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Analysis of Uranium in Sea Water

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TO date, all the reported analyses of uranium in sea water have been based on the methods of Hernegger and Karlik (1). Uranium concentration (required because it is present in sea water only to the extent of a few parts in 10^9) has been accomplished by an elaborate series of coprecipitations with ferric hydroxide, and the final estimation has been carried out by use of the fluorophotometer. Sample sizes ranging from 200 ml to 22 lit in volume have been required.

In the present work (2), concentration has been accomplished by extracting the uranium directly from the sea water into an organic solvent containing dibutyl-orthophosphoric acid (DBP) as prepared by the method of Stewart and Crandall (3). Uranium estimation has been by fission-fragment counting of the U^{235} present by placing the sample in the Argonne heavy-water reactor. Routine sample sizes of volume 20 ml can readily be used, and, with special precautions, it should be possible to analyze accurately volumes of 1 ml or less.

The uranium is extracted by mixing the sample with 0.5 ml of 0.7–0.8*M* dibutyl-phosphoric acid in CCl_4 . This is transferred *in toto* to a platinum counting plate, as is a subsequent "wash" of the same volume of CCl_4 . After bringing the material to dryness and heating the plate in a flame, the sample is ready for counting. Standard plates carrying known amounts of uranium are counted at the same time, as are blank plates prepared directly from the reagents.

A preliminary test of the method was made, utiliz-

ing artificial sea water having the composition listed by Sverdrup, Johnson, and Fleming (4), ignoring components present to less than 0.01 percent; U^{233} tracer was added to produce 616 alpha counts per minute, per 50-ml sample. Six such samples were treated in this way to concentrate the uranium, but, in this case, the plates were alpha-ray counted rather than being put in the fission-fragment counter. The average recovery for the six samples was 94.5 percent ($s = 1.8$ percent).

Table 1. Recovery of added uranium from acidified natural sea water.

Sample	U (μ g/lit)	
	Expected	Found
Unfortified 1953 Pacific Ocean water		2.36
		2.44
		2.43
		Mean = 2.41
Same + 0.33	2.74	2.82
	2.74	2.79
Same + 0.98	3.39	3.59
	3.39	3.53
Same + 1.77	4.18	4.18
	4.18	4.16
Same + 2.28	4.69	4.51
	4.69	4.55
Same + 3.26	5.67	5.60
	5.67	5.05

Table 2. Uranium content of some naturally occurring waters.

Sample	Size of sample	Acid added	Net fissions/min*	U ($\mu\text{g/lit}$)
1952 Pacific Ocean water	50 ml	None	8906	2.42
	50	None	9179	2.48
	50	0.44M HCl	8668	2.36
	25	.44M HCl	4902	2.60
1953 Pacific Ocean water	50	None	8854	2.40
	50	None	9268	2.52
	50	0.44M HCl	8780	2.39
	50	.44M HCl	9210	2.50
	25	.44M HCl	4740	2.58
	25	.44M HCl	4860	2.64
(Mean—all Pacific Ocean analyses)				2.49 ($s = \pm 0.09 = \pm 3.6\%$)
Great Salt Lake water	25	0.18M HCl	8960	4.79
	25	.18M HCl	9780	5.31
	25	.18M HCl	9150	4.97
Tap water	20	None	184	0.13
	20	None	157	.11
Distilled water	20	None	60	.04
	20	None	45	.03

* Corrected to allow for volume change where HCl was added.

A sample of natural Pacific Ocean coastal sea water was then acidified to 0.44M HCl and, after distributing the sample into a series of volumetric flasks, varying known amounts of natural uranium were added; 20-ml samples of these various solutions were then treated and assayed by fission-fragment counting. The results are given in Table 1.

The number of samples of natural salines available to us was very limited. Two samples had been taken in the surf on the Pacific Ocean side of the San Francisco Peninsula some 10 mo apart (1952 and 1953). One sample was collected in polystyrene bottles and stored in a Pyrex jar; the other sample was collected and stored in a soft glass jug. Neither sample was acidified until analysis. Great Salt Lake water was collected at the south shore and was acidified to 0.18M HCl when taken. Tap water and distilled water samples were taken at the Argonne National Laboratory, Lemont, Ill. The results on the uranium assays of these samples are given in Table 2. A uranium equivalence value of 71.8 fissions per minute, per millimicrogram of uranium was used, based on the average of counts taken on seven different plates made up from three different uranium stock solutions.

The Pacific Ocean assay figures given in Table 2 are higher than the majority of analyses of uranium reported by other investigators, but, since the samples were so few and since they were taken at the shore line, this may be of no significance. Hernegger and Karlik (1) originally reported values ranging from 0.87 to 2.15 $\mu\text{g/lit}$ for samples taken near the west coast of Sweden and in the Skagerrak. Föyn *et al.* (5) found values ranging from about 0.5 to 1.8 $\mu\text{g/lit}$

for samples taken from the same area and from the Adriatic Sea and the North Atlantic and North Pacific Oceans. Rona (6), using North Atlantic collected material, found lower and more erratic values. Koczy (7) had samples available from most of the oceans of the world and, on the basis of her results, concluded that the uranium concentration was quite constant, being of the order of 1.1 $\mu\text{g/lit}$ at the surface and reaching a maximum of 1.4 $\mu\text{g/lit}$ at a depth of about 1000 m. Nakanishi (8) reports values ranging from 1.75 to 3.37 $\mu\text{g/lit}$ for samples collected from the Pacific Ocean near Japan. The exact value is of some interest, since, as Petterson (9) has pointed out in a recent review, it is still not possible to account for all the radium present in certain deep-sea sediments on the basis of the amounts of the parent uranium and ionium in the sediment plus the "potential" radium in the superimposed water column as calculated from the reported values for the uranium content of sea water.

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