

Summarizing the experimental results: (1) there is no detectable amount of hypiodite in sea water; (2) the system iodine, iodide, hypiodite and iodate reaches a thermodynamical equilibrium rather quickly with iodide and iodate ions as predominant components; (3) even in the presence of oxygen, the oxidation of iodide to a higher oxidized state does not occur easily; otherwise iodate would be only one possible state of iodine in an oxygenated sea water. For reasons (2) and (3), iodine in sea water remains in practice in two states, namely, iodide and iodate.

Shaw and Cooper's view that the ratio of hypiodite to iodide is unity is thus untenable: as a matter of fact, even if the values are limited to those of the off-shore waters of Honshu^{1a}, to which they refer, the ratio varies from 0.88 to 1.75 with an average of 1.43, a value which cannot be easily made unity in round figures when the accuracy of determination is taken into consideration. Furthermore, among our later results from other regions^{1b}, which were apparently not available to them when formulating their views, we find many extreme values such as, for example, those for the 0 m. sample from station Satsuma 29, lat. 03° 38' N., long. 141° 56' E., 0.00 $\mu\text{gm. atom iodide-iodine/litre}$ with iodate-iodine/iodide-iodine = 0.00, while for the 0 m. sample from station Satsuma 5, lat. 13° 54' N. and long. 150° 57' E., iodate-iodine and iodide-iodine are respectively 0.21 $\mu\text{gm. atom/litre}$ and 0.04 $\mu\text{gm. atom/litre}$, with the ratio iodate-iodine/iodide-iodine equal to 5.2.

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- ^{1(a)} Sugawara, K., "Distribution of Some Minor Bio-Elements in Western Pacific Waters", Proc. Regional Symp. Physical Oceanography, Tokyo, 1955 (published by Unesco, 1957). (b) Sugawara, K., and Terada, K., *J. Earth Sci., Nagoya Univ.*, **5**, 81 (1957).
² Sugawara, K., Koyama, T., and Terada, K., *Bull. Chem. Soc. Japan*, **28**, 494 (1955).
³ Li, C. H., and White, C. F., *J. Amer. Chem. Soc.*, **65**, 335 (1943).

WINKLER¹ has demonstrated that a substantial part of the iodine naturally present in sea water is in an oxidized form which he considered to be iodate. I have suggested that the bactericidal nature of sea water towards coliforms is due to the presence of this iodate².

Shaw and Cooper³ have recently published a communication on the mechanism of iodine oxidation in sea water in which they demonstrate thermodynamically that aerial oxidation of iodide would take place at the *pH* of sea water. They recognize that the thermodynamically stable form of oxidized iodine at this *pH* is iodate, but on the grounds of the third-order kinetics of the hypiodite-iodate conversion, and the presence of biological activity, claim that iodate would not be formed. They consider that the oxidized form of iodine present would be an equilibrium mixture of iodine and hypiodous acid (hypiodite).

My work on the coast of New Zealand is not in agreement with these views, as the experimental evidence indicates that the oxidized form of iodine present in the local sea water is iodate, with no evidence for the presence of a detectable amount of

hypiodite. This experimental evidence is briefly as follows.

(a) Upon the addition of excess iodide to local sea water, a formation of the triiodide ion is not observed spectrophotometrically at 356 $m\mu$, or by the formation of a blue colour with starch, unless the solution is, in each instance, first acidified. If, as according to Shaw and Cooper, the iodine was present as hypiodite, then the above reactions would have been given without acidification. Solutions of iodate of equivalent concentrations to that found in sea water react only when acidified.

(b) When the amount of oxidized iodine is estimated as above, the concentration of oxidizing material found is too great to be other than iodate. In my earlier paper I showed that the amount of oxidizing material was equivalent to 150 $\mu\text{gm./litre}$ of iodine, that is, the amount of iodate which would be formed from 25 $\mu\text{gm./litre}$ of iodine, which is in agreement with the observations of Winkler¹ and others⁴. If this amount of oxidizing substance were hypiodous acid or hypiodite, then it would need to have been formed from 75 $\mu\text{gm./litre}$ of iodine, which is more than is usually regarded as being present.

In the light of the above evidence I consider that the local sea water contains iodate. Sulphamic acid was used for the acidifications as it effectively prevents interference from nitrite.

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- ¹ Winkler, L. W., *Z. angew. Chem.*, **29** (1), 205 (*Brit. Chem. Abs.*, A, ii, 389; 1916).
² Johannessen, J. K., *Nature*, **180**, 285 (1957).
³ Shaw, T. I., and Cooper, L. H. N., *Nature*, **180**, 250 (1957).
⁴ Harvey, H. W., "The Chemistry and Fertility of Sea Waters" (Cambridge Univ. Press, 1955).

TAKEN together, Sugawara and Terada's experiment A and Johannessen's evidence form more cogent reasons for believing iodate to be the oxidized form of iodine in the sea than the reasons we presented for believing hypiodous acid to be the oxidized form. However, as we indicated, the volatility of iodine from sea water seems to demand that a large part of the iodine should be in the form of hypiodite. Unless the volatility can be explained quantitatively in terms of an iodate-iodide mixture, the state of iodine in the sea cannot be considered as satisfactorily settled.

Moreover, we find that whereas Sugawara and Terada's conclusions upon the rate of oxidation of iodide in the sea are doubtful, their conclusions upon iodide-iodate-hypiodite equilibration have slender experimental foundation.

First, if iodide oxidation in the sea were as slow as Sugawara and Terada's laboratory experiment—and one that we have made—suggest, then we should expect that turbulent mixing would prevent variations in the amount of oxidized iodine between neighbouring portions of sea water. Sugawara¹, however, has presented results showing that the amount of oxidized iodine varies between samples taken simultaneously at the same station but differing in depth by only a few metres. He finds, for example, at the surface on station 1 a total concentration of iodine of 41.3 $\mu\text{gm./litre}$ and a concentration of iodide of 15.8 $\mu\text{gm./litre}$, whereas at 10 m. the total iodine is 41.4 $\mu\text{gm./litre}$