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COPPER AND ZINC CONTENT OF THE WATER IN THE LIGURIAN SEA

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ABSTRACT

During three cruises in the Ligurian Sea, samples containing copper and zinc trace elements were collected. They were analysed spectrophotometrically by the dithizone method. The sampling gear and technique are described; results are discussed, and earlier working methods are critically examined.

RESUME

Au cours de trois croisières dans le golf de Gênes, on a recueilli des échantillons d'eau de mer contenant des traces de cuivre et de zinc. Ces échantillons ont été soumis à une analyse spectrophotométrique par la méthode de la dithizone. Les auteurs décrivent les appareils et la méthode employés pour le prélèvement des échantillons; ils donnent et discutent les résultats obtenus et indiquent les avantages et les inconvénients des méthodes de travail précédemment utilisées.

I. INTRODUCTION

As trace elements, zinc and copper are of importance in the biological life cycle in the oceans. Both are taken up by living organisms and may be accumulated in tissues. Their radioactive isotopes are produced by nuclear energy plants and, if they get into the ocean water, may enter into the biological life cycle. Copper has no long-lived isotope and is therefore of less importance, but zinc has the radioisotope Zn^{65}, with a half-life of 245 days, which has been reported in fish tissues (e.g. by Tozawa, 1960). Hence the importance of knowing the natural concentration of the trace element in the oceans.

Copper and zinc trace elements were probably successfully isolated in sea water for the first time by Dieulafait (1879), (1880). He estimated the concentration of copper as being about 10 µg/l and zinc as 1.6-2.0 µg/l. The subject was taken up anew after the First World War. The most varying concentrations have been reported in the literature, the copper concentration varying from 0.2 µg/l (Wattenberg 1943) to 3000 µg/l (Black and Mitchell 1952) and zinc from 0 (Hiltner and Wichmann 1919) to 3800 µg/l (Bertrand 1938).

For a long time the analyses of Noddack and Noddack (1940) were considered to be the most accurate for sea water, but the work was done in shallow water in the Gullmarsfjorden on the Swedish west coast which can by no means be considered as representative sea water.

The most extensive and probably most accurate work was done by Morita (1950), (1953), (1961). The results indicate 0.4-1.5 µg/l for copper and 0.8-10.0 µg/l for zinc in ocean water in different parts of the world.

Very little is known about the forms in which trace elements may occur in sea water. It may be partly in inorganic ionic form or bound to a complex, or partly built into an orgxnic molevule; it may be partly in insoluble form as particulate matter, partly in colloidal form or in true solution. Some analysis techniques provide a quantitative total for all forms, others will give only the form which reacts with the reagent used for the analysis or which is extracted by the solvent. With some techniques, the element is co-precipitated with e.g. ferric hydroxide or aluminium hydroxide etc., and most forms of it can be precipitated or sedimented to the bottom of the vessel and collected on a filter. If ashing, fusing etc. is involved, the sample may be roughly treated, and the various forms of the element will be reduced to inorganic form and included in the analysis. The result will be almost quantitative. With other techniques, where the element is extracted with an organic solvent or is allowed to react directly with a reagent, only that part of it which ia extracted or reacts directly can be analysed; hence it may only be the inorganic part of the element that is estimated. The dithizone technique will probably give only the part of the elemnt which is in soluble form as ions present in the sea water.

II. STATIONS, AND SAMPLING TECHNIQUE

Two cruises with the research vessel "Calypso" were made, in May and September 1962. As part of the ordinary hydrographic and chemistry programme, surface samples of zinc and copper were taken for analysis at all stations. During cruise I, the samples were taken directly by means of a polyethylene bucket at the ship's side and stored in polyethylene bottles. Because of the great variations in the results, precautions were taken during cruise II to avoid contamination from the ship. The samples were taken with a Van Dorn plexiglass sampler; kindly provided by Dr. Bernhard, of the Comitato Nazionale per l'Energia Nucleare Laboratory in Fiascherino. Attached to a nylon wire, it was lowered over the ship's side to a depth of 20 m. An iron weight was fastened some 5 m under the sampler in order to get the gear down under water. The sampler was closed with a plasticcovered messenger from the deck. The samples were stored in 1-litre polyethylene bottles in a refrigerator at around 0°C until analysed.

A third cruise, concentrating on a single deep station, was made in March 1963 with the research vessel "Winnaretta Singer" in order to investigate the depth distribution of the metals. Using the same plexiglass sampler attached to a nylon wire, samples were taken at standard depths. As not enough nylon wire was available, ordinary hydrographic metal wire had to be used as a substitute. A nylon wire, 40 m long, was attached to the hydrographic wire, and the plexiglass sampler was fastened to the nylon wire 20 m from the connection. At the end of the nylon wire the ordinary iron weight for the hydrographic wire was fastened. At the end of the hydrographic wire, just beyond the connection point, an ordinary Knudsen reversing bottle was attached. The messenger for the plexiglass sampler was hung just under the connection point and connected to the Knudsen bottle. In this way the messenger for the plexiglass sampler could be released from the deck by releasing the Knudsen bottle with an ordinary messenger. The gear had to be lowered and lifted by hand to and from the point where the nylon rope was attached. This procedure took up a lot of time but probably eliminated all contamination from the metal wire. The samples (about 2 l each) were stored in polyethylene bottles in a refrigerator at about 0°C.

III. CHEMISTRY

Analysis of zinc by the mono colour method

Dithizone stock solution. 25 mg of analytical grade dithizone was dissolved in 500 ml carbon tetrachloride (BDH, passes test for dithizone). The solution was stored in a dark glass-stoppered bottle and the reagent was covered with a layer of water containing hydroxylamine hydrochloride.

Dithizone working solution. 10 ml of the dithizone stock solution was pipetted into a 100 ml volumetric flask and diluted with carbon tetrachloride to the mark.

Metal-free distilled water. Ordinary distilled water was re-distilled in an all-glass Pyrex system, and mixed with portions of dithizone working solution of about 10 ml each until no changes in the colour of the dithizone layer could be detected. The carbon tetrachloride layer was separated each time in a separation funnel.

Ammonia water. 1 ml of analytical-grade concentrated ammonia solution was added to 1 l metal-free distilled water.

Metal-free sea water. 1 l sea water was mixed with several 10-ml portions of dithizone stock solution. The pH of sea water is around 8 and in this slightly basic solution, part of the dithizone is absorbed in the water phase. This gives a brownish colour to the sea water which is removed by mixing the water with pure carbon tetrachloride.

Stock standard zinc solution. 209.6 mg zinc acetate p.a. was dissolved in 250 ml metal-free distilled water and acidified with 0.25 ml 0.5 N acetic acid. This solution contains 250 ug zinc/ml.

Working standard zinc solution. 1 ml stock standard solution was diluted to 250 ml with metal-free sea water. This solution contains 1 µg zinc/ml.

Preparation of the standard curve. 100 ml metal-free sea water and 10 ml dithizone working solution were run into a 250 ml separatory funnel and shaken vigorously for a minute. Most of the extract was drawn into another small separatory funnel containing 25 ml ammonia water and shaken with the solution for half a minute. The layers were allowed to separate and then the carbon tetrachloride extract was slowly run into a 1 cm cell. The extinction was measured in a Beckman DU spectrophotometer at a wavelength of 524 mµ, using distilled water as reference. This procedure was repeated with 1, 2, 3 and 4 µg zinc added to the 100-ml portion of metal-free sea water. In order to get the zero value of the reagents, 25 ml of the ammonia water was mixed directly with 10 ml of the dithizone working solution and the extinction of the organic layer was determined. As the zinc-free zero sample showed that the metal-free sea water still contained traces of zinc, the difference between the reading for the zero-sample and the reading for the ammonia water was subtracted from each reading. A standard curve was prepared with the 0 at the reading for the ammonia water.

Analysis of the sea water samples. 100 ml of sample at room temperature was treated in exactly the same way as the standards. The amount of Zn was evaluated from the standard curve, the actual figure being subject to modification in the event of there being a high copper content.

Analysis of copper by the mixed colour method

Dithizone working solution: As for zinc.

Concentrated acetic acid p.a.

Metal-free distilled water: As for zinc.

Metal-free sea water. 10 l sea water were acidified with 12 ml konconcentrated acetic acid and portions of it were trated with dithizone working solution until no colour changes in the dithizone layer could be detected. The dithizone layer was separated each time with a separatory funnel.

0.01 N sulphuric acid solution. 0.3 ml concentrated acid was added to 1 l metal-free distilled water.

Stock standard copper solution. 98.24 mg copper sulphate pentahydrate was dissolved in metal-free distilled water and diluted to 250 ml. The solution contains 100 µg copper/ml.

Working standard copper solution. 1 ml stock solution was diluted to 100 ml with metal-free sea water. This solution contains 1 µg copper/ml.

Preparation of the standard curve

1 l standard samples containing 0, 1, 2, 3 and 4 µg copper were prepared from the copper working standard solution and metal-free sea water. The samples were mixed with 10 ml dithizone working solution in 2 litre glass-stoppered volumetric flasks on a Köttermann shaker for 30 minutes. Using a large separatory funnel, the carbon tetrachloride extract was transferred to a smaller separatory funnel containing 25 ml 0.01-N sulphuric acid and shaken there for one minute in order to transfer any sinc that might have been extracted to the water phase. The extinction of the tetrachloride extract was measured in a 1 cm cell in the Beckmann DU photometer at 620 mµ, with distilled water as reference. In order to get the zero value for the reagent, 10 ml dithizone were mixed directly with 25 ml 0.01-N sulphuric acid. The difference between this value and the value for the zero sample was added to each reading, and a standard curve was prepared with the 0 at the reading for the reagent-0.

Analysis of sea water samples

1 l of the sample at room temperature was transferred to a 2 l volumetric flask; 1.2 ml concentrated acetic acid was added and the sample treated exactly as the standard samples. The extinction was measured. The copper was evaluated from the standard curve. If the copper content in a sample was so high that the colour of the dithizone changed considerably, a further 10 m of dithizone working solution was added to the sample.

Correction of the zinc values for high copper content

The zinc values of some of the samples which showed a high copper content had to be corrected. The following procedure was used. Standard samples containing 1-4 µg copper instead of zinc were prepared by the zinc analysis procedure. The samples were treated exactly as the zinc samples and their extinction was measured at 524 mµ. From all readings the zero reading was subtracted and a standard curve was prepared with the 0 at the origo.. From this curve the extinction of the samples with high copper content was estimated and this extinction value was subtracted from the zinc extinction value. This new corrected zinc extinction value was used in evaluating the true amount of zinc from the zinc standard curve.

The concentration of other trace elements in sea water is so low that they do not affect the dithizone analysis. The metal-dirhizone equilibria have been theoretically and experimentally investigated by Koroleff (1950), and the methods used here are based on his work.

IV. DISCUSSION OF THE RESULTS

Table I shows the co-ordinates of the stations and the results for cruises I and II. Table II shows the results, the temperatures and the salinities for the cruise III station.

It will be seen that the results for cruise I show large variations, giving an average surface value of 34.9 µg/l for zinc and 4.8 ug/l for copper. Station 2 on cruises I and II corresponds roughly to the cruise III station. The surface concentration of zinc at this point during cruise III is about half of the concentration during cruise I and even half of the mean value for cruise I. However, the values for some of the stations during cruise I are in the same range as the values for cruise III. The copper values agree better, the mean value being 4.8 ug/l as against, for station 2, 4.9 ug/l during cruise I, and a surface value of 3.32 ug/l during cruise III. The high values during cruise I were apparently caused by contamination from the ship's hull during the sampling; the weather was extremely bad and even with the simple bucket gear, proper sampling was difficult.

The average surface value appears to be at least 10 ug/l for zinc and 3 µg/l for copper in the Ligurin Sea, but it should be remembered that the accuracy of some of the results is questionable.

The results from cruise II, all taken at a depth of 20 m, are for cruises II and III much more consistent. The values at station 2 are 8.9 and 6.5 µg/l and the average value, at 20 m during cruise II is 6.1 ug/l for zinc. For copper the corresponding values are 0.69, 0.67, the average value being 0.75. For cruise II, the value for station 2 is taken as being that for station 2 in cruise III; the actual sample taken was obviously contaminated during the analysis and gave a value ten times too high. Hence it was omitted, and replaced by the assumed value of 0.67.

Fig. 1 shows the vertical distribution of copper, zinc, salinity and temperature at station 2, cruise III. All the curves reach a maximum at around 600 m. According to Wüst (1961), "intermediate Levantine water" is is formed at the surface near the island of Rhodes during the winter. This water sinks and forms an intermediate layer which can be recognized in almost the whole western Mediterranean by its high salinity and temperature. It flows out through the Straits of Gibraltar as a bottom current. In the Ligurian Sea this "intermediate Levantine water" has its centre at about 600 m, where the water has a salinity of over 38.50 ‰ and a temperature of over 13.5°C. Since this layer is formed originally at the surface, it is likely - like the Ligurian surface water - to have a high zinc and copper concentration. However, the authors have not produced any data for zinc and copper from the eastern Mediterranean. Under the regular thermocline at about 75-100 m the metal concentrations are very low and even (about 3.5 ug/l for zinc and 0.4 µg/l for copper). The "intermediate" water begins below 300 m and the zinc value increases to 11.9 µg/l at 600 m. The copper value increases to 0.52 at 400 m, decreases a little to 0.45 at 600 m and increases again to 0.52 at 800 m. At 1000 m, where the deep water begins, the zinc an copper values are 4 µg/l and 0.1 µg/l, respectively. The bottom water, easily distinguished by T-S diagrams, begins below 2000 m. The present technique revealed no differences in zinc and copper concentration as between deep water and bottom water.

The results for the Ligurian Sea agree well with those of Morita (1950, 1953, 1961) for sea water from different parts of the world.

Table I

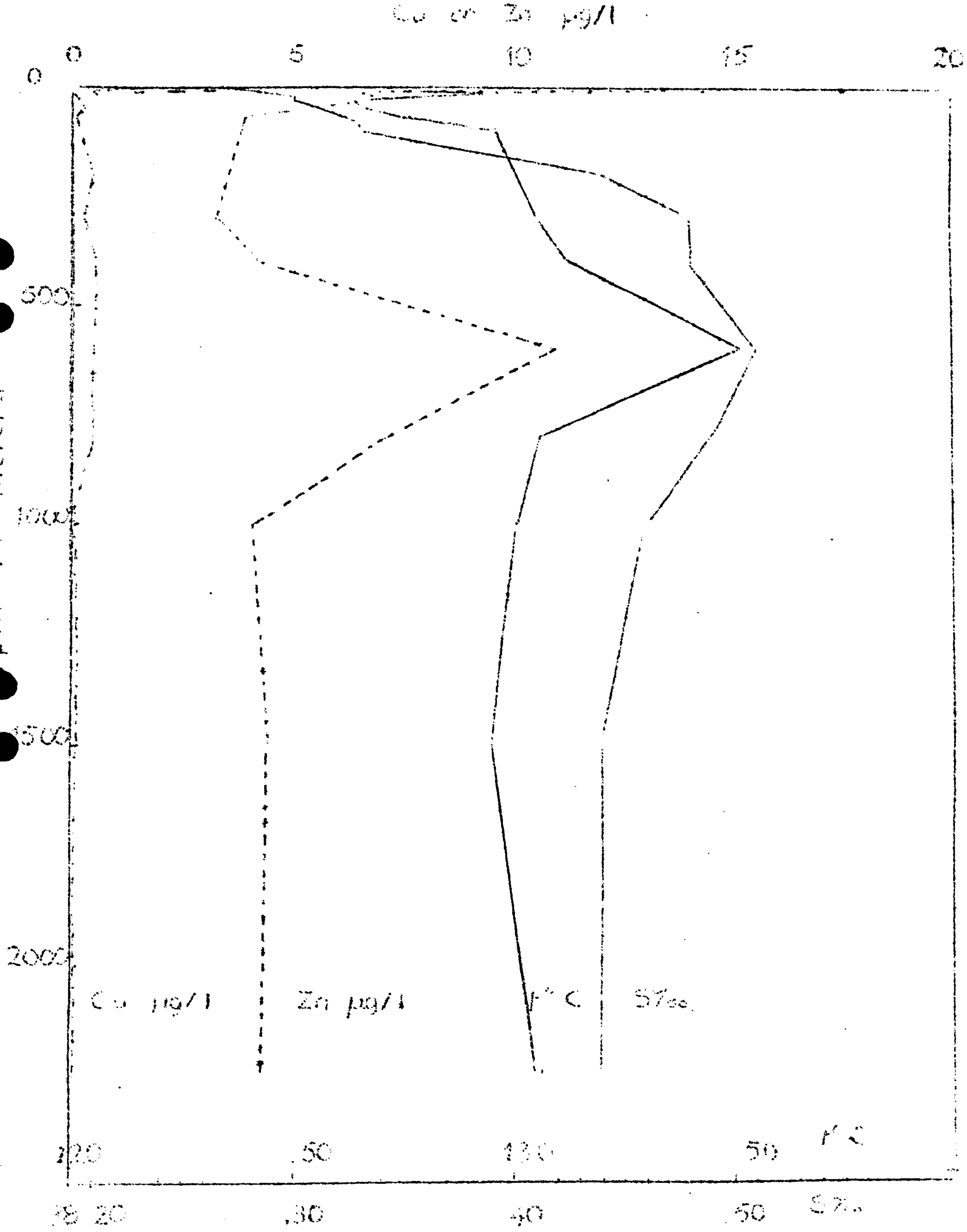
Station IAEA Nr	LatitudeN	LongitudeE	Cruise I R/V Calypso				Cruise II R/V Calypso			
			Date	Depth	Zn ug/l	Cu ug/l	Date	Depth	Zn ug/l	Cu ug/l
2	43°49.6′	07°38.2′	5.21.62	Om	9.6	1.2	10.1.62	20m	3.9	0.15
2	43°30.5′	08°03.0′	5.21.62	Om	35.	4.9	10.1.62	20m	8.9	(6.26)
3	43°22.1′	08°27.5′	5.22.62	Om	59.	4.8	10.2.62	20m	4.8	0.69
4	43°13.0′	08°52.2′	5.22.62	Om	27.	3.7	10.2.62	20m	4.7	1.05
5	43°04.1′	09°17.0	5.22.62	Om	39.	9.0	10.262	20m	10.6	1.20
6	42°48.5′	09°46.0′	5.22.62	Om	12.	1.0	10.2.62	20m	5.6	0.40
7	43°09.0′	09°40.5′	5.22.62	Om	30.	3.0	10.2.62	20m	5.4	0.74
8	43°38.3′	09°30.5′	5.22.62	Om	22.	2.0	10.2.62	20m	6.0	1.16
9	43°47.1′	09°35.0′	5.22.62	Om	86.	12.7	10.3.62	20m	5.2	0.50
10	43°57.0′	09°41.0′	5.23.62	Om	40.	8.5	10.3.62	20m	7.3	1.14
11	43°36.0′	08°38.0′	5.24.62	Om	24.	2.1	10.4.62	20m	4.7	0.50
Average for all stations				Om	34.9	4.8		20m	6.1	0.75

Table II

Cruise III 4.25.63 R/V Winnaretta Singer. Station IAEA Nr.2. Sonic depth 2300 m

Depth in m	Salinity ‰	Temperature °C	Zn ug/l	Cu ug/l
0	38.26	12.83	16.4	3.32
10	38.28	12.78	8.7	0.36
20	38.30	12.93	6.5	0.67
30	38.30	12.64	7.1	0.08
50	38.31	12.67	5.6	0.23
75	38.33	12.78	3.9	0.08
100	38.33	12.96	3.8	0.12
200	38.44	13.00	3.6	0.44
300	38.48	13.05	3.3	0.26
400	38.48	13.12	4.2	0.52
600	38.51	13.51	11.9	0.45
800	38.49	13.06	8.1	0.52
1000	38.46	13.01	4.1	0.00
1500	38.44	12.95	4.5	0.11
2250	38.44	13.05	4.3	0.03

Fig. 1.


Cu or Zn µg/l
0
5
10
15
20
0
500
1000
1500
2000
Depth in meters
Cu µg/l
Zn µg/l
t°C
S‰
12.0
.50
13.0
50
t°C
35.20
.30
.40
.50
S‰