CHEMICAL ANALYSIS OF RADIONUCLIDES IN SEA WATER

An Outline of the Chemical Analysis of Some of the Major Radionuclides that may be introduced in the Marine Environment by the Disposal of Radioactive Wastes or by Accidents of Nuclear Plants.

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January 1964

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INTRODUCTION

Natural and Artificial Radioactivity in the Sea

Natural radioactivity in sea water occurs mainly in radiopotassuim (K-40). The rest of the radioactive elements in sea water (Rb-87, U-238, Ra-226, C-14, U-235, and Th-232) contribute slightly more then 10 per cent of the natural radioactivity. This natural radioactivity of sea water is about 1/10th of the natural radioactivity of granite rocks.

TABLE 1

Natural Radioactive Nuclides in Ocean

(Note: Concentration in surface waters in 1953, prior to thermonuclear tests.)

Nuclide	Half-life in years	Concentration (g/ml)	Isotopic abundance (%)	Disintegrations per sec per ml
H^{3}	1.2×10^{1}	3.2×10^{-21}	1.0×10^{-16}	1.1×10^{6} β
C^{14}	5.5×10^{3}	3.1×10^{-17}	1.3×10^{-10}	5.2×10^{6} β
Be^{10}	2.7×10^{6}	1.0×10^{-16}		7.0×10^{-8} β
K^{40}	1.3×10^{9}	4.5×10^{-8}	1.2×10^{-2}	1.1×10^{-2} $\beta + \gamma$
Rb^{87}	5.0×10^{10}	3.4×10^{-8}	27.8	1.0×10^{-4} β
U^{238}	4.5×10^{9}	2.0×10^{-9}	99.3	2.5×10^{-5} α
Th^{230}	8.0×10^{4}	6.0×10^{-16}	$>3 \times 10^{-3}$	4.0×10^{-7} α
Ra^{226}	1.6×10^{3}	8.0×10^{-17}	~ 100	2.9×10^{-6} α
U^{235}	7.1×10^{8}	1.4×10^{-11}	0.7	1.1×10^{-6} α
Pa^{231}	3.4×10^{4}	5.0×10^{-17}	~ 100	8.0×10^{-8} α
Th^{227} (RdAc)		7.0×10^{-23}		8.0×10^{-8} α
Th^{232}	1.4×10^{10}	2.0×10^{-11}	~ 100	8.0×10^{-8} α
Th^{228} (RdTh)	1.9	4.0×10^{-21}		1.2×10^{-7} α
Ra^{228}	6.7	1.4×10^{-20}	$\sim 1.0 \times 10^{-2}$	1.2×10^{-7} β

Further contribution to radioactivity in the water comes from cosmic radiation, which, however, is absorbed quickly by the uppermost layers of the sea. Of the 35 mrad of the cosmic radiation coming to the surface, only 30% reaches a depth of 10 meters and 4% a depth of 50 meters.

The radioactivity of the sea bed varies with the type of sediment. Highest activities are found in deep water sediments, highest in red clay, followed by blue clays and calcareous oozes. The radioactivity of shallow water sediments with which commercial marine food resources may come into contact, have considerably lower natural radioactivity than the average soil on land.

Marine animals also receive, besides the external radiation, some radiation from internal sources, mainly from radiopotassium accumulated in the bones.

Artificially induced radioactivity, on the other hand, had its source up to now from nuclear explosions. In the near future, however, industrial nuclear wastes as well as reactor wastes from nuclear-powered vessels will be introduced into the marine environment and these will present serious potential hazards to human beings.

Artificial radioactivity in the sea is of interest to man for the following reasons:

a) It might affect health through consumption of sea food;

b) It might affect the ecological balance of marine resources; and

c) It can be used for the study of physical, chemical and biological processes in the sea.

DISCUSSION

The fate of radioactive materials introduced into the marine environment depends on five things: physical and chemical form of the material; initial mechanical dilution in the receiving waters; advection and turbulent diffusion; uptake by suspended silt and bottom sediments; and concentration by organisms.

a. The Physical and Chemical Form of the Material when Released and Initial Mechanical Dilution

Radioactive wastes may be released in the water either as particulate matter or as dissolved substances.

The particulate matter either floats or sinks. It can also be dissolved and be taken up by marine animals with food. The sinking speed depends on the specific gravity of the particles, their size and the turbulence in the sea. Ultimately, most of the particulate radioactive matter will sink to the bottom where it causes a higher activity in the surface layer of the sediment.

In the deep sea such sedimentation will remove radio-isotopes from the domain of harvested marine organisms. In the nearshore and continental shelf waters, however, it may tend to concentrate them in the bottom sediments from which they may be returned to the water or taken up by bottom-living food organisms.

Dissolved substances, which undergo dilution by different mixing processes in the sea, might enter into chemical reactions with other dissolved substances, might be precipitated, might be absorbed, and/or might be adsorbed by suspended matter, both living and dead and settle together with it to the bottom.

TABLE 2

Physical States of Elements in Sea Water

(USNRDL Doc. 436, pp. 1-28)

Element	Ionic %	Colloidal	Particulate
Cesium	70 70	7	23
Iodine	90	8	2
Strentu Strontium-	87	3	10
Antimony	73	15	112
Tellurium	45	43	12
Molybdenum	30	10	60
Ruthenium	0	5	95
Cerium	2	4	94
ZirconiuZirconium	1	3	96
Yltrium	0	4	96
Niobium	0	0	100

b. Advection and Turbulent Diffusion

In order to study the distribution of radioactivity in the oceans, one has to know also water mass movements.

Although the knowledge of the circulation of the deep ocean has increased in the past few years, the data are still too scarce and scattered to permit construction of a coherent picture.

Within the last few years, however, numerous measurements of the flow in the intermediate and deep layers have been made. Near-bottom deep-sea circulations studies involve the use of isotopic analyses of lead and thorium isotopes in the deep-sea sediments. The tramsfer of dissolved chemical species, characteristic of water mass adjacent to the bottom, to one or more of the solid phases of the deposit results in a record in the sediments of the travels of the bottom water.

Recently, they have used the observed distribution of radium in the ocean to evaluate the rate of mixing between deep and surface water. Under the assumption that all radium in ocean water originates from the ocean floor, a simplified form of the Fickian diffusion equation is used to compute deep vertical eddy diffusivity coefficients, which are found to be about 8 cm /sec. In the layer of minimum eddy diffusion (700-1500 m) , vertical transfer of radium is due to advection, which is estimated at 0.7-2.0 m/year. These results have been used to compute the consequences of depositing large quantities of Sr^{90} on the sea floor. It is shown that at the top of the deep layer, the maximum concentration of Sr^{90} is reached in about 25 years when the concentration per cm is 10^{-2} x Q, where Q is the total amount of waste deposited on the sea floor.

c. Uptake by suspended silt and bottom sediments

The mechanisms and patterns of bottom sediment transportation on continental shelves are poorly understood. The general circulation of the near-bottom water does not wholly control the movements of bottom sediments since tides, waves, storm surges and tsunami, impose controls which may in fact outweigh in importance the average circulation of near-bottom water. Important in such considerations is the recent conclusion independently proposed by several groups studying the sediment budget of North Sea beaches that up to half the sediments contributed to certain advancing beaches has been derived off shore from the floor of the North Sea. The possibility thus exists that detrital waste may reach adjacent beaches in undesirable quantities.

Because movement of bottom materials can be quite independent of the average water circulation since it partly depends on wave action and not wholly on water transport, it must be considered separately. Before extensive dumping is commenced, it would seem desirable to dump harmless trace material and observe from what distances appreciable material reaches the adjacent beaches.

d. Concentration by Organisms

The most serious potential hazards to human beings from the introduction of radioactive products into the marine environment are those that may arise through the uptake of radioisotopes by organisms used for human food. There are several reasons why these indirect hazards are more critical than the direct hazards:

1. The radiation received from a given quantity of an isotope ingested as food is much greater than the dose from the same quantity in the external environment;
2. Many elements, including some of those having radioactive isotopes resulting from nuclear reactions, are concentrated by factors up to several thousand by the organisms in the sea; and
3. The vertical and horizontal migrations of organisms can result in transport of radioactive elements and thereby cause distributions different from those that would exist under the influence of physical factors alone.

SAMPLING PROCEDURES

Analytical results do not have much meaning unless proper sampling procedures are followed. Samples should be representative of the composition of the selected medium, and should include--in the case of monitoring of radioactive wastes--not only water samples, but samples of the sediments, and of the marine organisms.

The size of the samples required is determined by the levels of radioactivity and the number of radiochemical separations to be performed.

a. Sampling Sea Water

Single random samples of sea water are of very little practical significance. Continuous sampling in terms of time and space is needed in order to provide information on the dynamic nature and impact on the environment over a period of time.

Taking representative samples from the sea water presents different problems since variable factors have to be taken into consideration. Tidal action, movement of estuarine and marine currents, wind movements are some of these variables that will affect sampling and the validity of the results. In sea water, much of the radioactivity is adsorbed by very fine particulate matter. For this reason differentiation has to be made as to whether the radioactivity is in the suspended matter or in solution in the water. Suspended matter, finely particulate and colloidal, organic and inorganic is present to some extent in sea water from all localities and has to be filtered. Filter papers are not satisfactory for critical work since only an approximate figure can be given for their pore size. Membrane filters are available with a stated maximum pore size and more recently so-called molecular filters and absorption materials have been introduced. Molecular filters are composed of incompletely cross-linked high polymer molecules of partially substituted cellulose acetate and can be prepared with a uniform pore size ranging from 0.5 to 5000 μ

Larger samples of water from different depths are required since small samples may not be enough for analysis. Often special equipment is needed. Nansen bottles are not applicable to this type of water sampling, first because they are made of metal and secondly, because they hold such small amounts. Special plastic samplers are used and scavenger techniques should be employed for chemical separations.

b. Sampling Sediments

Prior to sampling sediments in a radioactive disposal area, the nature of the bottom substrata should be found by using short gravity corers. If more than one type of sediment is found, the different types of sediment should be monitored separately. Only the surface layer of the sediment (2 cm thick) should be used for radiochemical analysis. For soft bottoms, Mortimer's mud-and-water sampler could be used. For sampling harder bottom, spring-loaded, orange-peel, or clamshell snappers are sufficient.

Sampling of sediments of the deep ocean floor may not be necessary since the marine life that comes in contact with it will not reach man. It is more important to sample sediments of the continental shelf and slope where most of the estuaries are located. In these areas marine organisms come in contact with the bottom, and the avenue of return to man is more direct.

c. Sampling of Aquatic Organisms

Samples of marine organisms are meaningless unless associated with a given volume of water from which they were taken. Otherwise, all that is proved by analyzing such samples is that marine organisms accumulate radionuclides, and no quantitative estimates can be made. In addition, since many of these organisms are mobile, they are not representative of the region in which they were collected. Plankton has very little mobility of its own, but is carried along water masses by current action. Therefore, quantitative sampling of plankton and especially phytoplankton should be carried out. Other less sessile aquatic organisms, such as Benthic fauna and flora, may give a good indication of the long-term history of radioactivity in a given locality close to the bottom. Also filter-feeders should be sampled. For obvious reasons, therefore, biological sampling is not indicative of current radioactivity in water, but is an index of average levels of contamination over a period of time.

There are many difficulties in separately sampling suspended matter, phytoplankton and zooplankton. Separation of inert suspended matter and plankton is achieved by two parallel samples: one with a millipore filter and the other with a fine quantitative plankton net. From the filters the gross activity of suspended matter is determined after conditioning of those filters in desiccators. To measure radionuclides in phytoplankton, great quantities of plankton are needed, and should therefore be sampled with a Carke Bumpus sampler fitted with a No. 25 or No. 20 net. The collected plankton should be measured by displacement volume, filtered and dried.

Seaweeds may be collected with commercial seaweed dredges in the areas desired. Differences in activity should be determined for the different parts of the seaweeds.

Fish should be collected by experimental gear as close to the disposal sites as possible. Special attention should be given to less mobile fish close to the disposal sites, and also to plankton feeders which might have been feeding in these areas.

Shellfish should be collected with a dredge in the vicinity of the disposal site. Both small and mature specimens should be measured since the smaller ones may accumulate radionuclides more rapidly than the adults.

Crustaceans should be caught with traps (lobster) and with dredges (shrimp) in the immediate vicinity of the disposalssites and also in deeper and shallower water, according to the expected migrations.

d. Sampling of Sea Water, Bottom Sediments and Marine Organisms for Gross-Activity Studies

In sea water the level of activity is very low and only the activity of radioactive potassium K-40 is detected by ordinary counting techniques. Only by using extremely large sampled and special low-level counting techniques is it possible to detect the activities of other radionuclides.

If, however, contamination of sea water occurs from the disposal of radioactive wastes, normal counting techniques can be used effectively. Underwater gamma counting could detect gross gamma contamination quickly. Beta counting of samples is better for detecting trace activities. The scavenging of sea water is very effective ~~to~~ in measuring trace activities. The addition of scavengers, such as iron plus barium or yttrium and the subsequent precipitation of mixed ferric hydroxide and barium sulfate or yttrium oxalate, can remove most of the active elements from contaminated water. By this method the radionuclides in water are concentrated in small amounts of precipitate. If it is desired, individual radionuclides can then be analyzed.

Gross alpha, beta and gamma counts can be made on dried sea bottom samples. The acid solution obtained by washing of these samples can also be subject to counting. It is suggested that sediments be separated by particle size and each fraction counted because certain long-lived isotopes tend to be concentrated in the sediments.

Plankton samples have to be dried or ashed, and then grodd alpha, beta and gamma counts can be made. Ashing should be made at low temperature to prevent evaporation of volatile compounds.

For seaweeds also ashing should be done at temperatures below 600 C and then counts can be made. Also analysis of radioiodine in seaweed is important since seaweeds concentrate it in large quantities.

The methods for sampling fish, shellfish and crustaceous fauna are the same as explained above. Similar counts are made on dried or ashed samples.

ANALYTICAL METHODS

The chemistry of the radioactive substances is not at all different from that of the nonradioactive species except in a few cases where the effects of the radiations must be taken into account. Radiochemical problems are often complicated by demands for speed far beyond the limits set by good analytical practice, by remote-control chemistry, by manipulation of vanishingly small amounts of material, and by the preparation of materials in peculiar chemical form. The most important thing is to prepare a given material which is pure--free from contamination of other radioactive species--rather than attempt to separate all of it. Because of the low level of concentrations in such work, it is essential that adequate precautions are taken, both before and during the analysis, against the contamination of sample, reagents, standards, all apparatus and glassware.

The selection of an analytical method for the qualitative and quantitative determination of a radionuclide must meet the following requirements:

1. It should be sensitive and specific;
2. It should be precise and accurate;
3. It should be rapid;
4. It should be economical in materials and instrumentation; and
5. It should be applicable to a wide variety of sample material.

These are the optimum conditions and unfortunately these requirements are not always fulfilled.

The complete radiochemical analysis of individual radionuclides in the marine environment is difficult and time consuming. In this paper only the radionuclides of greatest importance are being considered.

The following are outlines of the analytical methods that would be applicable to maring samples. For more details on these methods and the chemical pretreatment of the marine samples, the reader is referred to the literature.

Tritium

A common method of counting tritium is the following. A sample is prepared for counting in a vacuum line of the scintillation counter. The water sample is dropped on to the metallic calcium, and hydrogen and tritium are evolved. The gas flowing into the evacuated system is passed through a drying column to remove unreacted water, and is then allowed to flow into a tube similar to a Geiger-Müller tube until a pressure of 15 cm of mercury is reached. Ethylene and argon are added to give a total pressure of 22 cm of mercury. The beta activity is counted with a scaling circuit having an input sensitivity of ½ volt. A tube similarly filled with inert hydrogen is measured simultaneously to determine the environmental background. The background count is subtracted from the sample count to obtain the true sample count.

The method has an efficiency of approximately 40% and precision of 5% in the range of 1 to 250 µc of tritium per litre. Samples with higher concentrations may be determined with appropriate dilutions. The biological half-life of tritium is about 10 days.

Ruthenium

The determination of radioruthenium is usually made by gamma spectrometry. In the determination of ruthenium in seaweed ash, ruthenium tetroxide is extracted into carbon tetrachloride and precipitated as ruthenium dioxide, since ruthenium may be lost at high temperatures, the ashing procedure must be carefully followed.

After drying the ruthenium dioxide sample, Ru-106 is counted with a Geiger-Müller tube, through 29 mg/cm^3 of added absorber. The absorber is used to absorb beta-emission due to Ru-106 and Ru-103. Thus the measurement taken will be due to Rh-106, the 30-second daughter of Ru- 106, which is in equilibrium with the ruthenium.

The gamma-emission of Ru-103 is determined with a scintillation counter and from it the gamma-emission due to Rh-106 is subtracted. The gamma-emission due to Rh-106 is obtained by multiplying the beta-count by 8.375.

Strontium

Strontium is one of the more hazardous fission products and many methods have been devised for its determination. However, the following method has proved to give best results of sensitivity and precision.

a. Determination of strontium in bottom sediments

This method originally applying to the determination of strontium in soil may easily be modified for the determination of strontium in bottom sediments.

The sea water or the bottom sediment sample is stirred in the presence of strontium carrier with two portions of 6 M hydrochloric acid. The insoluble material is filtered off and calcium and strontium are precipitated as oxalates at a controlled pH of 4.

In the case of clay sediments, the solution may contain amounts of aluminum which, by complexing the oxalate ion, will prevent the precipitation of calcium and strontium. With such clays, the solution is first neutralized (before the addition of oxalic acid) with sodium hydroxide and excess sodium hydroxide added to make the solution 1 N in free alkali. Sodium carbonate is then added to precipitate the calcium and strontium, and the carbonates are filtered off. The carbonates are dissolved in dilute acid, oxalic acid added, and the pH adjusted to 4.0 when calcium and strontium are precipitated.

The oxalates are ignited and the calcium and strontium dissolved in dilute acid. Any residual iron and aluminum are removed as hydroxides and the calcium and strontium precipitated as carbonate and weighed.

The strontium is separated from the calcium by successive 75% nitric acid separations. Two barium chromate separations are made after additions of barium carrier, and these are followed by an iron scavenger to remove radium and its daughters. Yttrium carrier is added, and after allowing sufficient time for the Y-90 to grow in the yttrium is milked off and counted.

b. Determination of strontium-90 in marine organisms

The marine organisms are dried and then ashed to remove organic matter. The ash is dissolved in dilute nitric acid in the presence of strontium carrier, and the calcium and strontium precipitated as phosphate. The precipitate is dissolved in nitric acid and the acid concentration is increased to precipitate the strontium as nitrate. After further nitric acid separations, barium carrier is added and a barium chromate separation made. The separated strontium is stored in the presence of yttrium carrier to allow Y-90 to grow in. The yttrium is milked off and counted.

c. Determination of strontium-90 in marine plants

The marine organisms are dried and then ashed to remove organic matter. The ash is dissolved in dilute nitric acid in the presence of strontium carrier, and the calcium and strontium precipitated as phosphate. The precipitate is dissolved in nitric acid and the acid concentration is increased to precipitate the strontium as nitrate. After further nitric acid separations, barium carrier is added and a barium chromate separation made. The separated strontium is stored in the presence of yttrium carrier to allow Y-90 to grow in. The yttrium is milked off and counted.

d. Determination of strontium-90 in marine plants

Marine plants are dried and ashed. The ash is treated with dilute nitric acid in the presence of strontium carrier. The solution is evaporated nearly to dryness with perchloric acid and the silica filtered off. The calcium and strontium are precipitated as phosphate and the strontium removed from the mixed phosphates by a series of nitric acid separations. Barium carrier is added and a barium chromate separation made, followed by a ferric hydroxide scavenge to remove radium and its daughters.

The strontium is stored for at least 14 days in the presence of yttrium carrier, the yttrium is then milked off and counted. The strontium is precipitated as carbonate and mounted for counting when further Y-90 has grown in.

Cesium

This method may be used for direct analysis of Cs-137 in sea water after particulate matter has been removed. Marine organisms and seaweed may be analyzed after wet-ashing, sediments after dry-ashing.

Supernates from the nitrate precipitation of strontium will contain the radiocesium if cesium carrier has been added to the original solution of the sample. Where strontium and cesium are to be determined on the same sample, a wet-ashing procedure for tissue and vegetation may be followed. The strontium may then be precipitated as the carbonate and the filtrate containing the cesium analyzed.

The method is based on two separations involving the relative solubilities of the alkali alums and alkali chloroplatinates. Separation of cesium from the bulk of the alkali elements and the mixed fission products is accomplished by co-crystallization of cesium with ammonium aluminum sulfate. The ammonium salts are decomposed by heating. For counting, the cesium is reprecipitated from dilute hydrochloric acid as the chloroplatinate.

The cesium chloroplatinate precipitate is washed filtered and dried. Prior to counting the counter is standardized with a known amount of Cs-137 and 30 mg of cesium carrier precipitated as the chloroplatinate.

Thorium

Thorium has a low specific activity, therefore spectrometric measurements are utilized, after isolation of the thorium and reaction with a suitable chromogenic reagent such as morin or thorin. The methods described apply to urine samples but could easily be extended to sea water samples.

The sample is first freed from organic matter by a series of wet ashings with concentrated nitric acid. In the case of sea water this is not necessery. Two lanthanum fluoride precipitations remove the thorium from the other salts. Thorium in 0.2 N nitric acid is separated from any remaining salts and the lanthanum carrier by extraction with o.45M 2-thenoyltrifluoroacetone (TTA) in benzene. Thorium is stripped from the 2-thenoyltrifluoroacetone-benzene solution with 2N nitric acid and evaporated to dryness with perchloric acid to remove the last traces of organic material. Then the thorium is taken up in perchloric acid (pH 2.0) and determined colorimetrically as the thorium-morin complex.

A direct precipitation method has also been developed to replace the wet-ashing procedure, which is time-consuming and may also by a source of an ocassionally low result, possibly owing to the formation of a sparingly soluble, refractory thorium oxide during the heating. The acidified sample is boiled down to a small volume and the lanthanum fluoride is precipitated directly from this solution. This procedure gives a higher yield and greater precision than the wet-ashing procedure.

A third method involves treatment of the sea water sample with ammonia and the precipitate containing the thorium is dissolved in hydrochloric acid. After pH adjustment to 4-4.2, the thorium is extracted by cupferron in chloroform. The extract is ashed, and thorium is determined in the ash solution by colorimetry with thorin.

Plutonium

A method for measuring small amounts of plutonium in human urine, and applicable to aquatic solutions, involves the isolation of plutonium and its measurement by radioautographic means. Using this method, it is possible to measure 0.05 dpm of plutonium with relative confidence; special equipment, such as electrodeposition cells, radioautographic cameras, and microscopes must be provided. The isolation of plutonium is a rather complex procedure. The reader is referred to the literature for details.

A second method involves alkaline precipitation of the ash solution, cupferron extraction, and co-precipitation with lanthanum fluoride;

these steps successively eliminate the alkali metals, the alkaline-earth metals, and uranium before the activity due to plutonium is measured. Prior to counting, the efficiency of the counting equipment should be determined by measuring a plutonium sample of known activity. The activity in microcuries is:

$$\frac{N - N_o}{R \times 2.2 \times 10}$$

where N = average count of plutonium sample

N_o = background radiation

R = efficiency of the counting equipment

By this method 0.3×10^{-6} microcuries can be detected. The advantage of this method over the other one, lies in the fact that ordinary counting equipment can be used.

Iodine

The determination of radioiodine should be made by means of gamma spectrometry. In the radiochemical determination of radioiodine, the iodine is extracted into carbon tetrachloride, back-extracted into water, and finally precipitated as silver iodide. The amount of iodine in the weight of silver iodide is calculated and the final activity of I-131 can be determined from the following equation:

$$I^{131}\text{ activity} = \frac{C_{AgI} \cdot F_{AgI} \cdot f \cdot 100}{R_I \cdot V \cdot 2.22} \quad \mu\mu c \text{ per litre}$$

where C_{AgI} = net counts per minute for the silver iodide

F_{AgI} = standard factor dpm/cpm

f = correction factor for decay of I-131

R_I = recovery of iodine in %

V = sample in litres

The sum of the inorganic and organic I-131 activities gives the total I-131 activity in the sample.

a. Iodine in marine vegetation

An alkaline extract of vegetation is scavenged with aluminum hydroxide. Silver iodide is finally precipitated with silver nitrate, washed with alcohol, dried at room temperature, and its activity is measured.

Polonium

Polonium in solution of sea water is determined by allowing it to deposit by electrochemical exchange on various metallic discs, usually nickel, copper or silver.

The sample is digested, first with nitric and sulphuric acids and then with perchloric acid to remove all traces of organic matter. The residue is dissolved in water and potassium tellurate is added as a carrier. Polonium is co-precipitated with metallic tellurium on addition of sodium hypophosphite and this precipitate is dissolved in a saturated solution of bromine in hydrochloric acid; tellurium is precipitated by the addition of hydrazine hydrochloride and is removed by filtration. The acidity and volume of the filtrate are adjusted and polonium is deposited electrochemically on silver foil. The activity of the deposited polonium is determined in an alpha scintillation counter and is counted against a standard polonium source; differences in energies, backscatter, and geometry are accounted for in the overall bias of the method.

Radium

The procedure written below is for the determination of radium in urine but its use could be extended to the determination of radium in sea water.

Radium in solution is precipitated with ammonium hydroxide. The precipitate is dissolved with acetic acid and the pH is adjusted to 5 with ammonium hydroxide. Ammonium sulphate and barium chloride precipitate radium. The silica is removed and radium is purified by redissolving the precipitate with a mixture of sulfuric and hydrofluoric acids, in a sand bath. When fumes of sulfur trioxide appear, the sample is removed from the bath and is left until radium reprecipitates. The precipitate is washed, dried and is counted on a low-background alpha counter for one hour.

Uranium

The determination of natural uranium is based upon the fluorescence of uranium in fused sodium fluoride or in fused sodium fluoride-carbonate mixtures; this following method is one of the many standard methods appearing in literature; it is directly applicable to most types of aqueous samples.

The flyorimetric method for uranium utilizes the fluorescence produced when uranium is fused with sodium fluoride and exposed to ultraviolet light. This method was developed for urine specimens. However, it may be used for other materials after the uranium has been separated from large amounts of other elements.

For the treatment of samples which may contain uranium of higher specific activity than normal, an ether-extraction procedure prior to alpha counting is recommended.

Gross Activity

Procedures for the measurement of mixed or unidentified radioactive materials should be adopted only with the recognition that very grievous errors may be involved; such errors arise because radiometric standardization is impossible. Gamma spectrometry is of great utility in the qualitative and semi-quantitative examination of such samples.

The following procedure is useful for a crude measurement of fission products in aqueous solutions, keeping in mind the severe limitations imposed upon accuracy, sensitivity, and specificity.

In short, the measurement of gross-activity involves drying of the sample, ignition in a muffle furnace, and grinding for uniformity. The sample so produced is counted for beta activity and for alpha activity, by the conventional means.

INSTRUMENTATION

Once a radionuclide has been isolated it can be measured with the appropriate instrument.

Let R be a radioactive nuclide with λ the probability that this nuclide will spontaneously disintegrate in unit time. This λ is a constant characteristic of every nuclear species and is independent of the chemical or physical conditions of the medium. By disintegration, R will be transformed, either directly or indirectly, into a stable nuclide S. Should the transformation be indirect, that is, by way of other radioactive nuclides, R forms a radioactive family.

Let N be the number of atoms of R present at time t_o. This number will decrease exponentially with time owing to the disintegration of the atoms of R. The number of atoms, N, remaining after the passage of time t from t_o is given by the well-known formula: $N = N_o \cdot e^{-\lambda t}$ which is a first order reaction according to Physical Chemistry. Also $T = 0.693/\lambda$ where T is the half life and represents the time in which the number of atoms R remaining has diminished by 50 per cent from the original number N_o.

Standard equipment

The general requirements for laboratory counting equipment include high sensitivity to the measured radiation, high counting efficiency, stability, and low background counting rates. It is desirable that these requirements should be met in simple, easy-to-maintain, low cost instruments, but ideal conditions are not always realized.

a. End window geiger counter

This is a simple counting device with a high sensitivity for most beta radiation and a satisfactory sensitivity for alpha and gamma measurements. The counting efficiency for beta radiation is approximately 25% with the sample close to the window, and, in a suitable shield, background counting rates of about 20 cpm are possible. Lower backgrounds of about 5 cpm are found with the small-volume Geiger tubes.

b. Ionization chamber

This device is recommended only for radon alpha counting, where the sample is introduced into the chamber, although tritium may be counted similarly. In this application, all counter requirements can be met, with counting efficiencies of over 80% and backgrounds of less than 0.2 cpm.

c. Proportional counter

With or without a window, the gas-flow proportional counter is ideal for alpha and beta counting. All counter requirements are met, with counting efficiencies of about 50% and, with shielding, backgrounds of less than 10 cpm for beta and 0.2 cpm for alpha measurements. The ability to count alpha disintegrations in the presence of beta and gamma activity, and beta disintegrations in the presence of gamma activity is an added advantage.

d. Anticoincidence systems

Anticoincidence systems reduce the background counting rate for Geiger or proportional beta counting by a factor of more than five without changing other characteristics. These systems are, of course, more complex and more costly.

e. Alpha scintillation counter

This device can measure alpha disintegrations in the presence of beta and gamma activity. Using a standard photomultiplier and zinc sulphide phosphor, counting efficiencies of about 40% with backgrounds of less than 0.1 cpm are attainable. Other requirements are also fulfilled.

f. Gamma scintillation counter

Gamma scintillatorsc usually sodium iodide crystals, offer the most sensitive counting system for gamma rays. Flat or well-type crystals show counting efficiencies of 5 to 20%, but even with heavy shielding backgrounds of 100 to 200 cpm are common. Lower background counting rates are possible by use of energy discrimination, but this causes a marked increase in complexity and cost.

Standardization

The instruments used for assessing the radioactivity of samples register only a fraction of the number of disintegrations. To find the actual activity, it is necessary to standardize the instruments. The major points to be considered are:

a) the geometric efficiency of the counter;

b) the sample mounting; and

c) the type and energy of the emitted radiation.

The first two points are taken care of by exactly reproducing mounting techniques and counting samples and standard on the same counter. The diversity in energy of beta and gamma emission from different nuclides makes it essential that, in every possible case, standardization should be carrier out with calibrated standards of the same nuclide. In addition, the standard should be in the same chemical form as the sample.

BIBLIOGRAPHY

Artificial Radioactivity in the Marine Environment", Chapter 5, Oceanography, 1960 to 1970, NAS-NRC, 1959.

Arrhenius, G., M. N. Bramlette, and E. Picciotto, 1957, " Localization of radioactive and stable heavy nuclides in ocean sediments", Nature, 180, 85-86.

Arrhenius, G., and E. D., Goldberg, 1955, " Distribution of radioactivity in pelagic clays.", Tellus, 7, 226-231.

Barnes, H., "Apparatus and Methods of Oceanography", Interscience Publishers, Inc., New YOrk., 1959.

"The Biological Effects of Atomic Radiation.", Summary Reports 1960. National Academy of Sciences -- National Research Council, 1960.

Bleuler, Ernst, and Goldsmith, G., "Experimental Nucleonics", Rinehart & Co, Inc., New York 1952.

Britt, N. W (1955), "New methods of collecting bottom fauna from shoals or rubble bottoms of lakes and streams", Ecology 36, 524.

"The determination of polonium-210 in urine and other biological materials, Chemical Services Department, Operations Branch (1958), Windscale, Cumb., United KIngdom Atomic Energy Authority, Industrial Group Document IGO*AM/ W*167 C 1.

Dunster, H.J., "The disposal of radioactive liquid wastes into coastal waters", Paper 297, Proceedings of the Second International Conference on Peaceful Uses of atomic Energy, Geneva, 1958.

Greendale, A. E., and Ballow, N.E. (1954)., "Physical STates of Elements in Seawater". USNRDL Doc. 436, p 1-28.

Harley, J. H.& Foti, S. (1952) "Determination of micromicrogram quantities of radium". Nucleonics, 10, 45-47 (copyright 1952, McGraw-Hill Publishing Company, Inc.,)

Koczy, F. F. 1956. "Geochemistry of the radioactive elements in the ocean". Deep-Sea Research, 3, 93-103.

Kooi, J. (1958) "Quantitative determination of strontium-89 and strontium-90 in water". Analytical Chemistry, 30, 532.

Kooi, J. (1958) "A simple procedure for the determination of Sr-89 and Sr-90 in urine and sea water". Paper submitted to the Second United Nations International Conference on the Peaceful Uses of A tomic Energy, Geneva, document (A CONF. 15/P/549).

"Methods of Radiochemical Analysis". Report of a Joint WHO/FAO Expert Committee. WHO Technical Report Series, No. 173. Rome, 1959.

Perkins, R. W. and Kalkwarf, D. R. (1956). "Determination of thorium in urine". Analytical Chemistry, 28, 1989 (copyright 1956 by the American Chemical Society).

Picciotto, E.Edgard,. "Geochemistry of radioactive elements in the ocean and the chronology of deep-sea sediments". Laboratoire de Physique Nucleaire, Universite Libre de Bruxelles, Brussels, Belgium.

Piggot, C. S., and W. D. Urry. 1942 a. "Radioactivity of ocean sediments". V. Concentrations of the radioelements and their significance in red clay. American Journal of Science, 240, 93.

Price, G. R., Ferretti, R. J. and Schwartz, S. (1953) "Fluorophotometric determination of uranium". Analytical Chemistry, 25, 322 (copyright 1953 by the American Chemical Society).

"Radioactive waste disposal into the sea". Safety Series No. 5. International Atomic Energy Agency, Kaerntnerring, Vienna I, Austria 1961.

"Radioactive Waste Disposal into Atlantic and Gulf Coastal Waters," NAS-NRC Publication 655, 1959.

"Radioactive Waste Disposal from Nuclear Powered Ships . Publication 658. National Academy of Sciences, National Research Council.

"Synopsis of information on radioactive elements in sea water and in the marine food chain". prepared by Biology Branch, Fisheries Division, FAO, Luglio, 1962.

"The effects of atomic radiation on oceanography and fisheries", Publication No. 551, National Academy of Sciences, National Research Council, 1957.

United States Hydrographic Office. Publication No. 607, 1959.

Whitney, I. B., ed. (1957). In: "Manual of standard procedures", Analytical Branch, HASL, New York, United States Atomic Energy Commission, New York Operations Office (document NYO-4700).