

MONITORING OF SEA-WATER FOR IMPORTANT RADIOISOTOPES RELEASED BY NUCLEAR REACTORS

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IN view of possible increase in the discharge rates of radioisotopes into the sea, an analytical technique to measure very low concentrations of radioisotopes in sea-water has been developed.

The conventional method of scavenging, namely, the precipitation of mixed ferric hydroxide and barium sulphate, failed to prove itself because of its very slow filtration. The fact that marine manganese nodules are enriched with heavy metals and the rare earths¹ inspired us to examine commercial manganese dioxide, and it was found an effective and easily filterable scavenger for most of the radioisotopes which were reported to be present in reactor coolant water.

A radioisotope, carrier-free or of high specific activity, was added to 50 ml. of sea-water and then the mixture was shaken with 0.50 g reagent-grade powdered manganese dioxide for 10 min in a slightly alkaline condition (pH 8.2). Table 1 summarizes the results of experiments. Important corrosion products except chromium, and fission products other than strontium and caesium, were effectively picked up by 1 per cent (w/v) quantity of powdered manganese dioxide. Further experiments to find the optimum quantity of scavenger showed 0.35 per cent to be the minimum for effective removal.

Table 1. REMOVAL OF RADIOISOTOPES IN SEA-WATER BY SHAKING WITH POWDERED MANGANESE DIOXIDE

Radioisotope	Removed (%)
⁵⁴ Mn	100.1 ± 0.2
^{55,56} Fe	96.1 2.3
⁶⁰ Co	100.0 0.1
⁹⁰ Zn	99.9 0.1
⁹² Zr- ⁹³ Nb	99.9 0.1
¹⁰⁶ Ru- ¹⁰⁸ Rh	100.0 0.1
¹⁴⁴ Ce	99.8 0.1
⁹¹ Cr	14.5 1.2
⁸⁹ Sr	89.3 0.7
¹³⁷ Cs	1.8 0.1

Partial permissible concentrations of cobalt-60 and iron-59 in sea-water recommended by the U.S. National Academy of Sciences—National Research Council are respectively 3×10^{-9} and 5×10^{-9} $\mu\text{c./ml.}$ for harbours². Since 100 l. of sea-water had to be processed in order to detect referred concentrations of radioisotopes, granular manganese dioxide (20–60 mesh) was examined for its time-saving and scavenging efficiency in the filtration in a larger-scale operation. Three litres of sea-water containing cobalt-60 were mechanically agitated after the addition of ten grams of granular scavenger. After 105 min of agitation 98.2 per cent of the activity was removed from the liquid phase, and fixation on the scavenger still remained after standing overnight.

One hundred litres of sea-water were collected in Sagami Bay, off Enoshima, at $35^{\circ}16'N.$, $139^{\circ}28'E.$ on July 9, 1963, to check the feasibility in full-scale operation of the proposed method. To prevent loss by possible adsorption of trace activities to the container, collected waters in five polyethylene containers, 20 l. each, were treated *in situ* with 70 g each of granular manganese dioxide and transported to the laboratory. After 2-h agitation and settling overnight, the scavenger, 350 g altogether, was filtered off and transferred into a polyethylene assay cylinder of 3 in. diameter. This was placed on top of the crystal (3 in. × 3 in.) of sodium iodide, inside 1-in.-mercury and 4-in.-lead shields, and the γ -spectrum taken for 1,000 min by means of a 256-channel pulse height analyser.

Recognizable photo-peaks above the background response of the detector were 0.72–0.77 MeV, corresponding to zirconium-95 and its daughter niobium-95, and 0.52 MeV, corresponding to rhodium-106, the daughter of ruthenium-106. Comparison made with spectra from

Table 2. DETECTION LIMITS OF THE PROPOSED METHOD FOR CERTAIN RADIOISOTOPES WHICH MAY BE PRESENT IN SEA-WATER WHEN APPLIED TO 100-L. SAMPLE

Radioisotope	Photo-peak energy MeV	Detection limit in sea-water $\mu\text{c./ml.}$	Partial permissible concentration in sea-water* $\mu\text{c./ml.}$
⁶⁰ Co	1.17	1×10^{-9}	
	1.33	2×10^{-9}	3×10^{-9}
⁵⁹ Fe	1.10	2×10^{-9}	
	1.29	3×10^{-9}	5×10^{-9}
⁹⁰ Zn	1.12	1×10^{-9}	2×10^{-9}
⁹² Zr	0.72	2×10^{-10}	3×10^{-9}
⁹³ Nb	0.77		5×10^{-9}
¹⁰⁶ Ru	0.52(¹⁰⁸ Rh)	2×10^{-9}	1×10^{-8}

*For harbours, estuaries, and inshore waters within 12 miles of the coastline. Recommended by N.A.S.-N.R.C.¹.

adding known amounts of the radioisotopes to 350 g of scavenger showed the concentration of 1.5×10^{-9} $\mu\text{c.}$ zirconium-95 + niobium-95 and 4.9×10^{-9} $\mu\text{c.}$ ruthenium-106 per millilitre of sea-water, the latter being calculated by neglecting the presence of ¹⁰⁶Ru-¹⁰⁸Rh.

Detection limits of the proposed method are summarized in Table 2 for several important radioisotopes. The limits for cobalt-60 and iron-59 are from a half to one-third of the recommended partial permissible concentrations for harbours while those for the other radioisotopes are even less. This would indicate the practical usefulness of the proposed method for monitoring when distinction between cobalt-60, iron-59 and zinc-65 cannot be made easily, that is, when radioisotopes exist together. The detection limit for cerium-144 would lie above its permissible concentration of 1×10^{-9} $\mu\text{c./ml.}$ because of the high background counting rate in the spectral region of low gamma energy. Caesium-137 remains in the filtrate from the scavenger and can be determined by a molybdo-phosphate scavenging method followed by gamma spectrometry, a report of which is in preparation.

Neither the mechanism of pickup by manganese dioxide nor the physical states of trace elements in sea-water are clearly known and investigations are in progress. About 8×10^{-2} $\mu\text{c.}$ of cobalt-60 in a 2-l. sample of water from the thermal shield of a nuclear reactor was completely removed by the proposed method; this suggests the possibility of using manganese dioxide in place of organic ion-exchange resin in purifying hotter reactor water in closed-cycle reactor systems.

Sea-water samples were collected from three locations between the end of July and the beginning of August 1963: (1) the Sasebo Harbour, Kyushu District, an important port at which the United States nuclear-powered ships are expected to call, $33^{\circ}08'N.$, $129^{\circ}43'E.$; (2) the Inland Sea, off the Kure Harbour, an important fishing area, $34^{\circ}06'N.$, $132^{\circ}37'E.$; (3) Tsuruga Bay, near the expected power reactor site, $35^{\circ}44'N.$, $136^{\circ}03'E.$ Zirconium-niobium-95 and ruthenium-106, both of which are considered to have originated from radioactive fall-out released by nuclear weapon tests, were found in the samples in the following concentrations, respectively, 1.3 and 5.9×10^{-9} (location 1), 1.0 and 4.7×10^{-9} (location 2) and 2.6 and 11.8×10^{-9} $\mu\text{c./ml.}$ (location 3). The level of ruthenium-106 in the sea-water from location 3 indicated more than the recommended permissible level of 1×10^{-8} $\mu\text{c./ml.}$ for harbours. However, the result for ruthenium-106 could not be taken as more than a maximum estimate because it was calculated by neglecting the presence of ruthenium-103. The higher levels of the fission products in the sea-water from Tsuruga Bay may be contributed to the heavy snow-fall in winter and leaching by river of the accumulated radionuclides.

¹ Goldberg, E. D., *Physics and Chemistry of the Earth*, 4, 291 (Pergamon Press, 1961).

² *Nat. Acad. Sci.—Nat. Res. Council*, Publ. 658, Washington, D.C. (1959).