THE IRON CONTENT OF SEA WATER

By F. A. J. Armstrong

The Plymouth Laboratory

Concentrations of iron in sea water up to about 3 mg Fe/l. have been reported, most of the figures being in the range 10–100 μg Fe/l. The published analyses, with notes on the methods used where these are known, are summarized by Lewis & Goldberg (1954), who list thirty-nine sources up to 1953.

It is well known that much of the iron is in particles which can be removed by filtration. Attempts have been made to estimate the chemically more reactive and presumably biologically more available fraction of the metal. Often the coarser particles have been filtered off before analysis, and reagents of varying potency have been used to bring iron into solution for colorimetric determination. These procedures have sometimes excluded determination of the total concentration of iron in the water. It is known, however, that the phytoplankton can utilize particulate material for its requirements of iron (Allen & Nelson, 1910; Harvey, 1927; Goldberg, 1952).

Methods intended to determine total iron in sea water have been described by Thompson, Bremner & Jamieson (1932); Thompson & Bremner (1935); Cooper (1935, 1948); Rakestraw, Mahncke & Beach (1936); and Lewis & Goldberg (1954). Thompson and his collaborators evaporated the water with excess of sulphuric acid and heated to fuming, and Lewis & Goldberg used perchloric acid in a similar way. These methods should undoubtedly be effective, as should that used by Rakestraw *et al.* when applied to unfiltered water. Cooper, in his method for 'total iron' (for which expression he made specific reservations) used a less drastic attack and heated the sample with hydrochloric acid (0·008 N) and some bromine, excess of bromine being later boiled off. Some analyses of suspended matter in sea water (Armstrong & Atkins, 1950) showed that in surface water from a position in the English Channel there were present from 42 to 210 μg Fe/l. These amounts were so much greater than those previously found at the same position, by direct analysis, that it seemed desirable to make more analyses and to re-examine the analytical methods.

ANALYTICAL CONSIDERATIONS

Methods using wet ashing with sulphuric or perchloric acids should serve well for referee analyses. They are not, however, very convenient for routine use and reagent blanks tend to be high. A simple alternative way of bringing iron into solution which could be used for large batches of samples was sought. A possible method came from the observation that when the suspended

matter is filtered from sea water, the iron can be extracted completely from the solid residue with cold 1 N hydrochloric acid. This concentration is unmanageably great for acidification of a sea water sample of about 100 ml., so attempts were made to use 0·1 N acid. At this level blanks are low and partial neutralization is easier. 0·1 N acid was ineffective in the cold, although boiling for 1 h dissolved more than 90% of the iron present. Solution of iron appeared to be complete however when the acidified sample was heated in an autoclave for 5 h at 140° C. Since the treatment extracted appreciable and varying amounts of iron from borosilicate glassware, fused silica flasks had to be used. It proved convenient to add 1 ml. of concentrated hydrochloric acid to 85 ml. of sea water to give a concentration of 0·12–0·14 N. After digestion and adjustment of volume the addition of 10 ml. (20%, w/v) sodium acetate brought the solution to pH 3·8 ± 0·2, which was suitable for colorimetric determination.

Of the many very satisfactory colorimetric reagents for iron, 1:10 phenanthroline seemed to be the most suitable. It was extensively tested by Fortune & Mellon (1938), who found it effective (with ferrous iron) in the pH range 2–9. Of fifty-five ions which these authors tested for interference none of the undesirable ones, with the possible exception of fluoride, is present in sea water in troublesome quantity. 2-2′-Dipyridyl, of similar sensitivity and also interference-free, has a narrower pH range of 3·5–8·5 (Hill, 1930). It could be used, but extra sodium acetate might be desirable to raise the pH somewhat (since colour development tends to be slow at the higher acidities) and this would undoubtedly increase blanks.

Some tests with 1:10 phenanthroline were made to see whether fluoride would interfere with iron determinations at pH 3·8, and it was found that there was no effect up to a concentration of 7·6 mg F/l. (400 μg atom F/l.). This is 5 or 6 times the usual concentration in sea water, which is stated to be about 1·4 mg F/l. (74 μg atom F/l.) (Thompson & Taylor, 1933).

It was found that 1:10 phenanthroline could be used with confidence and that the method prescribed by Fortune & Mellon, using hydroxylamine hydrochloride for reduction of ferric iron, could be followed closely with sea water. The depth of colour, which does not fade, is unaffected by the salts in the water, and Beer's Law is obeyed in a simple filter absorptiometer.

METHOD

Apparatus

Polyethylene sample bottles. Fused silica flasks, 100 ml. Autoclave for temperature 140° C (40 p.s.i. or 2·8 kg/cm²). This should be of non-ferrous construction. Absorptiometer to take 10 cm cuvettes or longer. Glassware should be cleaned with strong hydrochloric acid before use and reserved for this work.

Reagents

Standard iron solution. 1 ml. ≡ 0·0001 g Fe. Dissolve 0·702 g $FeSO_4.(NH_4)_2SO_4.6H_2O$ in 1%, v/v, HCl and make to 1 l. with 1%, v/v, acid.

Sodium acetate 20%, *w/v*. Dissolve 200 g $CH_3COONa.3H_2O$ in water, make to 1 l., shake with about 10 ml. chloroform to saturate and filter on No. 42 Whatman paper.

Hydroxylamine hydrochloride 10%, *w/v*. Dissolve 10 g $NH_2OH.HCl$ in water and make to 100 ml.

1:10 *phenanthroline* 0·1%, *w/v*. Dissolve 0·25 g 1:10 phenanthroline in hot water, cool and make to 250 ml.

Analysis of sea water

Measure 85 ml. of the properly collected (see below) and well-shaken sample into a 100 ml. silica flask and add 1·0 ml. conc. HCl, preferably with a syringe pipette. Cover the flask and heat for 5 h in an autoclave at 140° C. After cooling, adjust the volume to 86 ml., transfer to a 150 or 250 ml. borosilicate flask and add 10 ml. 20% sodium acetate and 1 ml. 10% $NH_2OH.HCl$, using pipettes. Mix the solution, and measure the absorbance in a 10 or 15 cm cuvette at about 510 mμ (Ilford no. 603 or combination of 303 and 404 filters). This reading will allow correction for slight turbidity of the solution. Return the solution from the cuvette to the flask, add 3 ml. 0·1% 1:10 phenanthroline solution, mix, and measure the absorbance again after 10 min. The difference between the two readings, when corrected for the absorbance of the blank, measures the iron content of the sample.

Blank determination

Carry 85 ml. of iron-free distilled water through the same procedure. If it is found that release of iron from the flasks is negligible digestion of blanks may of course be omitted.

Calibration

In a series of 100 ml. graduated flasks, place measured amounts of the standard iron solution (or of a freshly prepared known dilution of it), to give a range of known iron concentrations. They may be chosen on the assumption that about 60 μg Fe in 100 ml. are required to give an absorbance of 1·0 in a 10 cm cuvette in a filter absorptiometer at about 510 mμ. Add distilled water to a volume of about 80 ml., and then add HCl, sodium acetate, $NH_2OH.HCl$ and 1:10 phenanthroline in the quantities given above. Adjust the volumes to 100 ml., mix and measure absorbance after 10 min. Construct a calibration curve. This should be a straight line. If so, it is convenient to recalculate the slope as the concentration of iron in an 85 ml. sea-water sample required to give an absorbance of 1·00. The product of this factor and the corrected absorbance of a treated sea-water sample is the concentration of iron in the sample. Calibration should be repeated occasionally as a check on the constancy of the absorptiometer. If the curve is linear a check at one iron concentration is enough.

TESTS OF METHOD

The effectiveness of the digestion in extracting iron from refractory marine material was tested by comparing the amount brought into solution by digestion with that found after ignition and fusion with potassium bisulphate. For this test two samples, one of marine silt and the other of equal parts of dried whole fish meal and dried ground sea weed, were homogenized by grinding. Fibrous material in the second sample was removed with a 100-mesh sieve. Portions of 50–100 mg were weighed and assayed by the two methods. The

results, expressed as iron contents of the samples, are given in Table 1, and show that recovery of iron by the digestion method was sensibly complete.

For trials with sea water, two carboys of freshly collected water were well shaken and kept vigorously stirred whilst samples were drawn off by siphon. From each carboy three samples of 2 l. each were taken for filtration as described below, and three sets of eight samples for replicate determinations

TABLE 1. RECOVERY OF IRON FROM MARINE MATERIALS

	Iron content (%)							
	Ignition and bisulphate fusion				Acid digestion at 140° C			
Material								
Silt	1·26	1·28	1·26	1·25	1·24	1·27	1·25	1·27
Sea weed and fish meal	0·061	0·077	0·060	0·069	0·079	0·078	0·067	0·060

TABLE 2. COMPARISON OF METHODS FOR DETERMINATION OF TOTAL IRON IN SEA WATER

(Iron found, μg Fe/l.)

	Filtration, bisulphate fusion, etc.	Acid digestion at 140° C	Fuming with H_2SO_4 (Thompson et al.)	HCl and Br_2 (Cooper)
Carboy A	89	81	71	13
	100	78	100	15
	83	83	98	21
	—	80	83	15
	—	82	83	17
	—	89	79	18
	—	93	76	19
	—	95	84	13
Mean	91	85	84	16
S.D.		±6	±9	±3
Carboy B	140	106	130	50
	164	152	132	34
	118	139	168	6
	—	143	137	9
	—	140	140	17
	—	145	137	21
	—	142	132	22
	—	139	132	21
Mean	141	138	138	23
S.D.		±14	±12	±14

by the digestion method (85 ml.), Thompson & Bremner's sulphuric acid method (100 ml.) and Cooper's 'Total Iron' method (150 ml.). The 2 l. samples were filtered on 'Gradocol' membrane filters (A.P.D. approx. 1 μ) and the filtrates reserved. Each membrane with the suspended matter on it was ignited in platinum and the residue fused with bisulphate. Iron in the melt was determined, blanks being carried through all stages. To the iron concentrations thus found were added those found in the filtrates by the digestion method. Any material passing the filter was necessarily very finely subdivided and was assumed to be readily dissolved. (The amount of iron

found in these filtrates varied from 4 to 8 μg Fe/l., and may be compared with
the 2–5·5 μ Fe/l. found after filtration through 'Millipore' membranes of
0·5 μ A.P.D. by Lewis & Goldberg.) This procedure gave an independent
estimate of total iron in the samples, although it is probably not very accurate
because so much manipulation is involved.

The samples for digestion were carried through the method described
above. Those for test by Thompson & Bremner's method were heated to
fuming as prescribed in the original method. Silica flasks were used. The
colorimetric finish with thiocyanate, however, was set aside in favour of the
1:10 phenanthroline procedure after neutralization of excess acid with
ammonia, iron in this reagent being allowed for. The samples for Cooper's
'Total Iron' method were treated as described in his 1948 paper, dipyridyl
being used.

The results are given in Table 2. Taking into consideration the marked
scatter in the figures it can be seen that the filtration, Thompson & Bremner's
and the new digestion methods agree well, but that the HCl-bromine 'Total
Iron' method is not rigorous enough, as Cooper himself surmised (1948,
p. 281).

COLLECTION OF SAMPLES

Circumspection is obviously needed when samples are taken from a steel ship
and in a hydrographic water bottle on a steel wire. Ordinary glass sample-
bottles are unsuitable, even after washing with acid, since they are appreciably
attacked by sea water. Iron in the glass is released, remaining on the walls of
the bottle, probably as a film of ferric hydroxide, but easily contaminating the
sample. Moreover, Goldberg (1952) showed that iron added to sea water is
rapidly adsorbed by glass. Polyethylene bottles, though not ideal, may be
used. Analysis of some new bottles showed the plastic to be iron-free, but it
should be remembered that the bottles may be made on iron or steel moulds.
It is advisable to wash out all bottles with strong hydrochloric acid before use
(a little wetting agent such as cetyl ammonium bromide with the acid is
helpful) and to test for extractable iron by filling with 0·1 N-HCl and heating
for several hours in a water bath at 100° C and then determining iron in the
solution. It has been noticed that polyethylene bottles which had been used
repeatedly for collection of water for other analyses had an internal deposit of
ferruginous material which came out only after prolonged acid treatment.

Deposition of iron on the walls of polyethylene bottles takes place rapidly
from raw sea water. Experiments showed that in a week one-quarter of the
iron originally present was so deposited; storage for 4 weeks showed losses of
one-half to two-thirds. The iron deposited is difficult to recover, only half of
it being removed by standing with 0·1 N-HCl for several days with occasional
shaking. It is advisable therefore to complete iron determinations soon after
collection. When this cannot be done the samples should be acidified when

collected. For long storage it would probably be advisable to use the full amount of acid, i.e. 1·0 ml. conc. HCl per 85 ml. of sample, but for 3 weeks' storage a smaller amount is sufficient. Table 3 shows the effectiveness of addition of 1 ml. of 10%, v/v, HCl per 100 ml. sample. This amount of acid may be disregarded when acidifying before digestion and its contribution to the reagent blank is usually negligible.

TABLE 3. IRON DETERMINATIONS ON SUBSAMPLES OF SEA WATER BEFORE AND AFTER STORAGE FOR 3 WEEKS WITH ADDITION OF 1 ML. (10%, V/V) HCl PER 100 ML.

Before storage   74, 94, 92, 81, 105, 86, 85, 88, 67, 88   Mean 86 s.d. ± 11 μg Fe/l.
After 3 weeks' storage 105, 83, 86, 86,   80, 81, 86, 88, 88, 84   Mean 86 s.d. $\pm$ 7 μg Fe/l.

VARIABILITY OF RESULTS

Tables 2 and 3 include standard deviations. The sets of samples analysed are hardly random ones, but subsamples of larger portions which were vigorously stirred whilst subsampling. Those of Table 2 were, as stated, from carboys (20–25 l.), whilst those of Table 3 were from a bucket (8 l.). A set of ten samples, each of 85 ml., from ten consecutive buckets of water taken from the sea surface at Station E 1 whilst the ship was stopped gave a mean iron content of 65 ± 22 μg Fe/l. Sampling took about 15 min.

The variability of replicate iron determinations has been discussed by other workers, and was turned to account by Cooper (1948) who assessed, by statistical treatment, the size and distribution of iron-containing particles in the water. Lewis & Goldberg (1954) were at some pains to obtain replicate samples from deep water and gave a statistical analysis of their data from nine Pacific Ocean stations.

RESULTS OBTAINED

Iron concentrations found by the digestion method in samples from the Plymouth Laboratory stations L2 to L6 and at the International Hydrographic Station E 1 during 1955 and 1956 are given in Table 4. As would be expected there is appreciably more iron in the coastal waters. There is a seasonal variation, more iron being found in the winter months, which may be caused by the increased run-off from the land and greater turbulence in winter. There is often, at Station E 1, more iron at the surface, as observed by Cooper (1948). Iron concentrations are very much higher than those reported by Cooper for 1933 and 1934 and 1946 and 1947. This is ascribable to the difference in the analytical methods.

Results from two other stations in the English Channel and from three positions off the Brittany coast in the northern part of the Bay of Biscay are given in Table 5. Figures from four deep-water stations in the Bay of Biscay are given in Table 6.

TABLE 4. IRON CONTENT OF SEA-WATER SAMPLES FROM POSITIONS NEAR PLYMOUTH 1955–6

(In μg Fe/l.)

St. no.	N. lat.	W. long.	Miles from Plymouth	Depth (m)	18 Jan.	16 Feb.	15 Mar.	12 Apr.	9 May	13 June	13 July	11 Aug.	15 Sept.	18 Oct.	17 Nov.	21 Dec.
L2	50° 20′	4° 10′	2	0	203	160	58	146	—	33	64	157	53	169	177	424
L3	50° 18′	4° 11′	5	0	82	174	59	65	—	21	17	92	35	176	129	212
L4	50° 15′	4° 13′	8	0	90	107	67	68	—	7	16	100	157	94	102	100
L5	50° 11′	4° 18′	12	0	92	92	43	111	—	8	11	140	115	85	77	59
L6	50° 06′	4° 21′	17	0	124	326	60	25	—	5	30	107	97	65	62	94
E1	50° 02′	4° 22′	22	0	78	111	39	89	13	13	1	58	75	25	127	100
				5	49	77	23	36	17	198	6	31	22	19	26	26
				10	60	61	27	15	19	19	4	24	29	33	22	38
				20	—	—	—	—	—	—	3	51	15	48	35	64
				25	85	77	31	17	15	7	—	—	—	—	—	—
				50	34	90	26	50	21	16	7	31	57	84	56	83
				70	73	108	29	84	46	25	4	60	28	175	54	87
Integral mean, Station E1					—	92	28	41	22	28	5	42	36	72	45	70

St. no.	Depth (m)	17 Jan.	21 Feb.	26 Mar.	11 Apr.	16 Apr.	24 Apr.	22 May	23 July	22 Aug.	25 Sept.	23 Oct.	13 Nov.	10 Dec.	Mean
L2	0	239	129	209	106	103	54	69	40	84	70	104	120	86	127
L3	0	150	60	101	86	108	27	45	21	64	65	38	86	74	83
L4	0	121	60	33	129	98	19	32	73	57	37	30	42	64	71
L5	0	83	56	35	88	100	16	42	53	54	20	30	47	46	63
L6	0	76	64	31	52	50	28	38	75	76	13	44	64	78	70
E1	0	28	57	31	16	20	7	15	69	126	77	24	31	48	51
	5	36	36	10	9	13	5	50	14	134	20	8	32	31	37
	10	35	31	10	9	11	4	31	25	10	21	7	34	31	24
	20	37	26	20	11	13	8	13	21	15	18	10	43	23	27 }
	25	—	—	—	—	—	—	—	—	—	—	—	—	—
	50	52	36	13	14	12	7	20	28	16	18	8	53	79	36
	70	75	32	18	20	22	19	16	33	25	17	13	59	41	46
Integral mean, Station E1	—	46	33	16	13	14	9	20	26	29	12	47	48	35

F. A. J. ARMSTRONG

TABLE 5. IRON CONTENT OF SEA-WATER SAMPLES FROM POSITIONS IN ENGLISH CHANNEL AND OFF BRITTANY COAST

(Depth in metres. Iron content in μg Fe/l.)

49° 27' N., 4° 42' W. 14 Nov. 1956		48° 34' N., 5° 13' W. 14 Nov. 1956		48° 18' N., 5° 18' W. 14 Nov. 1956	
Depth	Iron	Depth	Iron	Depth	Iron
0·5	45	0	66	0	90
5	33	5	30	5	27
10	45	10	56	10	25
20	34	20	52	20	31
50	37	50	53	50	35
90	19	100	14	100	35
		110	35	105	41

47° 50' N., 5° 22' W. 14 Nov. 1956		47° 35' N., 4° 20' W. 15 Nov. 1956	
Depth	Iron	Depth	Iron
0	61	0	126
5	61	10	26
10	62	20	28
20	61	50	40
50	49	75	24
100	86	100	109
125	158	105	126

TABLE 6. IRON CONTENT OF SEA-WATER SAMPLES FROM POSITIONS IN THE BAY OF BISCAY

(Depth in metres. Iron content in μg Fe/l.)

48° 00' N., 10° 05' W. 29 Apr. 1955		47° 33' N., 07° 27' W. 8 May 1955		46° 27' N., 08° 04' W. 27 June 1955		47° 30' N., 08° 00' W. 28 May 1956	
Depth	Iron	Depth	Iron	Depth	Iron	Depth	Iron
0	46	10	17	0	23	90	21
10	13	100	154	10	7	170	6
100	45	200	290	50	11	260	7
600	10	265	22	100	7	350	9
745	10	275	7	200	146	490	4
885	13	355	17	300	15	660	4
1025	11	435	29	400	13	860	5
1280	7	600	27	500	21	1100	9
1670	11	720	22	585	8	1500	6
2060	8	810	50	655	26	1890	7
2650	1	910	39	780	10	2180	11
2950	21	1050	34	930	27	2580	9
3250	58	1190	77	1080	9	3190	4
3540	37			1150	9	3700	7
				1320	15	4000	8
				1520	9	4570	5
				1720	16		
				1945	5		
				2245	7		
				2540	6		
				2840	10		
				3140	13		
				3440	12		
				3700	5		
				3990	18		
				4270	9		
				4460	4		

SUMMARY

A method, suitable for routine use, of determining total iron in sea water is described. The water is acidified to about 0·13N with hydrochloric acid and is heated for 5 h in an autoclave at 140° C. Iron is determined absorptiometrically with 1:1 phenanthroline after reduction with hydroxylamine hydrochloride.

Tests of the method, collection and storage of samples and the variability of results are described.

Iron contents of water samples from the English Channel and the Bay of Biscay are reported.

REFERENCES

ALLEN, E. J. & NELSON, E. W., 1910. On the artificial culture of marine diatoms. *J. mar. biol. Ass. U.K.*, Vol. 8, pp. 421–74.

ARMSTRONG, F. A. J. & ATKINS, W. R. G., 1950. The suspended matter of sea water. *J. mar. biol. Ass. U.K.*, Vol. 29, pp. 139–43.

COOPER, L. H. N., 1935. Iron in the sea and in marine plankton. *Proc. roy. Soc.* B, Vol. 124, pp. 419–38.

—— 1948. The distribution of iron in the waters of the Western English Channel. *J. mar. biol. Ass. U.K.*, Vol. 27, pp. 279–313.

FORTUNE, W. B. & MELLON, M. G., 1938. The determination of iron with O-phenanthroline. *Industr. Engng Chem. (Anal.)*, Vol. 10, pp. 60–4.

GOLDBERG, E. D., 1952. Iron assimilation by marine diatoms. *Biol. Bull., Woods Hole*, Vol. 102, pp. 243–8.

HARVEY, H. W., 1927. The supply of iron to diatoms. *J. mar. biol. Ass. U.K.*, Vol. 22, pp. 205–19.

HILL, R., 1930. A method for the estimation of iron in biological material. *Proc. roy. Soc.* B, Vol. 107, pp. 205–14.

LEWIS, G. J. & GOLDBERG, E. D., 1954. Iron in marine waters. *J. mar. Res.*, Vol. 13, pp. 183–97.

RAKESTRAW, N. W., MAHNCKE, H. E. & BEACH, E. F., 1936. Determination of iron in sea water. *Industr. Engng Chem. (Anal.)*, Vol. 8, pp. 136–8.

THOMPSON, T. G. & BREMNER, R. W., 1935. The occurrence of iron in the waters of the north-east Pacific Ocean. *J. Cons. int. Explor. Mer*, Vol. 10, pp. 39–47.

THOMPSON, T. G., BREMNER, R. W. & JAMIESON, M., 1932. Occurrence and determination of iron in sea water. *Industr. Engng Chem. (Anal.)*, Vol. 4, pp. 288–90.

THOMPSON, T. G. & TAYLOR, H. J., 1933. Determination and occurrence of fluorides in sea water. *Industr. Engng Chem. (Anal.)*, Vol. 5, pp. 87–9.