

# YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

## JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.  
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



# DETERMINATION OF COBALT IN SEAWATER

By

HERBERT V. WEISS AND JOHN A. REED

*U. S. Naval Radiological Defense Laboratory  
Chemical Technology Division  
San Francisco, California*

## ABSTRACT

Cobalt has been isolated from seawater by cocrystallization with  $\alpha$ -nitroso- $\beta$ -naphthol. Quantitative determination by a nitroso-R-salt method for each of two seawater samples has indicated the cobalt content to be 0.038  $\mu\text{g/l}$  after radiometric correction for losses incurred in the isolation process.

The cobalt content of seawater has been variously estimated as 0.1  $\mu\text{g/l}$  (I. and W. Noddack, 1940) and 1.0  $\mu\text{g/l}$  (Malyuga and Makarova, 1954); and a more definite range of 0.38 to 0.67  $\mu\text{g/l}$  has been reported by Ishibashi (1953), but details of his analytical method were not completely documented.

This report describes a procedure that determines accurately the concentration of this element in seawater. It depends on the cocrystallization of elements with organic reagents (Weiss and Lai, 1960), a general process applicable to the isolation of ultramicroquantities of an element from solution. After separation of cobalt along with small amounts of certain other elements from seawater, the cobalt is purified by ion exchange and is determined quantitatively by colorimetric analysis.

In preliminary study of the cocrystallization of minute quantities of cobalt, the organic precipitant  $\alpha$ -nitroso- $\beta$ -naphthol was selected because it forms an insoluble compound with cobalt, a condition which satisfies the basic requirement for efficient cocrystallization. Test solutions consisted of 0.1 l of seawater containing  $\text{Co}^{60}$  tracer with less than  $10^{-10}$  g inert cobalt added. To these test solutions four different weights of organic reagent dissolved in acetone, ranging from 0.4 to 3.2 mg, were introduced. The solutions were boiled for 10 min. After cooling, the crystallized organic reagent was collected and its radioactive content assayed in a gamma scintillation counter.

The cocrystallization of cobalt as determined by this measurement was quantitative when 1.6 to 3.2 mg of the reagent were used (Table I).

TABLE I. RECOVERY OF COBALT-60 FROM 0.1 LITER OF SEAWATER BY COCRYSTALLIZATION WITH VARIOUS CONCENTRATIONS OF  $\alpha$ -NITROSO- $\beta$ -NAPHTHOL

$\alpha$ -Nitroso- $\beta$ -Naphthol Added (mg)	Co <sup>60</sup> Recovery (%)
0.4	89.0 $\pm$ 0.5
0.8	94.8 $\pm$ 0.5
1.6	99.4 $\pm$ 0.5
3.2	99.5 $\pm$ 0.5

This isolation procedure was subsequently applied to the determination of cobalt in larger volumes of seawater. Surface seawater was collected in scrupulously cleaned 20 l polyethylene bottles 40 miles due west of San Francisco in July 1959. To avoid contamination, the collection was made several hundred yards from the ship. (It was previously established with radiotracer in seawater that cobalt does not adsorb on the surface of this polyethylene.)

Two samples, one 50 l and the other 100 l in volume, were submitted to the following process. For convenience, each sample was subdivided into aliquots of one liter. Then  $10^3$  c/m of Co<sup>60</sup> tracer (specific activity, 19,500 mc/g) was added to each aliquot to permit final correction for chemical losses. One ml of 1.6%  $\alpha$ -nitroso- $\beta$ -naphthol in acetone was added, and the solution was boiled for 10 min, after which the beaker was placed on an ice-bath for 15 min. After the crystallized reagent was collected by filtration through fine sintered glass, the filtrate was discarded. The walls of each beaker were then washed with hot nitric acid and the wash was passed through the sintered glass funnel to dissolve the organic residue. This washing treatment was repeated twice. The washings and dissolved reagent of the aliquots from each of the original samples were combined. To each of the combined samples 5 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were added and the solution was evaporated until fumes of SO<sub>3</sub> appeared. Several milliliters of a 50:50 mixture of concentrated HClO<sub>4</sub> and HNO<sub>3</sub> were slowly added to the hot solution to completely ash the organic residue. The samples were then heated to complete dryness, and each contained about 2 g of inorganic residue. Radioactive count of the residue from the 50 l

sample, compared with a  $\text{Co}^{60}$  standard of the same volume, indicated that 99% of the cobalt was isolated. Each ashed residue was dissolved in distilled water. Only a small quantity of the solid was not soluble, and since the undissolved material accounted for only 3 to 5% of the cobalt, it was discarded.

The dissolved samples were purified by ion exchange and enough concentrated HCl was added to make the samples about 10N. Sodium chloride, which crystallizes from solution with this treatment, was separated from the supernatant liquid by centrifugation; it was then washed several times with concentrated HCl and discarded. The HCl wash was added to the main solution. The strongly acidified solution was passed through an anion exchange column in the  $\text{Cl}^-$  form under previously described column conditions (Kraus and Moore, 1953). The column was first eluted with 6N HCl to remove nickel. Cobalt was then selectively eluted with 4N HCl while possible contaminants (iron, zinc and copper) remained adsorbed on the column. The recovery of cobalt was again determined radiometrically at this stage of the analysis. The 50 l sample contained 87.0% of the original quantity of cobalt, the 100 l sample 90.8%.

The eluted cobalt, evaporated to near dryness, was quantitatively analyzed by a nitroso-R-salt method (Shipman and Lai, 1956). Following a blank correction for all chemicals that entered the analysis in the amounts used as well as adjustment for the cobalt yield as determined radiochemically, the content of each of the seawater samples was determined to be 0.038  $\mu\text{g/l}$  of cobalt. The main errors in the analysis, attributable to the radioactive counting statistics and the spectrophotometric measurements, were approximately 0.5% and 3%, respectively.

After spectrophotometric analysis,<sup>1</sup> the samples were prepared for unequivocal qualitative identification of the isolated material by spectrographic assay. The samples were combined and the nitroso-R-salt was removed by ashing with nitric and perchloric acid. Cobalt was separated from residual salts introduced in the colorimetric analysis by adsorption on an anion exchange resin (as above) and then eluted directly with 30 ml of 4N HCl. The eluate was evaporated to a small volume, deposited on copper electrodes and analyzed spectrographically. The results confirmed the presence of cobalt.

<sup>1</sup> The authors wish to express their appreciation for the spectrographic analysis to J. Conway and G. V. Shalimoff of the Lawrence Radiation Laboratory, University of California.

Traces of other elements (Al, Ca, Fe, Mg, Mn, Ni, Si, Ti, Zr) were also identified. However, the influence of these elements in the colorimetric determination of cobalt by this method was tested, and none interfered at concentrations far in excess of the trace quantity which was present. Thus, the quantitative value given for each seawater sample analyzed is presented with reasonable reliability.

## REFERENCES

ISHIBASHI, M.

1953. Minute elements in seawater. *Rec. oceanogr. Works Japan*, 1: 88-92.

KRAUS, K. A. AND G. E. MOORE

1953. Anion exchange studies, VI. The divalent transition elements manganese to zinc in hydrochloric acid. *J. Amer. chem. Soc.*, 75: 1460-1462.

MALYUGA, D. P. AND A. I. MAKAROVA

1954. Cobalt content of soils and plants ashes of tuva. *Doklady Akad. Nauk SSSR*, 98: 811-813.

NODDACK, I. AND W.

1939. Die Häufigkeiten der Schwermetalle in Meerestieren. *Ark. Zool.*, 32A(1)4: 1-35.

SHIPMAN, W. H. AND J. R. LAI

1956. General photometric microdetermination of cobalt with nitroso-R-salt. *Anal. Chem.*, 28: 1151-1152.

WEISS, H. V. AND M. G. LAI

1960. The cocrystallization of ultramicroquantities of alkaline earth elements with potassium rhodizonate. *Anal. Chem.*, 32: 475-478.