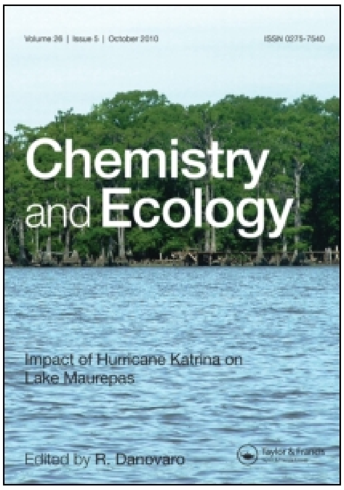

**Chemistry and Ecology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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**To cite this Article** Barbolani, Emilia and Piccardi, Giovanni(1986) 'Assessment of Iodine Direct Titration in Sea Water by Constant Current Potentiometry', Chemistry and Ecology, 2: 3, 175 — 179

**To link to this Article: DOI:** 10.1080/02757548608080722

**URL:** http://dx.doi.org/10.1080/02757548608080722

*Chemistry in Ecology*, 1986, Vol. 2, pp. 175–179
0275-7540/86/0203-0175 $18.50/0

Printed in the United Kingdom

# Assessment of Iodine Direct Titration in Sea Water by Constant Current Potentiometry†

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Dissolved iodine in sea water, about 60 $\mu g\,L^{-1}$, usually exists in equal proportions as iodate and iodide ions. For their determination several techniques have been proposed (Riley, 1975); among them the volumetric one which depends upon the release of elementary iodine by the addition of acid and iodide ions to the iodate present in the sample. The liberated iodine is titrated with thiosulphate the equivalence point being detected photometrically (Matthews and Riley, 1970; Wong and Brewer, 1974) or it can also be reduced with an excess of thiosulphate and the residual thiosulphate back-titrated with iodate amperometrically (Barkley and Thompson, 1960; Truesdale and Spencer, 1974; Tsonkova and Kulev, 1981). To titrate total iodine in the sample the iodide must be previously oxidized to iodate with bromine (Barkley and Thompson, 1960; Tsonkova and Kulev, 1981) or permanganate (Schnepfe, 1972). In the amperometric procedure Truesdale and Spencer (1974) observed that platinum electrodes often do not respond reliably.

To avoid this drawback and the error introduced by the back-titration, direct titration using controlled current potentiometry with

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† Presented at the Symposium on Analytical Problems in the Marine Environment, Genoa, 23–24 May, 1983.

two indicator electrodes is described in the present study. The titrating agent is a $10^{-4}$ N phenylarsine oxide solution which is much more stable than a sodium thiosulphate solution of similar concentration. The determinations are carried out with a microcomputer-controlled titrator composed of a Rockwell AIM 65, a Metrohm dosimat 655, a Metrohm potentiometer 605 and an $x$–$y$ recorder W + W 314. The titrant is added stepwise in equal volumes each time. Successive additions are effected only when the potential variation is less than a programmed value.

In the titration at constant current with two indicator electrodes of a reversible system with an irreversible one, a large break in potential is found at the equivalence point (Delahay, 1954). This break is anticipated with increasing current at a given dilution and with increasing dilution at constant current. However in titration of very dilute iodine solution the potential break shift from the equivalence point may be calculated. In fact the equation of the current-potential curve for a fast system when oxidant and reductant are contemporaneously present (Heyrovský and Kûta, 1966) is

$$E - E_{1/2} - \frac{0.059}{n} \log \frac{i - I_d}{i_d - i} \tag{1}$$

where $i_d = k[\mathrm{ox}]$ and $I_d = -k'[\mathrm{red}]$.

At the beginning of the titration:

$$x = 0, \qquad [i_d]_0 = kC_0 \quad \text{and} \quad [I_d]_0 = -k'C_0'.$$

During the titration, before the equivalence point:

$$0 < x < 1, \qquad [\mathrm{ox}] = C_0(1 - x) \quad \text{and} \quad [\mathrm{red}] = C_0' + C_0x.$$

These values can now be substituted in Eq. (1) giving

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{\dfrac{i}{[i_d]_0} - \dfrac{[I_d]_0}{[i_d]_0} + \dfrac{k'}{k}x}{1 - x - \dfrac{i}{[i_d]_0}} \tag{2}$$

The logarithm of the second term of the Eq. (2) goes towards infinity when the denominator of the fraction is going towards zero, i.e. when

$$x = 1 - \frac{i}{[i_d]_0}.$$

The lower the value of the fraction $i/[i_d]_0$ the nearer shall be the asymptote of the curve $E$ vs $x$ to the true equivalence point ($x = 1$). This condition is obtained by decreasing the magnitude of the titration current $i$ and increasing the size of the electrodes thus producing an increase of $[i_d]_0$. We have observed that by using electrodes of identical size (each one $cm^2$ 2) and a 0.5 $\mu$A constant current the end point, represented by a large potential break, occurs before the equivalence point and the error is lower than 1% for an iodate concentration higher than $1.4 \times 10^{-5}$ M. With more diluted solutions, as in the example in Figure 1, the flex of the titration curve occurs before the equivalence point; this is indicated by the beginning of the rectilinear final part of the curve. This was experimentally confirmed by several titrations of identical amounts of iodine at various dilutions. On an arbitrary scale, as in Figure 1, the curve obtained from Eq. (2) is shown with the titration curve. The $[i_d]_0$ value in such an equation was measured polarographically using, as a working electrode, the same platinum electrode that works as cathode in the potentiometric titration. In order to find the optimal conditions for the determinations of $IO_3^-$ and $I^-$ in sea

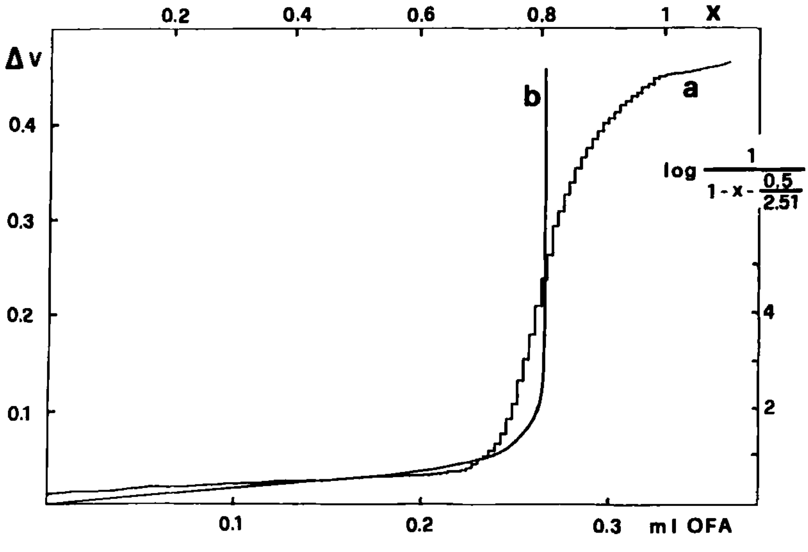

FIGURE 1 Titration of 100 ml of a solution $2.99 \times 10^{-7}$ M $KIO_3$ in NaCl 3%: (a) titration curve with phenylarsine oxide, (b) curve calculated from Eq. (2).

water, known concentrations of $KIO_3$ or/and KI in 3% NaCl solutions were examined. The determination of iodine, which is completely released from $IO_3^-$ by an excess of $I^-$ only in acid medium, must be carried out at $pH < 3$. We have observed that in such conditions the determinations of low $IO_3^-$ levels is affected by errors in excess, since in acid medium the added iodide is also slowly oxidized to iodine by the oxygen dissolved in water. Bubbling nitrogen is then necessary before the addition of iodide. Truesdale and Spencer (1974) showed that the results of iodate determinations are heavily dependent upon the concentration of KI added if it is less than $1.5\,g\,L^{-1}$. Therefore in their procedure a $6\,g\,L^{-1}$ concentration of KI is recommended. Since the iodate content of a reagent grade KI is $\leq 0.0003\%$ (ACS Specifications 1960), the suggested addition of KI introduces of itself an $IO_3^-$ amount of the same magnitude of iodate to be detected. In our experimental method (direct titration) such a source of error is avoided since 1 ml of 1% solution in 100 ml sample is sufficient to ensure the complete formation of $I_3^-$. Several titrations on 100 ml of 3% NaCl containing iodate in the range of 3 $\mu$g iodine have been carried out.

Acidification at $pH = 2.5$ was performed by sulphamic acid in order to eliminate $NO_2^-$ which may be present in sea water. As previously reported the dissolved oxygen was removed by aeration of the solution with nitrogen for 15 minutes and then 1 ml of 1% KI solution was added. The solution was allowed to stand 2 minutes and then the titration with $5 \times 10^{-4}$ N OFA was performed. The iodide determination involves a previous oxidation to iodate and then a treatment, in acid medium, with an excess of iodide as previously described. Bromine was employed as oxidant agent, similarly by other authors. (Barkley and Thompson, 1960; Tsonkova and Kulev, 1981). However oxidation by means of bromine vapour, as proposed by Barkley and Thompson (1960), was not suitable because of the loss of iodine, the first product of oxidation, due to volatilization by the action of vapours. Therefore we preferred to use bromine water freshly prepared by bubbling $Br_2$-saturated air into redistilled water. The sample was evaporated on a water bath to one fifth of the original volume to remove excess bromine completely. According to our experience the addition of a small quantity of $NH_4Cl$ aids the removal because it is oxidized by the bromine to nitrogen. The two determinations previously described are carried out on mixtures of $IO_3^-$ and $I^-$ in the same range of concentrations as can be found in sea water, by using aliquots of the same sample. In this case, after oxidation by $Br_2$, the sum $IO_3^- + I^-$ is obtained, iodide being calculated from the difference between the two titrations.

Preliminary tests indicate the reliability of this method for determinations in sea water samples. A wider investigation is in progress in our Institute in order to obtain more information about the actual selectivity of this method. In the authors' opinion this can be achieved by analyzing several sea water samples of different origin.

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