawater.

7.1.5
Thorium

In recent years, there has been an increasing level of interest in the use of ^{234}Th/^{238}U disequilibrium in the marine environment to study geochemical processes with short time scales (up to 100 days), particularly those associated with carbon cycling in the oceans [34–36] and the partitioning of pollutants between the dissolved and particulate phases [37, 38]. However, the analysis of ^{234}thorium is constrained by its short half-life and its low concentration in seawater, so appropriate analytical techniques must be rapid and sensitive and preferably should allow shipboard analysis.

   Secondary ion mass spectrometry has been used to determine low levels of ^{230}thorium and ^{232}thorium in seawater [39].

   Thermal ionisation mass spectrometry has been used to determine pg/kg levels of ^{230}thorium and ^{232}thorium in seawater [40].

   Pates et al. [41] have described a liquid scintillation spectrometry method for the determination of ^{234}thorium in seawater with ^{230}thorium as the yield

tracer. ^{234}Thorium is separated from the dissolved phase by a ferric hydroxide precipitation and is then purified using ion exchange chromatography. The counting source is prepared by taking the sample to dryness in a vial, redissolving in acid, and mixing with a scintillation cocktail. The instrument employed has a relatively low background (11 cpm) and the ability to separate α from β activity on the basis of pulse shapes. The ^{234}thorium + ^{234m}protactinium counting efficiency is 50% over the counting window employed. The limit of detection, using the above parameters, a 20 litre sample, and a 400-min count, is found to be 0.04 dpm/l. It was also demonstrated that less advanced instruments, without α/β separation, can also be used effectively.

Bacon and Anderson [42] determined ^{230}thorium and ^{228}thorium concentrations, in both dissolved and particulate forms, in seawater samples from the eastern equatorial Pacific. The results indicate that the thorium isotopes in the deep ocean are continuously exchanged between seawater and particle surfaces. The estimated rate of exchange is fast compared with the removal rate of the particulate matter, suggesting that the particle surfaces are nearly in equilibrium with respect to the exchange of metals with seawater.

Because of the large volumes of water that were required, an in situ sampling procedure was used. Submersible, battery powered pumping systems [43, 44] were used to force the water first through filters (62 μm mesh Nitex followed by 1.0 μm pore-size Nucleopore) then through an adsorber cartridge packed with Nitex netting that was coated with manganese dioxide to scavenge the dissolved thorium isotopes, and finally through a flow meter to record the volume of water that was filtered. Natural ^{234}thorium served as the tracer for monitoring the efficiency of the adsorbed cartridges. Standard radiochemical counting techniques were used [45]. On average 4% of the ^{234}thorium, 15% of the ^{228}thorium, and 17% of the ^{230}thorium were found in the particulate form, i.e., the percentage increases with increasing radioactive half-life. However, the percentages varied considerably from sample to sample and were found to be strongly dependent on total suspended matter concentration.

Traditionally, ^{234}thorium has been analysed by gas proportional counting of β-particles emitted by ^{234m}protactinium, using sample volumes ranging between 20 and 100 litres, depending on detector efficiency and background [38, 46, 47]. Since the analysis requires preconcentration and purification of the sample and electrodeposition onto a planchette, a yield monitor is required – typically ^{228}thorium, ^{229}thorium, or ^{230}thorium. The samples then require a minimum of two counts – one to determine the β activity and another to determine the α activity – and each count requires independent calibration of detection efficiency. Modern gas proportional counting instruments are capable of providing low backgrounds (–0.3 cpm) and extremely good accuracy and precision (–2%) and have been used at sea [47].

An alternative approach is γ spectrometry using HpGe γ photon detectors. This technique meets most of the requirements for ^{234}thorium analysis

since no chemical manipulation of the sample is required and the detectors are sufficiently rugged to be used at sea. However, the low absolute intensity of the 63 keV γ photon emissions (3.8%), combined with the relatively low detection efficiency of γ spectroscopy systems, results in large sample volumes (300–600 litres) being required for the analysis [48, 49]. These sample sizes can be achieved through the use of in situ pumps and manganese cartridges [49] which scavenge thorium from seawater [50]. These systems avoid the problems of bottle-associated sampling artefacts, such as thorium losses to the vessel walls and particles sinking below spigots, and enable sampling of rare large particles. However, the pumping system is relatively expensive and time-consuming to use, restricting the number of depths that can be sampled simultaneously. In addition, only a simple split of particulate and dissolved fractions can be archieved, with more detailed size fractionation, such as that required for the determination of colloidal ^{234}thorium, requiring an alternative method. This second point is of particular relevance with the growing realisation that (i) colloids play a critical role in both carbon cycling and trace metal scavenging, and (ii) ^{234}thorium/^{238}uranium disequilibrium is a useful technique for elucidating this role [51–53].

Liquid scintillation spectrometry is a technique suitable for the analysis of both α and β emitters, with much higher detection efficiencies than either α or γ spectrometry using semiconductor detectors or gas proportional counting. For α emitters, the liquid scintillation spectrometric detection efficiency is $\sim$100%, while for β emitters with $E_{max} > 156$ keV (^{14}C), detection efficiency is $> 95\%$.

7.1.6
Bromide

Foti [54] has studied the feasibility of concentrating traces of radioactive bromide ions by passing the seawater sample through a column of inactive AgBr (to effect isotopic exchanges). The effects of column height and of flow rate, volume and/or residence time of the seawater on the extent of exchange were examined; each of these variables had a significant effect.

7.1.7
Phosphate

Flynn and Meeham [55] have described a solvent extraction phosphomolybdate method using iso-amyl-alcohol for monitoring the concentration of 32-phosphorus in sea and coastal waters near nuclear generating stations.

Benitez-Nelson and Buesselet [56] have developed a new method for the collection, purification, and measurement of natural levels of ^{32}P and ^{33}P in marine particulates, and dissolved constituents of seawater. ^{32}P and ^{33}P

activities were measured using a ultra-low-level liquid scintillation counter. Measurement by liquid scintillation counting allows, for the first time, simultaneous measurement of both ^{32}P and ^{33}P. Furthermore, ^{33}P activities are measured with high efficiency (> 50%), regardless of the amount of stable phosphorus in the sample. Liquid scintillation also produces energy specific β spectra which has enabled us to identify previously unrecognised β-emitting contaminants in natural samples. In order to remove these contaminants, new methods of purification have been developed which utilise a series of precipitations and anion and cation exchange columns. Dissolved seawater samples were extracted from large volumes of seawater (> 5000 litres) using iron-impregnated polypropylene filters. On these filters, it was possible to load between 25 and 30% $Fe(OH)_3$ by weight, over twice that loaded on previously utilised materials. Using these collection, purification, and liquid scintillation counting techniques, it was possible to obtain specific ^{32}P and ^{33}P activities with less than 10% error (2a) in rainwater and 20% error (2a) in seawater.

7.2
Fallout Products and Nuclear Plant Emissions

7.2.1
Americium and Plutonium

Livingston and Cochran [50] collected large seawater samples by using a cable-supported electrical pumping system for subsequent determination of thorium, americium, and plutonium isotopes. Particles were removed by filtration and actinides were collected by absorption on manganese dioxide-coated filters. The samples were then analysed by standard radiochemical and a spectrometric techniques.

Schell et al. [57] have described a sorption technique for sampling plutonium and americium, from up to 4000 litres of water in 3 h. Battelle large-volume water samples consisting of 0.3 μm Millipore filters and sorption beds of aluminium oxide were used. Particulate, soluble, and presumed colloidal fractions are collected and analysed separately. The technique has been used in fresh and saline waters, and has proved to be reliable and comparatively simple.

7.2.2
^{137}Caesium

Dutton [58] has described a procedure for the determination of ^{137}caesium in water. This procedure comprises a simple one-step separation of the radio-caesium from the sample using ammonium dodecamolybdophosphate or potassium cobaltihexacyanoferrate; ^{137}caesium and ^{134}caesium are measured

by γ-ray counting of the dried adsorbent with a NaI(Tl) crystal coupled to a γ-ray spectrometer. Levels of [137]caesium activity down to about 1 pCi per litre can be determined in seawater and lake, rain, and river waters without sophisticated chemical processing.

A further method for the determination of caesium isotopes in saline waters [60] is based on the high selectivity of ammonium cobalt ferrocyanide for caesium. The sample (100–500 ml) is made 1 M in hydrochloric acid and 0.5 M in hydrofluoric acid, then stirred for 5–10 min with 100 mg of the ferrocyanide. When the material has settled, it is collected on a filter (pore size 0.45 μm), washed with water, drained dried under an infrared lamp, covered with plastic film and β-counted for [137]caesium. If [131]caesium is also present, the γ-spectrometric method of Yamamoto [61] must be used. Caesium can be determined at levels down to 10 pCi/l.

Mason [62] has described a rapid method for the separation of [137]caesium from a large volume of seawater. In this procedure the sample (50 litres) is adjusted to pH 1 with nitric acid, and ammonium nitrate (100 g) and caesium chloride (30 mg) added as carrier. A slurry is prepared of ammonium molybdophosphate (7.5 g) and Gooch-crucible asbestos (715 g) with 0.01 M ammonium nitrate and deposited by centrifugation on a filter paper fitted in the basket of a continuous-flow centrifuge. The sample is centrifuged at 600–3000 rpm and the deposit washed on the filter with 1 M ammonium nitrate (60–70 ml) and 0.01 M nitric acid (30–40 ml). The caesium collected on the filter is then prepared for counting by the method of Morgan and Arkell [63]. With this method the caesium can be extracted in less than an hour.

Krosshaven et al. [64] used scintillation spectrometry employing germanium detectors to measure [137]caesium and [90]strontium in coastal seawaters.

Aleksan'yan [65] has discussed a method for determining [90]strontium and [137]caesium in seawater or river water involving isolation of the radionucleides, in the presence of strontium and caesium carriers, by precipitation as the carbonate and ferrocyanide respectively. The carbonate is dissolved in 0.5 N hydrochloric acid and the strontium in this solution is precipitated as oxalate, the precipitation ignited and a solution of the product in 2 N hydrochloric acid is set aside for accumulation of [90]yttrium; this is precipitated as hydroxide (and again as oxalate) for β-counting.

The ferrocyanide precipitate containing [137]caesium is ignited at < 400 °C, the residue is extracted with boiling water, then evaporated and a solution of the residue in acetic acid is treated to precipitate caesium (as $Cs_3Bi_2I_9$) for β-counting.

Huang et al. [66] removed [137]caesium from 4 litre samples of seawater by adsorption onto a filter coated with copper (II) and then determined it by with 47% recovery by γ-ray spectrometry.

Riel [67] studied in situ extraction combined with γ-ray spectrometry in an underwater probe for the determination caesium and chromium in seawater.

7.2.3
[60]Cobalt

Hiraide et al. [68] used continuous flow coprecipitation-floatation for the radiochemical separation of [60]cobalt from seawater. The [60]cobalt activity was measured by liquid scintillation counting with greater than 90% yield and a detection limit of 5 fCi/l seawater.

Tseng et al. [69] determined [60]cobalt in seawater by successive extractions with tris(pyrrolidine dithiocarbamate) bismuth (III) and ammonium pyrrolidine dithiocarbamate and back-extraction with bismuth (III). Filtered seawater adjusted to pH 1.0–1.5 was extracted with chloroform and 0.01 M tris(pyrrolidine dithiocarbamate) bismuth (III) to remove certain metallic contaminants. The aqueous residue was adjusted to pH 4.5 and re-extracted with chloroform and 2% ammonium pyrrolidine thiocarbamate, to remove cobalt. Back-extraction with bismuth (III) solution removed further trace elements. The organic phase was dried under infrared and counted in a germanium/lithium detector coupled to a 4096 channel pulse height analyser. Indicated recovery was 96%, and the analysis time excluding counting was 50-min per sample.

7.2.4
[55]Iron

Testa and Staccioli [70] used Microthene-710 (microporous polyethylene) as a support material for bis-(2-ethylhexyl) hydrogen phosphate in the determination of [55]iron in environmental samples.

7.2.5
[54]Manganese

[54]Manganese has also been determined by a method [71] using coprecipitation with ferric hydroxide. The precipitate is boiled with hydrogen peroxide and the iron is removed by extraction with isobutyl methyl ketone. Zinc is separated on an anion exchange column and the manganese is separated by oxidising it to permanganate in the presence of tetraphenylarsonium chloride and extracting the resulting complex with chloroform prior to a spectrophotometric finish. Both [65]zinc and [54]manganese are counted with a 512-channel analyser with a well-type NaI(T1) crystal (7.6 × 7.6 cm). Recoveries of known amounts of [65]zinc and [54]manganese were between 74% and 84% and between 69% and 74%, respectively.

Flynn [72] has described a solvent extraction procedure for the determination of [54]manganese in seawater in which the sample with bismuth, cerium, and chromium carriers, is extracted with a heptane solution of bis(2-ethylhexyl) phosphate and the manganese back-extracted with 1 M hydrochloric acid. After

oxidation with nitric acid and potassium chlorate, manganese is determined spectrophotometrically as permanganate ion.

7.2.6
[237]Neptunium

May et al. [73] used neutron activation analysis to determine [237]neptunium in waste waters. The determination used the [237]Np(n, γ)[238]Np reaction. The detection limit was 5×10^{-6} µg of [237]neptunium, which corresponds to 2.5×10^{-6} µg/kg for 200 ml seawater samples.

Holm et al. [74] used α spectrometry for the determination of [237]neptunium in seawater. The actinides are preconcentrated from a large seawater sample by hydroxide precipitation. The neptunium was isolated by ion exchange, fluoride precipitation, and extraction with TTA. [238]Neptunium or [235]neptunium was used to determine the radiochemical yield.

7.2.7
Plutonium

The plutonium concentration in marine samples is principally due to environmental pollution caused by fallout from nuclear explosions and is generally at very low levels [75]. Environmental samples also contain microtraces of natural α emitters (uranium, thorium, and their decay products) which complicate the plutonium determinations [76]. Methods for the determination of plutonium in marine samples must therefore be very sensitive and selective. The methods reported for the chemical separation of plutonium are based on ion exchange resins [76–80] or liquid–liquid extraction with tertiary amines [81], organophosphorus compounds [82, 83], and ketones [84, 85].

Wong [77] has described a method for the radiochemical determination of plutonium in seawater, sediments, and marine organisms. This procedure permits routine determinations of [239]plutonium activities (dpm) down to 0.004 dpm per 100 litres of seawater (50 litre sample), 0.02 dpm per kg sediments (100 g samples), and 0.002 dpm per kg of organisms (1 kg sample). The plutonium is separated from seawater by coprecipitation with ferric hydroxide and from dried sediments or ashed organisms by leaching with nitric acid and hydrochloric acid [86]. After further treatment and purification by ion exchange, the plutonium is electro-deposited onto stainless steel disks for counting and resolution of the activity by α-spectrometry. For 30 samples the average deviation was generally well within the 1SD counting error. For seawater the average recovery was $52 \pm 18\%$ and for sediments and organisms it was $63 \pm 20\%$. The most serious interference is from [228]thorium, which is present in most samples and is also a decay product of the [236]plutonium tracer.

Livingstone et al. [87] carried out double tracer studies to optimise conditions for the radiochemical separation of plutonium from large volumes of seawater.

In this procedure ^{242}plutonium is added to determine the overall recovery of plutonium from the sample, and the recovery of ^{242}plutonium at any point in the procedure is measured by the addition of a similar amount of ^{236}plutonium at that point, the final recovery of ^{236}plutonium being used to calculate the recovery of ^{242}plutonium at the time of the addition of ^{236}plutonium. Experience with this double-tracer experiment has permitted improvement in the ability to recover plutonium from 50 litre samples for α-spectrophotometric analysis of ^{239}plutonium, ^{240}plutonium, and sometimes ^{238}plutonium.

Anderson and Fleer [88] determined the natural actinides ^{237}actinium, ^{228}thorium, ^{230}thorium, ^{232}thorium, ^{234}thorium, ^{231}palladium, ^{238}uranium and ^{234}uranium, and the α-emitting plutonium isotopes in samples of suspended marine particulate material and sediments. Analysis involves total dissolution of the samples to allow equilibration of the natural isotopes with added isotope yield monitors followed by coprecipitation of hydrolysable metals at pH 7 with natural iron and aluminium acting as carriers to remove alkali and alkaline earth metals. Final purification is by ion exchange chromatography (Dowex AG1-X3) and solvent extraction for palladium. Overall chemical yields generally range from 50% to 90%. The method has been successfully interfaced with methods to include the determination of fallout elements of ^{55}iron, ^{137}caesium, ^{90}strontium and ^{241}americium on the same samples.

Testa and Staccioli [70] have pointed out that Microthene-710 (a microporous polyethylene) as a support material for triphenylphosphine oxide in cyclohexane medium has a potential application for the determination of plutonium in fallout samples.

Hirose and Sugimura [89] investigated the speciation of plutonium in seawater using adsorption of plutonium (IV)-xylenol orange and plutonium-arsenazo (III) complexes on the macroreticular synthetic resin XAD-2. Xylenol orange was selective for plutonium (IV) and arsenazo (III) for total plutonium. Plutonium levels were determined by α-ray spectrometry.

Kim et al. [116] determined plutonium isotopes in seawater by an online sequential injection technique with sector field ICP-MS.

Delle Site et al. [90] have used extraction chromatography to determine plutonium in seawater sediments and marine organisms. These workers used double extraction chromatography with Microthene-210 (microporous polyethylene) supporting tri-octylphosphine oxide, a technique that has been used previously to isolate plutonium from other biological and environmental samples [91]. ^{236}Plutonium and ^{242}plutonium were tested as the internal standards to determine the overall plutonium recovery, but ^{242}plutonium was generally preferred because ^{236}plutonium has a shorter half-life and an α-emission (5.77 MeV) which interferes strongly with the 5.68 MeV (95%) α-line of ^{224}radium, the daughter of ^{228}thorium. However, the 5.42 MeV-lines of ^{228}thorium interfere with those of ^{238}plutonium (5.50 MeV) and so a complete purification from thorium isotopes is required.

Plutonium sources were counted by an α-spectrometer with good resolution, background, and counting yield. The counting apparatus used had a resolution of 40 keV. The mean ($\pm$ sd) background value was 0.0004 ± 0.0003 cpm in the [239]plutonium and [240]plutonium energy range and 0.0001 ± 0.0001 cpm in the [238]plutonium energy range. The mean (iso) counting yield, obtained with [239]plutonium, [240]plutonium reference sources counted in the same geometry, was found to be 25.08 ± 0.72%.

To determine the overall recovery obtained by this procedure (chemical recovery and electrodeposition yield) a known activity of [242]plutonium was added to the different samples; the plutonium sources were counted by α-spectrometry for 3000 minutes and the percentage overall recovery was calculated from the area of [242]plutonium peak. The percentage overall recovery for 3-litre samples of seawater was 63 ± 10%. Owing to the very low activity of the samples, the determination of [239]plutonium, [240]plutonium, and [238]plutonium in the reagents is very important in calculating the net activity of the radionuclides.

The method proposed was checked by analysing some seawater reference samples prepared by the IAEA Marine Radioactivity Laboratory (Monaco) for intercomparison programmes. The values reported by IAEA and the experimental values obtained by Delle Site et al. [90] were in good agreement.

Buesseler and Halverson [92] have described a thermal ionisation mass spectrometric technique for the determination of [239]plutonium and [240]plutonium in seawater. The mass spectrometric technique was more sensitive than α spectrometry by more than order of magnitude.

7.2.8
[106]Ruthenium and Osmium

Kiba et al. [93] has described a method for determining this element in marine sediments. The sample is heated with a mixture of potassium dichromate and condensed phosphoric acid (prepared by dehydrating phosphoric acid at 300 °C). The ruthenium is distilled off as RuO_4, collected in 6 M hydrochloric acid-ethanol and determined spectrophotometrically (with thiourea) or radiometrically. Osmium is separated by prior distillation with a mixture of condensed phosphoric acid and $Ce(SO_4)_2$. In the separation of ruthenium–osmium mixtures recovery of each element ranged from 96.8 to 105.0%.

7.2.9
[90]Strontium

Silant'ev et al. [94] have described a procedure for the determination of [90]strontium in small volumes of seawater. This method is based on the determination of the daughter isotope [90]yttrium. The sample is acidified with

hydrochloric acid, heated and, after addition of iron, interfering isotopes are separated by double coprecipitation with ferric hydroxide. The filtrate is acidified with hydrochloric acid, yttrium carrier added, the solution set aside for 14 days for ingrowth of [90]yttrium, and $Y(OH)_3$ precipitated from the hot solution with carbon dioxide free aqueous ammonia. Then $Y(OH)_3$ is reprecipitated from a small volume in the presence of hold-back carrier for strontium, the precipitate dissolved in the minimum amount of nitric acid, the solution heated and yttrium oxalate precipitated by adding precipitated oxalic acid solution. The precipitate is collected and ignited at 800–850 °C to Y_2O_3. The cooled residue is weighed to determine the chemical yield, then sealed in a polyethylene bag and the radioactivity of the saturated yttrium measured on a low-background β-spectrometer. If the short-lived nuclides [140]barium and [140]lanthanium are thought to be present in the seawater sample, lanthanum carrier is introduced after the first $Y(OH)_3$ separation, and the system is freed from [140]lanthanum by precipitation of the double sulfate of lanthanum and potassium from a solution saturated with potassium sulfate.

Gordon and Larson [95] used photon activation analysis to determine [87]strontium in seawater. Samples (2 ml, acidified to pH 1.67 or 2.54 for storage) were filtered and freeze-dried. The residues, together with strontium standards, were wrapped in polyethylene and aluminium foil and irradiated in a 30 MeV bremsstrahlung flux of γ-radiation. After irradiation, the samples were dissolved in 50 ml of acidified water and [87m]strontium was separated by precipitation as strontium carbonate for counting (γ-ray spectrometer, Ge(Li) detector and multichannel pulse-height analyser). The standard deviation at the 7 ppm strontium level was ±0.47.

Pinones determined [90]strontium in seawater [96]. The seawater sample is filtered and a known amount of strontium nitrate is added to the filter as a carrier. Precipitation of the radiogenic elements, followed by addition of fuming nitric acid, separates strontium nitrate from the radiogenic elements. The [90]strontium is measured by the change in activity of the radiogenic daughter, [90]yttrium.

Chassery et al. [97] studied the [87]Sr/[86]Br composition in marine sediments, observing excellent agreement between results obtained by ICP-MS and thermal ionisation mass spectrometry. Low level α-spectrometry with lithium drifted germanium detectors has been used to determine [90]strontium in seawater [59].

7.2.10
Uranium

Spencer [98] has reviewed the determination of uranium in seawater.

Bertine et al. [99] have discussed the determination of uranium in deep sea sediments and water utilising the fission track technique. In this technique a weighed aliquot (50–100 mg) of the powdered sample is made into a pel-

let with sufficient cellulose (as binder). The pellet is placed in a high-purity aluminium capsule and covered by polycarbonate plastic film (Lexan, $10\,\mu m$ thick).

Adsorbing colloid flotation has been used to separate uranium from seawater [101].

To the filtered seawater (500 ml; about $1.5\,\mu g$ U) is added 0.05 M ferric chloride (3 ml), the pH is adjusted to 6.7 ± 0.1 and the uranium present as $(UO_2(CO_3)_3)^{4-}$ is adsorbed on the colloidal ferric hydroxide which is floated to the surface as a stable froth by the addition of 0.05% ethanolic sodium dodecyl sulfate (2 ml) with an air-flow (about $10\,ml\,min^{-1}$) through the mixture for 5 min. The froth is removed and dissolved in 12 M hydrochloric acid-16 M nitric acid (4:1) and the uranium is salted out with a solution of calcium nitrate containing EDTA, and determined spectrophotometrically at 555 nm by a modification of a Rhodamine B method. The average recovery of uranium is 82%; co-adsorbed WO_4^{2-} and MoO_4^{2-} do not interfere.

Adsorbing colloid flotation has also been used by Williams and Gillam [102]. The fusion track method has also been used by Hashimoto [100]. In this method the uranium is first coprecipitated with aluminium phosphate [103], the precipitate is dissolved in dilute nitric acid and an aliquot of the solution is transferred to a silica ampoule into which small pieces of muscovite are inserted before sealing. The uranium is then determined by measuring the density of fission tracks formed on the muscovite during irradiation of the ampoule for 15 min at $80\,°C$ in a neutron reactor. The muscovite is etched with hydrofluoric acid for 1 h before the photomicrography; the density is referred to that obtained with standard solution of uranium. There is no interference from thorium, and no chemical separations are required. An average concentration of $3-40 \pm 0.12\,\mu g$ uranium per litre was obtained, in good agreement with the normally accepted value.

Leung et al. [104] and Kim and Zeitlin [105] described a method for the separation and determination of uranium in seawater. Thoric hydroxide $(Th(OH)_4)$ was used as a collector. The final uranium concentration was measured via the fluorescence (at 575 nm) of its Rhodamine B complex. The detection limit was about $200\,\mu g/l$.

Korkisch and Koch [106, 107] determined low concentrations of uranium in seawater by extraction and ion exchange in a solvent system containing trioctyl phosphine oxide. Uranium is extracted from the sample solution (adjusted to be 1 M in hydrochloric acid and to contain 0.5% of ascorbic acid) with 0.1 M trioctylphos-phine oxide in ethyl ether. The extract is treated with sufficient 2-methoxyethanol and 12 M hydrochloric acid to make the solvent composition 2-methoxyethanol-0.1 M ethereal trioctylphosphine acid-12 M hydrochloric acid (9:10:1); this solution is applied to a column of Dowex 1-X8 resin (Cl$^-$ form). Excess of trioctylphosphine oxide is removed by washing the column with the same solvent mixture. Molybdenum is removed by elution with 2-methoxyethanol-30% aqueous hydrogen peroxide-12 M hydrochloric

acid (18:1:1); the column is washed with 6 M hydrochloric acid and uranium is eluted with molar hydrochloric acid and determined fluorometrically or spectrophotometrically with ammonium thiocyanate. Large amounts of molybdenum should be removed by a preliminary extraction of the sample solution (made 6 M in hydrochloric acid) with ether.

Spectrophotometric analysis following extraction with Aliquot 336 has been used to determine uranium in seawater [108]. Kim and Burnett [109] used X-ray spectrometry to determine the uranium series nucleides including ^{238}uranium, ^{226}radium and ^{210}lead in marine phosphorites.

Bowie and Clayton [110] used γ-ray spectrometry to determine uranium, thorium, and potassium in sea bottom surveys.

Chen et al. [111] determined ^{238}uranium, ^{234}uranium and ^{232}thorium in seawater by isotope dilution mass spectrometry. Uranium measurements were made by using a ^{233}uranium/^{236}uranium double spike to correct for instrumental fractionation. The ^{234}uranium/^{238}uranium ratio could be measured routinely to $\pm5\%$ for 0.03 μg of total uranium in a 1-h data acquisition time, which is considerably shorter than α-counting. The ^{232}thorium is measured to $\pm20\%$ for 0.001 μg of ^{232}thorium.

7.2.11
Miscellaneous

Spencer and Brewer [112] have reviewed the determination of radionucleides in seawater and discuss sampling and storage methods together with tables of radionucleides that have been determined in the oceans.

Becker and Dietze [113] used a micro mist nebuliser with ICP high resolution mass spectrometry to determine sub-picogram/l levels radionucleides in seawater.

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