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DETERMINATION AND OCCURRENCE OF COBALT IN SEA WATER

By

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ABSTRACT

Methods have been investigated to ascertain the most desirable procedure for determining the trace concentrations of cobalt in sea water. The nitroso-R-salt method of Sandell was adopted and modified for sea water analysis. Samples of water were secured with the nonmetallic water sampler of Thompson and Chow. Preliminary studies of the waters of the San Juan Archipelago and of Puget Sound showed cobalt concentrations ranging from 0.0039 to 0.0054 $\mu\text{g-at Co/l.}$

Since little is known of the biogeochemistry of cobalt in the ocean, study of a method to determine its amount in sea water was initiated with the view of eventually investigating its role in the sea. The available data on the occurrence of cobalt in sea water are summarized in Table I. These data vary by more than one order of magnitude and this variation may be due to local conditions, to seasonal changes, or to deviations resulting from the analytical methods employed.

TABLE I. CONCENTRATIONS OF COBALT IN SEA WATER ACCORDING TO
PREVIOUS INVESTIGATORS

<i>Place of Collection</i>	<i>$\mu\text{g-at/kg}$</i>	<i>Investigator</i>
Black Sea	0.059	Malyuga, 1945
Barents Sea	0.025	Malyuga, 1945
Skagerrak (Gullmarsfjord)	0.0017	I. & W. Noddack, 1939
Pacific Ocean	0.0085	Ishibashi, <i>et al.</i> , 1951
English Channel	<0.005	Black and Mitchell, 1952

¹ Contribution No. 240, Department of Oceanography, University of Washington, Seattle, Washington.

Portions of this work were performed under contract NONR-477(10), Project NR 083-012, Office of Naval Research.

It is known that Vitamin B₁₂ is a cobalt complex, and it is said that marine animals and plants are important as sources of this vitamin (Ivey, 1950). Bertrand and Mâcheboeuf (1925) stated that animals have far less nickel than cobalt in their tissues, but later I. and W. Noddack (1939) showed that the concentration of cobalt in marine animals is about one-tenth that of the nickel content. Black and Mitchell (1952) found that the concentration of cobalt in seaweeds was equivalent to about one-fourth that of nickel. Malyuga, in his systematic work on algae (Vinogradov, 1953), found cobalt and nickel in relatively high quantities, equivalent to about 9 $\mu\text{g-at/kg}$ of living matter or ten times this amount in the ash; the cobalt and nickel were present in 1:1 concentrations. Tsuchiya and Makuta (1951) and Maxwell (1952) have made extensive studies of cobalt in marine products, finding from 0.2 to 6 $\mu\text{g-at/kg}$ of material examined.

METHOD OF ANALYSIS

Reagents. All should be of reagent grade quality and should be tested for absence of cobalt.

Ammonium Hydroxide: - Dilute the concentrated reagent with an equal volume of water.

Buffer Solution: - Dissolve 35.6 g disodium phosphate dihydrate and 6.2 g boric acid in 500 ml 1N NaOH and dilute to one liter.

Citric Acid: - Dissolve 42 g of the crystals in 100 ml of water.

Distilled water: - Use redistilled water prepared in an all-glass still for all operations.

Dithizone: - 0.02% solution in pure carbon tetrachloride (= 200 mg/kg).

Hydrochloric Acid: - Dilute one part 12N HCl with two parts water.

Nitric Acid: - Concentrated reagent grade.

Nitroso-R-Salt: - Prepare 0.2% aqueous solution; store in cold and dark.

Perchloric Acid: - 70% reagent grade.

Sodium Carbonate: - Dissolve 50 g of reagent grade anhydrous sodium carbonate in one liter of redistilled water.

Sodium Citrate: - Dissolve 10 g of sodium citrate in 100 ml of water.

Sodium Hydroxide: - Dissolve 40 g in water and then dilute to one liter in volumetric flask.

Sulphuric Acid: - Concentrated reagent grade.

Standard Cobalt Sulphate Solutions:

Solution A. Weigh out exactly 1.2811 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, dissolve in water and dilute to one liter in a volumetric flask.

Solution B. Pipet 100 ml of Solution A into a volumetric flask and dilute to exactly one liter.

Solution C. Pipet 10 ml of Solution B into a volumetric flask and dilute exactly to one liter. This solution has a concentration of 0.001 $\mu\text{g-at Co/ml}$ of water solution.

Solutions B and C should be freshly prepared immediately before use.

Procedure. Six to ten liters of freshly collected sea water were obtained with a nonmetallic sampling device (Thompson and Chow, 1955) in order to avoid contact of the water with any metal. The sample was then filtered through millipore filters (H.A. type). The cobalt in the filtrate was coprecipitated with the naturally occurring magnesium in the waters by adding 50 ml of sodium carbonate solution per liter of collected sea water. Filtration and precipitation should be performed immediately after collecting in order to prevent changes in the cobalt content of the water by biological activity (Laevastu and Thompson, 1956).

The precipitate was allowed to settle for 8 to 10 hours and the supernatant solution was then decanted through a millipore filter. The bulk of the precipitate remaining in the container as well as that retained on the filter was dissolved in hydrochloric acid.

The nitroso-R-salt method for the determination of cobalt (Sandell, 1950) was modified to obtain an estimate of the element in sea water. Procedure with the modifications was as follows:

After the solution was complete, 15 ml of sodium citrate solution was added and the pH was adjusted to 8.4 to 8.5 with ammonium hydroxide; the final volume should approximate 90 ml. The cobalt was removed from this solution by adding 20 ml of dithizone reagent and shaking the solution in a wrist-action shaker for 20 minutes. The dithizone carbon tetrachloride was separated from the solution. Another portion of the dithizone reagent was added and the solution was again shaken for the same length of time. This process was repeated a third time. The carbon tetrachloride extracts were combined and evaporated at a low heat; the residue was treated with one ml of concentrated sulfuric acid and one ml of perchloric acid, and heating continued until it was colorless. When it had cooled,

one ml of citric acid and 1.5 ml of phosphate-boric acid buffer were added; the pH was adjusted to 8.0 with ammonium hydroxide; then 0.5 ml of nitroso-R-salt solution was added and the resulting mixture was boiled for one minute. One ml of concentrated nitric acid was then added and the mixture was boiled again for another minute. The solution was cooled and diluted to exactly 30 ml with distilled water. The color resulting from the presence of cobalt was stable for at least nine hours. The optical density was measured in a Beckman DU Spectrophotometer in 10 ml cells at a wavelength of 415 $m\mu$. If any suspended material was present in the final solution it was removed by filtration before measurements were made with the Beckman Spectrophotometer.

Calibration of Beckman DU Spectrophotometer. The following volumes of the cobalt standard solution C were taken: 1.00, 2.00, 3.00, 5.00, 10.00, 15.00 and 25.00 ml; each was pipetted into a separate container. Then 15 ml sodium citrate was added and the solution was diluted to 90 ml. The solutions were then treated with the thiozine reagent and the procedure was continued in exactly the same manner as that outlined above. From the different readings obtained with the Beckman Spectrophotometer, a calibration curve showing the optical densities for various concentrations of cobalt was prepared for a wavelength of 415 $m\mu$.

SUMMARY OF RESULTS

Preliminary studies on several samples of water collected in the San Juan Archipelago and on other samples from Puget Sound gave a mean value of 0.0048 $\mu\text{g-at Co/kg}$, the values ranging from 0.0039 to 0.0054. Using previous data for nickel (Laevastu and Thompson, 1956) for waters in the same regions, a nickel-cobalt ratio of 1 to 0.14 is obtained. This ratio approximates that obtained by other investigators for marine animals and plants and also for marine deposits (Young, 1954). More extensive studies on the occurrence of cobalt with respect to localities, seasonal variations, marine organisms and deposits are contemplated. From present data and those reported elsewhere, it is expected that the cobalt concentrations will vary in different localities and depths and will show variations related to biological activities and to seasons, particularly for waters at the surface and at depth.

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