

The Copper Content of Sea-water.

By

W. R. G. Atkins, F.I.C., F.R.S.,

Head of the Department of General Physiology at the Plymouth Laboratory.

INTRODUCTION.

THE existence of copper in plants and animals has long been known. For an account of early analyses in seaweeds and marine animals reference may be made to Quinton (1912). In recent years the study of the distribution of copper has become of increasing importance in connection with researches on its nutritional value. Analyses have been given of the copper content of many vegetables and fruits (Remington and Shiver, 1930) and of the oyster in relation to the cure of nutritional anæmia (Levine, Remington and Culp, 1931). Orton (1924) collected a number of results bearing on the copper content of oysters. Some of these values are extraordinarily high and the oysters have a greenish appearance from the excess copper, which however may be removed after relaying on clean grounds. There is, however, always a small residual amount of copper, the function of which is unknown. The source is probably particulate inorganic matter in the abnormal cases and the food in those with a normal copper content. This would point to the existence of copper in diatoms and algal spermatozoa, such as those of the Fucaceæ. Copper too is a constituent of the respiratory pigment in Crustacea. Its source is again to be sought in the phytoplankton. One would therefore expect to find a seasonal change in the copper left free in sea-water. Except in the case of the respiratory pigment it was not however known whether the copper was present as an essential or accidental constituent of the cell. Sommer (1931), however, also Lipman and Mackinney (1931), have recently shown that copper is essential for the growth of higher plants, such as barley and flax. Orr (1929) has pointed out our lack of knowledge as to how the concentration of copper in pasture soils varies. It is not known whether some soils contain too little copper.

The first comprehensive survey of the distribution of copper appears to be that of Dieulafait (1879). He proved its presence in both igneous and sedimentary rocks. All but one out of a large number examined gave a detectable amount of copper on 100 g. sample; the amount varied from one to fifty times. His spectroscopic method enabled him to identify in an absolute manner as little as 10^{-6} g. of copper. He refers to the early

(1850) detection of copper, in the ash of *Fucus*, by Malaguti, Durocher, and Sarzeau, and to the similar work by Forchhammer (1864).

As a consequence of the universal presence of copper in rocks, Dieula-fait pointed out its existence in ancient and modern seas. After many failures he succeeded in demonstrating its presence in brine, from salt marshes, of density 1.36. The method is based upon precipitation with sulphuretted hydrogen and redissolving in nitric acid. Seeing that his brine was concentrated so that 1 litre represented 200 to 250 l. of natural sea-water, his results give 10–12.5 mg. of copper per cubic metre. These he considers minimum values, obtained by finding the least volume of brine in which he could qualitatively detect copper.

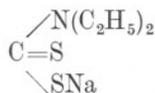
When the copper content of sea-water was first sought for by the writer in 1928 the only analysis known was one by the Government Chemist, London (Orton, 1924), which gave approximately 0.2 parts per million or 200 mg./m³. This value related to a sample of water, from 70 metres depth, taken by me near the Wolf Light off the Lizard Hd., English Channel, on November 12, 1921.

METHODS OF ANALYSIS FOR COPPER.

The above sample was analysed for copper by concentrating 800 ml. of filtered water to 150 ml. The tint of 50 ml. was then compensated, after the addition of three drops of concentrated hydrochloric acid, by the addition of very dilute potassium bichromate. It was then saturated with sulphuretted hydrogen and compared with similar tubes containing known amounts of copper.

When a number of samples have to be examined the avoidance of filtration and evaporation is however desirable, so the potassium ethyl xanthate method of Scott and Derby (see Scott, 1922) was tried. It was found that as little as 0.01 mg. copper per 100 ml., namely, 100 mg./m.³ gave a noticeable brown tint. This seemed an appropriate degree of delicacy and during 1928 a number of samples were thus examined. Values from about 40–110 mg./m.³ were obtained, but the tints were so faint that complete reliance could not be placed on the results. The surface values were as a rule lower than the deeper, and beyond 50 mg. the difference from the blank became practically indistinguishable. Moreover, with this reagent, there is always a very faint tint in absence of copper—when made up in glass distilled water.

Later on Callan and Henderson's (1929) colorimetric method was tried, using sodium diethyl-dithio-carbamate



This is a readily soluble white crystalline substance, used in 0.1 per cent slightly alkaline aqueous solution; it is perfectly colourless and 10 ml. added to 100 ml. of glass distilled water gives no tint, nor is any tint given with our Laboratory supply from a copper still with block tin spiral condenser. With this reagent 0.01 mg. copper per 100 ml. gives a far more intense colour than it does with potassium ethyl xanthate. The sensitivity is about twice as great, and the fact that the reagent is colourless is an added advantage. It was examined in 12 cm., 100 ml. Nessler tubes, in 15 cm., 100 ml. Hehner tubes, and in 30.5 cm., 200 ml. Hehner tubes. With the 15 cm. tubes it was possible to distinguish 0.002 mg. in 100 ml., viz. 20 mg./m³ of copper from the blank, but not in the Nessler tubes. In the long Hehner tubes 0.001 mg. in 100 ml., viz. 10 mg./m³ could be distinguished at the 200 mark as giving a distinct yellowish tint, and a very slight tint at 150 mark; at 100 mark it was indistinguishable from the blank. One would therefore expect this reagent, used with long tubes, to be a possible one for use with sea-water if it contains 50–200 mg./m³. No colour is however given, even with winter samples, when the copper content should be at a maximum, under conditions that would definitely detect 20 mg./m³. There is therefore a disagreement between the Government Chemist's result and my own xanthate and carbamate values. The latter are, however, in good agreement with the following xanthate analysis. A carboy of sea-water, from Station E1, surface, taken on March 23, 1931, was concentrated to one-fifth of its volume and, after making allowance for a blank correction, was found to contain 50 mg./m³ of copper, corresponding to 10 mg. for original sea-water.

Again, use was made of the standard method of electro-deposition. One litre of the same carboy of water was raised nearly to boiling and was electrolysed for one hour at 2.0 volts, the copper being deposited upon platinum gauze. Electrolysis of the hot solution was continued for a further two hours with fresh gauze. Electrolysis with a third piece of gauze was continued for an hour.

The copper deposited was dissolved in copper-free water acidified with the purest sulphuric acid. After neutralisation the volume was made up to 10 ml. in each case and the copper was estimated colorimetrically. The first and second periods of electrolysis deposited, respectively, 0.0040 and 0.0057 mg. copper, the third gave none, total 0.0097 mg. from one litre or 9.7 mg./m³. The current must be continued till the liquid has been lifted away from below the electrodes to avoid loss by redissolving of the copper. The method of electro-deposition is very simple and the colour intensity is so intense that accuracy is greater than in the volume concentration method.

It remains to explain the discrepancy between the earlier results and the

concordant results just mentioned. My attention was drawn by L. H. N. Cooper to some bolts on the inside of the standard water-bottle. The gun-metal bolts were corroded and covered with verdigris. Consequently all samples are liable to contain, and according to the analysis given do contain, traces of added copper. The sea-water used in the later analyses was from a glass carboy filled, from the surface, with a wooden bucket. The water-bottle is carefully washed with fresh water after each cruise, but the sample I took for the Government Chemist was taken on the fourth day of a cruise, after we had taken shelter in Falmouth Harbour for two days, which gave opportunity for the accumulation of an additional amount of verdigris.

It remains to consider the presence of iron in sea-water as a source of error in direct examination. According to Ansbacher, Remington and Culp (1931) with the xanthate method, 0.050 mg. of iron gives the same colour as 0.0123 of copper. On testing the carbamate method, however, the writer found that it required a concentration of 1.32 mg. per litre of ferric iron to give as much colour as 0.01 mg. per litre of copper. The interference is therefore negligible. It is, of course, absent altogether when the copper is deposited electrically.

SUMMARY.

1. On comparing the potassium ethyl xanthate and the sodium diethyl-dithio-carbamate methods for estimating copper the latter was found to be preferable because (a) It is at least twice as delicate, (b) The reagent is absolutely colourless, (c) In very dilute solution ferric iron causes little or no disturbance.

2. Estimation of copper may be carried out by electro-deposition from one litre of sea-water at about 90–100° C. for three hours at 2.0 volts with subsequent re-solution and colorimetric estimation using the carbamate method.

3. In agreement with the spectroscopic determinations of Dieulafait in 1879, it was found that sea-water contains about 10 mg. per cubic metre of copper.

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