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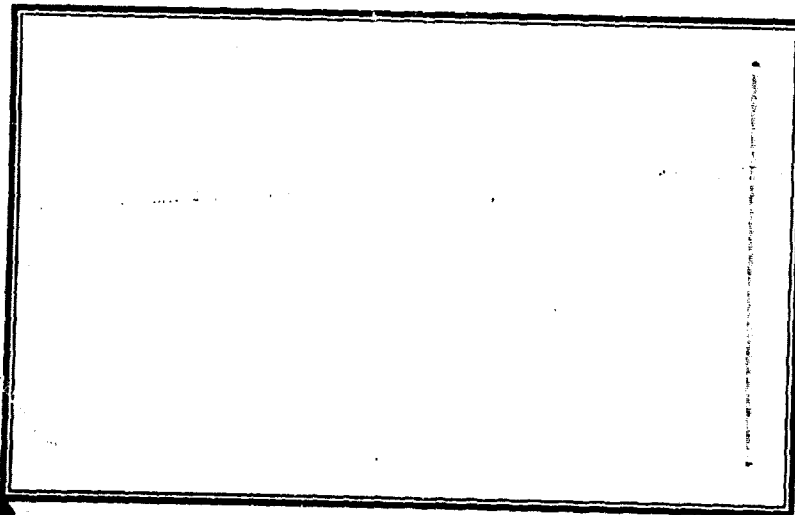
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Chemical Detection of Ferrous Objects
in the Sea

By

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ABSTRACT

If the corrosion of iron or steel objects in sea water gives a detectable change in the iron content of the water, search for these objects might be aided by a rapid chemical analysis of water samples. In examining the feasibility of such a method, the following points have been considered.

An estimate of the order of magnitude of the effect, if the products of corrosion are uniformly distributed in the sea water near the corroding object.

The character and the amount of iron normally found in sea water under various conditions.

The character of the analytical methods of sufficient sensitivity to detect the amounts of iron to be expected.

The nature of the corrosion process and an assessment of the probable form of the corrosion product.

Dispersive effects in slowly moving fluids are mentioned. These considerations lead to the following conclusions.

A submerged ferrous object might be expected to produce an average change in iron content in neighboring water of 0.1 micrograms per liter. Wide fluctuations from this figure might be expected. Furthermore an effect even of this order of magnitude would be expected only if the

corrosion product was found in true solution or as a fine colloid.

Iron normally present in sea water must be divided into two categories: (a) "dissolved" iron, that which passes through a filter of arbitrarily selected pore size and (b) "particulate" iron retained on the filter. In recent work employing a filter which stopped particles larger than 0.5 micron in some dimension, the concentration of dissolved iron was found to be of the order 4 micrograms per liter. In deep water of the Pacific the total iron content was 8 micrograms per liter. In coastal waters the iron content was found to be highly variable.

The most sensitive colorimetric determination of iron cannot be conveniently used at concentrations below 3 micrograms per liter. The accuracy of the method is apparently about 50% at these levels. The method is at best somewhat time-consuming and requires laboratory facilities.

A consideration of the thermodynamic data for the various reactions involved in the corrosion process, as influenced only by dissolved oxygen and not by reactive organic matter, leads to the conclusion that the corrosion product cannot be in true solution unless it is held complexed by organic matter. The principal corrosion products must be solid or colloidal hydrous oxides or else held in combination with organic matter.

It is recommended that no more effort be spent on attempting to develop a purely chemical method for the detection of submerged ferrous objects. In view of the apparent dearth of information on the nature of the products of the corrosion of iron and steel, it is recommended that a careful survey be made of existing knowledge with a view toward assessing the desirability of further experimental work on the subject. In particular it is suggested that this survey be made with special emphasis on the possible effects of organic matter present in sea water.

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1. Possible Concentration of Iron near a Corroding Object.

It is evident that any estimate of possible concentrations of dissolved matter to be found in water, as a result of the slow corrosion of a metal object, which leaves all details as to convective and diffusive mixing out of account can at best be only very rough. However, in the absence of any details for a special case it is not worthwhile to do more than produce a rough guess. The following estimation, due to D. F. Ream, is of this practical character. If one considers a sunken mine, taken to be cylindrical steel object half covered by the silt of the bottom, one may suppose that corrosion products are picked up at the average rate of corrosion into a volume of water equal to that of the uncovered object and that this volume is changed at a rate determined by the linear velocity of the water in the neighborhood of the object. For an object 5 feet in length and 1 foot in diameter corroding at a rate of 1 pound of iron per year, immersed in water with a linear velocity of 1.7 feet per second, the resulting iron concentration turns out to be 0.06 micrograms per liter. This result, of course, depends on the supposition that the corrosion products are uniformly distributed in the sea water. That this last is an improbable situation will be seen below. It seems much more likely that the primary products of corrosion are small bits of hydrous iron oxide which are carried away in a highly non-uniform manner.

The above estimate, however, gives a basis on which to discuss the possibilities which may be encountered. It is now necessary to compare this estimate of possible iron concentration with the iron actually found in sea water not necessarily near a submerged iron object

2. Iron in the Sea.

A very complete summary of previous work on the iron content of marine waters together with important new results has recently been published by George J. Lewis and Edward D. Goldberg (Sears Foundation: *Journal of Marine Research*, 13, No. 2, pp 183-197(1954)). Table I, taken from this paper, will be found on the next page.

The differentiation between soluble and total iron is, of necessity, arbitrarily dependent on the type of filter used and varies with the investigation. It is apparent, however, that the concentration of iron classifiable as particulate is generally about twice that of the soluble iron. The total iron is seen to vary enormously from point to point in the seas. Within the Northwest Pacific, which has been most thoroughly examined, variations of nearly forty-fold have been found.

Lewis and Goldberg report new results of their own which are of great significance in the present connection. These workers, using a 0.5 micron filter, determined the soluble iron content of shore water collected from the Scripps Pier at La Jolla, California. Expressed in micrograms per liter these values varied from 0.7 to 5.2 with an average of 3.3. From the nature of the analytical method employed it is most probable that the variations found represent a true fluctuation in normal iron content. It is not apparent how rapidly this fluctuation takes place. Lewis and Goldberg also report a value of 3.7 micrograms per liter for the average of bottom water in the Pacific at depths of 4000 and 4500 meters, with a fluctuation of about 50% about this value.

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TABLE I. * IRON DETERMINATION IN MARINE WATERS

NORTHEAST ATLANTIC

Location	Depth (meters)	Fe in mg/L	
		Soluble	Total
1. Mediterranean	1	-----	2.0
2. English Channel	?	-----	0.10
3. Irish Sea	?	-----	3.25
4. English Channel	70	-----	0.10
5. English Channel	0-68	0.003	-----
		-0.006	
6. Tropical N. Atlantic (Meteor Profiles 12, 13, 14)	-----	-----	0.06
7. Norwegian Sea	0-400	0.0049	0.0085
8. Barents Sea	?	-----	0.010-
			0.020
9. North Atlantic	?	-----	0.003-
			0.011
			(Surface
			0.013-
			0.014
			Bottom)
			0.014
			0.008
			0.020
NORTHWEST ATLANTIC			
10. English Channel	0-70	0.007	
11. Swedish Coast	?	-----	
12. English Channel	0-120	0.000	
13. Gulf of Maine	1-340	-----	0.019
14. U. S. Coast	0-3830	0.005	0.021
15. U. S. Coast	Surface	0.003	-----
NORTHEAST PACIFIC			
16. Washington Coast	0-300	-----	0.073
17. Coasts of U. S. A., Canada, Alaska	0-2000	0.026	0.091

From Lewis, G. J. and E. D. Goldberg, Iron in Marine Waters, Reprint from Sears Foundation, Journal of Marine Research, Vol. 13, No. 2, November 1, 1954. Pp. 183-197.

TABLE I. * IRON DETERMINATION IN MARINE WATERS
NORTHWEST PACIFIC

	Location	Depth (meters)	Fe in mg/L	
			Soluble	Total
18.	Seto Inland Sea	0-27	-----	0.145
19.	Ryukyu Island	0-200	-----	0.138
20.	Osaka-Wan Inland Sea	0-65	-----	0.060
21.	Osaka-Wan, Osaka	0-10	-----	0.083
22.	Seto-Naikai (Inland Sea)	0-150	-----	0.333
23.	Kyushu Island	0-100	-----	0.146
24.	Osaka-Wan	0-16	-----	0.089
25.	Saruga-Wan, Honshu, Japan	0-978	-----	0.027
26.	Osaka-Wan, Osaka	0-7	-----	0.372
27.	Osaka Bay (off Osaka)	Surface	-----	0.091
28.	Seto Inland Sea	0-33	-----	0.046
29.	East China Sea (Kyushu Inlets)	0-68	-----	0.024
30.	Sea of Japan (Fukuoka, Kyushu)	0-20	-----	0.009
31.	Sea of Japan (Maizura Bay, Honshu)	0-30	-----	0.212
32.	Southern Japan (Open Ocean)	0-1009	-----	0.010
33.	Southern Japan (Osaka Bay, Kii Suido)	0-75	-----	0.033
34.	Southern Japan (Kii Suido)	0-70	-----	0.009
35.	Seto Inland Sea	0-49	-----	0.069
36.	Northern Japan (Murooran Harbor, Hokkaido)	0-12.5	-----	0.810
37.	Northern Japan (Murooran Harbor, Hokkaido)	0-12.5	-----	0.310
38.	Off SE. Honshu and S. Shikoku	0-1554	-----	0.0095

It is apparent that not only is the normal iron content of sea water far in excess of the increase to be expected from the corrosion of a ferrous object, but also that the normal fluctuation is far above this expected increase. It follows that only if a rapid and accurate analytical method is available would there be any hope of detecting fluctuations due to corrosion. Even this last possibility would demand much preliminary testing under controlled conditions before any reliance could be placed on observations made in this way. It is also apparent that in coastal waters the least reliable results would be obtained.

3. Analytical Methods.

Only colorimetric methods need be considered in connection with the determination of the small amounts of iron under consideration. Of these the two best depend upon the formation of intensely colored complex compounds with α, α bipyridyl and with bathophenanthroline (4,7 - diphenyl, 1,10-phenanthroline). The bipyridyl method is useful for amounts of iron in the range 5-100 micrograms. Amounts from 0.3 to 6 micrograms may be determined by the use of bathophenanthroline.

Both of these methods were used by Lewis and Goldberg in their work, and these authors give details for the procedures as applied to the determination of particulate iron and of soluble iron. The determination of particulate iron involves a digestion with perchloric acid. The determination of soluble iron involves the evaporation of the sample followed by considerable chemical treatment and finally an extraction of the colored compound into isoamyl alcohol.

Neither of these procedures could be classed as a rapid analysis. It is difficult to see how they could be applied to the problem at hand.

Another method which should be considered in this connection is a reflectrimetric determination of sub-microgram amounts of iron developed by L. Meites and T. Meites. In this method a very small volume of a ferric solution is placed on a piece of paper previously impregnated with ferrocyanide. The absorbance of the blue spot formed is measured with an appropriately adapted Beckman Model B spectrophotometer. In the experiments volumes of iron solution (in 0.01 M HCl of only 2 microliters were applied to the treated paper. With precautions and after the application of a correction due to the liberation of iron by oxidation of the ferrocyanide, the technique can detect 0.5 milli micrograms of iron. We may reasonably suppose that sufficiently accurate measurement can be made at 5 millimicrograms in 2 microliters. To apply the method in its original form we require a ferric solution in 0.01 M HCl at a concentration of 2500 micrograms per liter. Thus the iron of sea water would have to be concentrated 1000-fold and converted to the ferric condition. This is certainly not an impossible process, but just as certainly one which would require time and careful manipulation. Again it seems unlikely that the method could profitably be applied to the practical problem at hand.

In summary, we may state that no method now exists which can be applied to produce a rapid analysis of sea water for its iron content in the concentration range which must be considered and with the accuracy apparently required. Polarographic methods might be developed, but none has come as yet to the author's attention.

4. The Condition of Iron in the Sea and the Possible Course of the Corrosion Process.

Much indirect illumination is shed on the condition of iron in sea water by a somewhat detailed consideration of the equilibria involving the purely inorganic forms of iron. This has been done by L. H. N. Cooper

(Proc. Roy. Soc. London, 124B, 299 (1937-38)). The principal conclusion of Cooper's work is to the effect that the total quantity of iron in true solution after equilibrium has been attained does not exceed the following values

3×10^{-8}	micrograms Fe per liter at pH	8.5
4×10^{-7}	" " " "	8.0
4×10^{-5}	" " " "	0
5×10^{-3}	" " " "	6.0

Since the pH of sea water is near 8 it is evident that the actual content of dissolved iron as defined by the assumptions of Lewis and Goldberg is more than a million-fold greater than the equilibrium value.

The considerations which lead to the above figures may be summarized as follows, it being understood that organic matter is not to be considered.

(1) The solubility product of ferrous hydroxide is of no importance in sea water. The ferrous iron concentration is controlled by the oxidation potential of the system and the solubility of ferric hydroxide.

(2) Ferric iron in the dissolved state exists principally as Fe^{+++} and $\text{Fe}(\text{OH})^{++}$, the total ferric iron being given by

$$[\text{Fe}^{\text{III}}_{\text{T}}] = \frac{[\text{H}^+] + K_1' [\text{Fe}^{+++}]}{[\text{H}^+]}$$

K_1' is the first hydrolysis constant for Fe^{+++} and the ionic strength in question. According to Latimer (Oxidation Potentials, 2nd Ed., Prentice-Hall, Inc., New York, 1952, p. 224) $K_1 = 4.0 \times 10^{-3}$

Cooper calculates values for the solubility products

$$S_2 = a_{\text{Fe}(\text{OH})^{++}} \cdot a_{\text{OH}^-}^2 = 10^{-26.8}$$

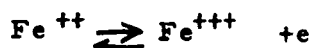
$$S_3 = a_{\text{Fe}^{+++}} \cdot a_{\text{OH}^-}^3 = 10^{-38.6}$$

From these one finds for sea water at pH = 8

$$a_{\text{Fe}^{++}} = 10^{-13.9}$$

$$a_{\text{Fe(OH)}^{++}} = 10^{-8.3} \text{ (microgram atom/liter)}$$

(3) Using the oxidation potential for the reaction



and considering the ferric iron to have the concentration for a saturated solution, one arrives at a relation for the ferrous ion concentration as a function of pH and oxidation potential of the system.

At the reversible oxygen potential in sea water at pH 8 the corresponding activity of ferrous iron is 2×10^{-14} , far less than the value implied by the solubility product of Fe(OH)_2 , $S = 1.8 \times 10^{-15}$, whence $A_{\text{Fe}^{++}}$ at pH8 should be $\sim 10^{-3}$. Thus ferrous hydroxide is unstable in sea water and is rapidly converted to ferric hydroxide.

Since sea water free of complexing agents cannot account for the observed presence of iron, consideration must be given to the possible existence of chloro complexes, complexes with fluoride, and, most important, iron in some sort of organic combination. The chloro- and fluoro- complexes are probably of no significance at pH 8.

It is interesting to notice that it has been quite definitely shown by several workers that marine diatoms assimilate iron only in particulate form. Indeed, an estimate has been made of the size of particle required by Asterionella japonica; this is 2 microns (Goldberg, Biol. Bull. 102, 247 (1952)). Since particulate ferric hydroxide must be one of the primary corrosion products of an iron object in sea water, it would be of considerable

interest to investigate the effect on this process of the presence of both animate and inanimate organic matter capable of "complexing" ferric hydroxide.

It should be noted that the term "dissolved" iron, used by Lewis and Goldberg, applies to particles smaller than 0.5 micron. This dimension is 10^3 -fold larger than the dimensions of atoms and ions, and thus includes particles of colloidal size as well as truly dissolved (molecularly dispersed) material.

Any study of the motion of molecularly or colloidially dispersed matter in slowly moving water should take into account the phenomenon of convective dispersion. Peculiar effects can be produced by the superposition of molecular diffusion and convective flow. The mathematical problems involved are complicated and only a few special cases have been worked out. As an example may be mentioned the work of G. J. Taylor (Proc. Roy. Soc. London, A 219, 186-203 (1953)) in which is considered the dispersion of soluble matter in fluid moving slowly through a tube. Both theoretically and experimentally it is shown that the distribution of the soluble matter in the direction of the axis of the pipe assumes the shape of the normal curve of error. In this case the very interesting result is obtained that the spread of soluble matter is decreased rather than increased by the molecular diffusion.

It has been shown in this report that a study of the convection of dispersed iron in sea water is not justified for the purposes at hand. In cases, however, where slow convection must be studied, the dispersive effects should be evaluated and taken into account where necessary.

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