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A METHOD FOR THE ESTIMATION OF TOTAL SOLUBLE COBALT IN SEA-WATER*

T. M. KRISHNAMOORTHY, V. N. SASTRY AND T. P. SARMA

Bhabha Atomic Research Centre, Health Physics Division, Bombay-74 (AS)

THE estimation of cobalt in sea-water has been done by various workers[1-4] using colorimetry and activation analysis methods. In view of the extremely low content of cobalt in sea-water ($0 \cdot 1$–$1 \cdot 0$ μg./1), co-precipitation methods have been used for preliminary concentration of the element. Yamagata and Iwashima[5] added powdered manganese dioxide to sea-water which scavenges cobalt along with other trace elements. The recoveries are established to be 100% using cobalt-60 in the chloride form as tracer. Krishnamoorthy and Viswanathan[4] have co-precipitated cobalt along with magnesium hydroxide by adding KOH solution to sea-water and the recoveries are established to be 93% using cobalt-58 in the chloride form as tracer.

Cobalt is one of the biologically active elements which is taken up by the phytoplankton and algæ from sea-water. Preliminary laboratory studies[6] indicated that cobalt can be associated in significant amounts with soluble organic matter. From the work reported in the literature, it is not established whether cobalt associated with soluble organic matter is also carried in the initial concentration steps used. Experiments have been carried out to find whether any differences exist in the recovery of cobalt if it is present in the ionic form as well as in the organic form.

Three litres of sea-water filtered through Whatman No. 42 filter-paper is spiked with $Co^{58}Cl_2$ tracer and magnesium is precipitated as hydroxide using 10 ml. of 4 N NaOH. Cobalt-58 gamma activity in the precipitate is counted and compared with the standard added. The recoveries are found to be 96–98% and these results are given in Table I.

TABLE I

Co-precipitation of cobalt-58 with magnesium hydroxide

No.	Co-58 activity in solution after 40 hrs. equilibration cpm	Co-58 activity in Mg (OH)$_2$ ppt. cpm	Activity in supernatant liquid (before filtration) cpm	Activity in supernatant liquid (after filtration) cpm
1	106,652	102,500 (96%)	1875 (1·8%)	1200 (1·2%)
2	108,000	105,600 (98%)	656 (0·7%)	488 (0·5%)

Activity of cobalt-58 added to the solution 106,700 cpm.

Chlorella sp. is grown in sea-water spiked with $Co^{60}Cl_2$ tracer to get organically bound cobalt.[6] The supernatant of the culture solution is filtered through $0 \cdot 22$ μ millipore membrane filter. An aliquot of the culture solution containing soluble cobalt (organically bound and/or otherwise) is added to 3 litres of filtered sea-water and magnesium is precipitated as hydroxide as above. The precipitate is allowed to settle for 2 hours and the supernatant liquid decanted. The slurry

contents of hydroxide precipitate is centrifuged and precipitate dissolved in 50 ml. of 6 N HCl. The solution is evaporated to dryness, taken up in 10 ml. of water and cobalt-60 activity is measured by gamma counting (3% standard deviation). The sample and standard activities are counted under the same conditions of volume and geometry for comparison. In the supernatant liquid, second and third magnesium hydroxide precipitations are carried out and the slurry is treated and counted as above. The data are summarised in Table II.

TABLE II

Co-precipitation of organically bound cobalt with magnesium hydroxide

Expt. No.	Process	Co-60 activity		Recovery %
		Added cpm	Recovered cpm	
1	First Mg(OH)$_2$ precipitation	438	195	44·5
	Second Mg(OH)$_2$ precipitation	..	127	29·0
	Third Mg(OH)$_2$ precipitation	..	23	5·3
	Total	..	..	78·8
2	First Mg(OH)$_2$ precipitation	438	185	42·0
	Second Mg(OH)$_2$ precipitation	..	130	29·1
	Third Mg(OH)$_2$ precipitation	..	27	6·2
	Total	..	..	77·3

As seen from Table II, the first hydroxide precipitate is carrying down only 43% of the total cobalt-60 activity whereas the second and third precipitates carry 29% and 5·7% respectively. The experiment demonstrates that 96–98% recoveries obtained by spiking the system with ionic tracers are not applicable when cobalt can be present as organically bound in the system.

In view of the above, the following experiments are conducted to release the organically bound cobalt into ionic form so that all the cobalt can be co-precipitated in the initial concentration step.

To 3 litres of filtered sea-water is added 1 ml. cobalt-60 culture filter solution. Oxidising agents such as saturated bromine water, KMnO$_4$ in neutral medium and K$_2$S$_2$O$_8$ in sulphuric acid medium are added and oxidations carried out under different conditions. The percent recoveries by single co-precipitation step are determined as earlier and the results are summarised in Table III.

As seen from Table III, saturated bromine water and potassium permanganate in neutral

TABLE III

Recovery of cobalt-60 from Chlorella sp. *culture filtrate with various oxidising agents*

Expt. No.	Oxidation process	Carrier precipitate	Co-60 culture activity		Recovery %
			Added cpm	Recovered cpm	
1	50 ml. of saturated bromine water, heated for 30 mts.	Mg(OH)$_2$	243	197	82·0
2	do.	Mg(OH)$_2$	243	209	85·8
3	75 ml. of saturated bromine water, heated for 2 hrs.	Mg(OH)$_2$	256	218	85·1
4	do.	Mg(OH)$_2$	256	208	82·1
5	50 ml. of saturated bromine water, 30 mts. heating, 500 mg. of iron added	Fe(OH)$_3$ and Mg(OH)$_2$	185	157	84·9
6	do.	Fe(OH)$_3$ and Mg(OH)$_2$	185	156	84·8
7	1 ml. of 5% KMnO$_4$, heated for 1 hr. and 0·2 gm. MnCl$_2$ added	MnO$_2$	375	320	85·4
8	do.	MnO$_2$	375	307	82·0
9	7·5 gm. of K$_2$S$_2$O$_8$ and 20 ml. of conc. H$_2$SO$_4$, boiled for 2 hrs.	Mg(OH)$_2$	300	303	101·0
10	do.	Mg(OH)$_2$	150	147	98·0
11	do.	Mg(OH)$_2$	150	148	98·7

medium are not very effective oxidising agents (oxidation $\leqslant 85\%$). On the other hand, potassium persulphate in sulphuric acid medium is quantitative in oxidising capacity.

These observations indicate that it is necessary to use the oxidising agent potassium persulphate in sulphuric acid medium prior to any initial concentration and subsequent processing.

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