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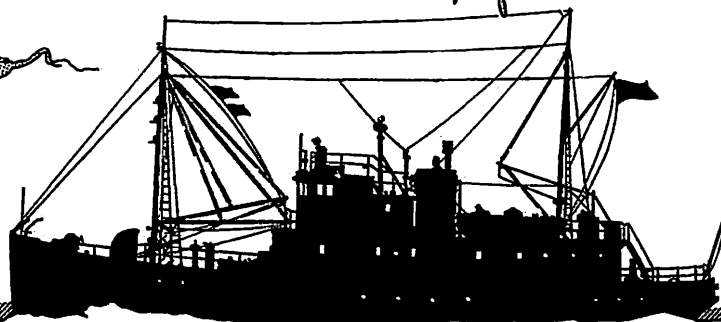
DEPARTMENT OF OCEANOGRAPHY UNIVERSITY OF WASHINGTON

Technical Report No. 64
ON THE COASTAL GENERATION OF
INTERNAL TIDES

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DETERMINATION OF CHEMICALLY COMBINED
IODINE IN SEA WATER BY AMPEROMETRIC
AND CATALYTIC METHODS

Office of Naval Research
Contracts N8onr-520/III
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Reference 60-23
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Maurice Rattray, Jr.

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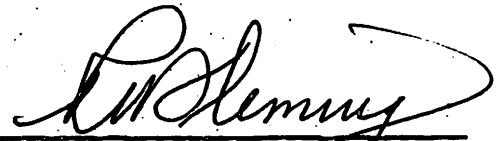
BY AMPEROMETRIC AND CATALYTIC METHODS

by

Richard A. Barkley and Thomas G. Thompson

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RICHARD H. FLEMING
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Determination of Chemically Combined Iodine in Sea Water by Amperometric and Catalytic Methods

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Iodine, in the form of iodides and iodates, exists in sea water in very small concentrations. In previous studies iodine has been concentrated from large samples by precipitation, extraction, or distillation. Using amperometric or catalytic methods the iodine may be determined directly on relatively small samples in much less time and with elimination of loss of iodine inherent in other methods. For extensive oceanographic studies the two methods may complement one another. The amperometric method permits ready determination of iodine in the form of iodate and iodide. The catalytic method permits determination of total iodine more rapidly and accurately than the amperometric method. The difference between the total iodine and the iodate-iodine gives the iodide-iodine. Some data are given for the distribution of iodine in the Northeast Pacific.

Two methods for the determination of chemically combined iodine were examined for application to the analysis of sea water. The amperometric method permits direct titration of free or liberated iodine at extremely low concentrations by applying the very sensitive electrode system developed by Potter and White (11). The system responds to the presence of $10^{-11}M$ concentrations of elemental iodine. The catalytic method of Lang (10), later studied by Sandell and Kolthoff (12), utilizes the acceleration of the reaction between ceric sulfate and arsenous acid by iodine.

Investigations of the iodine content of sea water were begun soon after the discovery of the element by Courtois in 1812. Vinogradov (20) summarizes the results of analyses of oceanic iodine published up to 1933. In 1932, Evans (5) reviewed the methods for iodine analysis used by previous investigators and reported his own findings for sea water from the Strait of Juan de Fuca. More recently, Sugawara and Terada (15) used silver nitrate to determine the iodide and total iodine content of a large number of samples from the Northwest Pacific, while Dubravacic (4) used the catalytic method to analyze sea water from the Adriatic. Although the

results of the investigations since 1916 vary from about 10 γ per liter of iodine to slightly less than 100 γ per liter, most of the values range between 40 and 60 γ per liter, with Sugawara and Terada's values (which are the most numerous), averaging about 43 γ per liter. Dubravacic (4) found 63 γ per liter in a surface sample from the Adriatic.

Prior to the development of the catalytic method for the determination of iodine, no method was sensitive enough to permit a direct determination of the element in sea water. Iodine was concentrated by precipitation, extraction, or distillation from relatively large samples and final estimation was done either colorimetrically or volumetrically.

Before Sugawara and Terada (15) presented their extensive data on iodide and iodate, few attempts had been made to determine the forms of iodine present in the oceans. Winkler (21) reported the inorganic iodine in the waters of the Adriatic as 9 γ per liter of iodide and 41 γ per liter of iodate; no iodine was found in organic combination. Cameron (3) found 2.5 γ per liter of iodide and 22.5 γ per liter of iodate in surface water of the Strait of Georgia, British Columbia. Sugawara and Terada (15) determined iodide and total iodine by precipitation as silver iodide. The iodide content of their samples varied from about 10 to 100% of the total iodine. They considered the noniodide iodine in their samples to be iodate.

Shaw and Cooper (13) suggested that the iodate thus reported was, in fact, hypiodous acid, as the reaction by which iodate would be formed in sea water is trimolecular and could be expected to proceed at a very low rate; they pointed out, however, that iodate would be the thermodynamically stable form of iodine in the oceans. Despite the empirical data presented in rebuttal by Sugawara and Terada (16) and by Johannesson (9), Shaw and Cooper (14) consider that many of the questions which they raised remain unanswered, although they agree that iodate appears to be the oxidized form of iodine in the sea.

THE AMPEROMETRIC METHOD

The amperometric method of Potter

and White (11) was used for the determination of traces of iodine in sea water. A potential of about 0.3 volt applied across two platinum electrodes causes a current to flow through the circuit. The current changes abruptly at the end point of the iodine-thiosulfate titration. In place of a galvanometer, which is normally used, Potter and White placed a resistor in series with the electrodes and measured the change in potential across the resistor. By using a vacuum-tube voltmeter capable of detecting a change in potential of 1 mv., together with a 50-megohm resistor, changes in current flow through the circuit of 10^{-11} ampere could be detected. Thus, the circuit provides a sensitivity some three orders of magnitude greater than that normally attained in amperometric titrations using a galvanometer and permits the direct titration of the $5 \times 10^{-7}M$ concentrations of iodine present in sea water. The electrode response near the end point was approximately 4×10^{-11} ampere for each change of 1×10^{-11} mole of free iodine in the solution, or a measurable change of 2 mv. for each 1×10^{-11} mole change in iodine concentration.

The determination was performed by allowing iodate in the acidified sample to react with excess iodide, liberating 6 equivalents of iodine for each equivalent of iodate originally present. A known excess amount of thiosulfate was then added and the excess was determined by back-titration with standard iodate solution. The iodate content of sea water could be determined directly, while the total iodine content was determined by first oxidizing all the iodine to iodate by means of bromine. Thus, using two aliquots of the same sample, iodine in the form of iodate and total inorganic iodine could be readily determined.

DETERMINATION OF IODATE IN SEA WATER

Apparatus. Figure 1 shows the arrangement of the apparatus together with the electrode assembly. The electrodes consisted of short lengths of platinum wire sealed into glass tubing with 1 cm. of wire exposed. The resistors were of ordinary commercial manufacture, with tolerances of 10% of the nominal value.

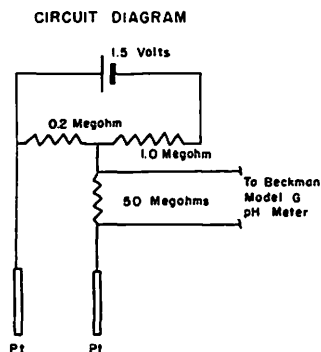


Figure 1. Circuit diagram and arrangement used for amperometric titration

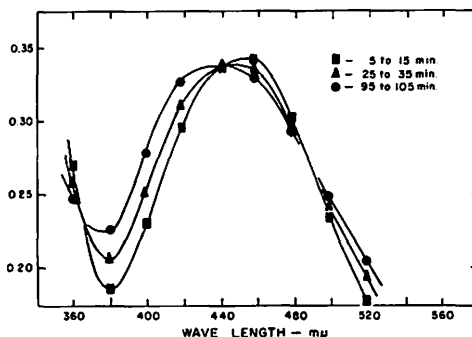
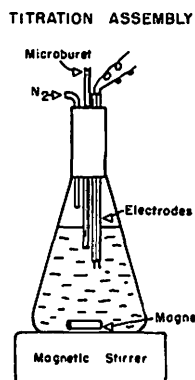


Figure 2. Brucine spectrum with time variation

To protect the assembly against moisture, the resistors were wrapped with insulating tape and the leads from the electrodes to the resistors were enclosed in flexible plastic tubing whose ends were also wrapped with tape. The required voltage was supplied by an ordinary dry cell. The dry cell was replaced every 2 or 3 months as a precautionary measure. Potentiometric measurements were made with a Beckman Model G pH meter. A 1-ml. air-controlled microburet, which delivered 0.005-ml. increments, was made and calibrated as described by Upton (19).

Reagents. SODIUM THIOSULFATE. A 0.1*N* stock solution was prepared by dissolving 25 grams of the pentahydrate salt in 1 liter of freshly boiled distilled water. About 1 ml. of carbon disulfide was added as a preservative. A 0.0002*N* working solution was prepared daily, first by diluting 10 ml. of the stock solution to exactly 100 ml. with freshly boiled distilled water, and then by diluting 20 ml. of the resulting solution to exactly 100 ml.

STANDARD IODATE SOLUTION. A 0.0500*N* stock solution was prepared by dissolving 1.9496 grams of potassium acid iodate in exactly 1 liter of water. A working solution, 0.000500*N*, was prepared by successive dilutions.

ACETIC ACID. A 25% solution was made by diluting 250 ml. of glacial acetic acid to 1 liter.

NITROGEN. Water-pumped tank nitrogen was bubbled through pyrogallol and distilled water, and then into the apparatus to remove oxygen from the solution to be titrated.

POTASSIUM IODIDE. Iodate-free reagent grade crystals were used directly to provide the required excess of iodide for titration.

Procedure. A 100-ml. sample of sea water was placed in a 125-ml. Erlenmeyer flask and acidified by the addition of 10 ml. of 25% acetic acid. Dissolved oxygen was removed by passing nitrogen through the solution for 15 minutes. Then 1 ml. of 0.0002*N* thiosulfate solution was added, followed by two or three crystals of potassium iodide. With the electrodes in position, the titration was performed by adding increments of iodate solution until the potentiometer needle showed a deflection; thereafter,

small increments were added, with careful measurement of the potential 30 seconds after each addition. The end point was located by plotting potential against volume added, the intercept of the pre- and the post-end point curves being taken as the required volume for titration.

The volume of iodate solution used in titrating the unknown sample, subtracted from the volume required to titrate the same volume of thiosulfate in a blank determination, was the iodate equivalent of the sample.

In adjusting the pH meter for the titration, the bridge was rebalanced each time the potential changed significantly to prevent disturbance in the electrode circuit by the unbalanced bridge. The resistance of the potentiometer must be higher than that in the electrode circuit, otherwise the meter will act as a shunt and the results will be meaningless.

Prior to initial use, the electrodes were pretreated as suggested by Potter and White (11) and needed no further attention. The electrodes were always kept immersed. Between titrations, the electrodes were simply rinsed with distilled water.

Standardization. The reagents used in the titration were standardized against each other at each step in the dilution of the stock solutions to the working concentration, with the stock acid iodate as the original standard.

In the standardization of the 0.0002*N* thiosulfate solution in nine determinations, 1 ml. of the solution in redistilled water required a mean of 0.349 ml. of standard iodate solution, the minimum value being 0.344 ml. and the maximum 0.360 ml. The standard deviation was 0.012 ml.

DETERMINATION OF TOTAL IODINE IN SEA WATER

The apparatus used is the same as described previously.

Reagents. In addition to the reagents and standards listed above, reagent grade bromine was purified by shaking with potassium bromide and distilling in an all-glass apparatus.

Procedure. A 100-ml. sample of sea water was placed in a 125-ml. Erlenmeyer flask and acidified by the addition of 10 ml. of 25% acetic acid.

Table I. Recovery of Added Iodide by the Amperometric Method

Iodine Added, γ	Iodine Found, γ	Error, γ
0.00	0.54	+0.54
2.00	1.96	-0.04
4.00	3.96	-0.04
6.00	6.05	+0.05
8.00	8.09	+0.09
10.00	10.00	0.00
0.20	0.26	+0.06
0.50	0.49	-0.01
1.00	1.12	+0.12
0.00	0.57	+0.57

Bromine vapor was then poured into the flask (with swirling to mix the vapor with the sample) until the latter had a distinct coloration. The sample was evaporated on a water bath to one half the original volume to remove excess bromine completely, then the sample was diluted to 100 ml. with distilled water, and the titration was conducted as described above.

In oxidizing the sample with bromine, the pH of the solution should not be less than about pH 2, as Evans (6) has shown that the reaction is reversible in strongly acid solutions and that elemental iodine is lost when the sample is heated too vigorously to remove excess bromine.

Ten determinations for total iodine were run on the same sample of sea water, which had a chlorinity of 16.82‰. The mean value for total iodine was 48.3 γ per liter, the minimum result being 45.5 γ per liter and the maximum 51.0 γ per liter. The standard deviation was 2.1 γ per liter.

To test the procedure for total iodine, known amounts of iodide were added to redistilled water and the solutions were analyzed. The results (Table I) indicate that the error of the determination is almost constant in the range 0.5 to 10 γ in 100-ml. samples.

THE CATALYTIC METHOD

Browning and Cutler (2) showed the rate of reaction between the arsenous and ceric ions to be exceedingly small. Feigl (6) postulated a mechanism for the iodine-catalyzed reaction. Reaction rates have been measured in various ways for the determination of iodine (7, 8, 12). The effects of chloride on

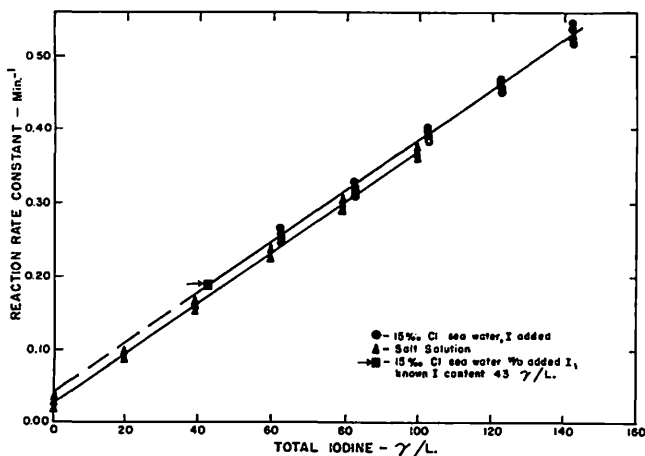


Figure 3. Reaction rate constant vs. total iodine content

the determination of iodine were discussed by Dubravacic (4).

The reaction rate is a function of the concentrations of iodine, ceric ion, and arsenous acid. Iodine, however, does not vary in concentration in any one sample, because it acts as a catalyst. Arsenous acid is added in large excess of the amount required to react with the ceric sulfate so that the changes in arsenous acid concentration during the course of the reaction are negligible. Under these circumstances the reaction appears to proceed with first-order kinetics, which obey the integral equation:

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[\text{CeIV}]_1}{[\text{CeIV}]_2}$$

The first-order reaction rate constant, k , can be computed by measuring the ceric ion concentrations at various times during the reaction. The rate constant, in turn, can be empirically related to the iodine concentration in the sample.

Brucine was the most satisfactory reagent for measuring the ceric ion concentration. It reacted instantly with any remaining ceric ion to quench the catalytic reaction and at the same time produced a coloration which was directly proportional to the ceric ion concentration. The color was stable for 2 hours or more. Figure 2 shows the spectrum of the brucine coloration and its changes with time. The maximum absorption occurs initially near 460 $m\mu$, shifts to about 450 $m\mu$, and finally to about 440 $m\mu$ after 30 and 100 minutes, respectively. A region near 440 $m\mu$ shows little change in absorption with time and this wave length was thus chosen for measurements. The effect of temperature upon absorptivity between 17° and 32° C. was negligible.

Osmium, iodine, and bromine (1, 12) act as catalysts, with osmium being the most active and bromine the least. To ensure the presence of constant concentrations of bromide in the samples of sea water (17, 18) as well as of other

ions in sea water which occur in constant proportions, the samples were always diluted to the same chlorinity. Sea water which had been treated with silver nitrate to remove the halides showed no catalytic activity.

DETERMINATION OF TOTAL IODINE IN SEA WATER

Apparatus. A Beckman Model DU spectrophotometer with 1-cm. glass cells was used to measure the absorptivity. An 80-liter water bath with stirrer and heater, maintained at 30.00° ± 0.05° C., was used to control reaction temperature. The reaction vessels were 32 × 160 mm. test tubes which were fitted into holes in a sheet of foamed polystyrene floated in the water bath. The ceric reagent was supported inside the bath to keep it at the required temperature. Aliquot portions of the reaction mixtures were removed from the test tube with a 5-ml. dispenser manufactured by the California Laboratory Supply Co. These T-shaped dispensers were attached to the mouth of each test tube reaction vessel, filled by rotating the assembly through an angle of 90°, and emptied by returning the assembly to the vertical position. The dispensers delivered volumes reproducible within 1%.

Reagents. ARSENOUS ACID. First, 19.8 grams of reagent grade arsenic trioxide were dissolved in 200 ml. of warm distilled water containing 8.0 grams of sodium hydroxide; then the solution was diluted to about 800 ml., acidified with 94 ml. of 18N sulfuric acid, and, after cooling, diluted to 1 liter.

SULFATOCERIC ACID. A 0.016N solution in 1.5N sulfuric acid was prepared by dissolving 10.1 grams of reagent grade ceric ammonium sulfate dihydrate in 200 ml. of distilled water to which had been added 41.4 ml. of 36N sulfuric acid. The solution was diluted to 1 liter, allowed to stand for 3 days, and then filtered through a Millipore filter.

BRUCINE REAGENT. Exactly 2.5 grams of brucine were dissolved in 500 ml. of distilled water containing 14 ml. of 36N sulfuric acid. This solution must be kept in brown glass

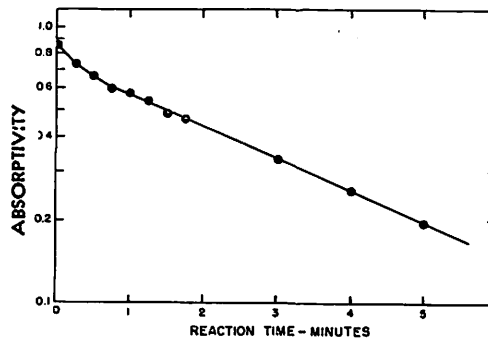


Figure 4. Typical reaction curve

bottles, where it remains usable for 2 to 3 weeks.

Procedure. The samples of sea water were filtered through a Millipore filter, their chlorinities were determined, and 25 ml. of each sample were diluted with redistilled water to give a chlorinity of 15 ‰; 25 ml. of the diluted sample were placed in a large test tube, 20 ml. of the arsenous acid reagent were added, and the solutions were thoroughly mixed. The test tubes were then placed in the water bath for 30 minutes.

The reaction was initiated by adding 5 ml. of the ceric reagent, mixing as rapidly as possible, and replacing the reaction vessel in the water bath. A stop watch was started just as the ceric reagent was added. Subsequently, a minimum of four 5-ml. aliquots of the reaction mixture were removed at predetermined intervals and quenched by pouring each into a small test tube containing 1 ml. of brucine reagent. The aliquots were taken by starting to fill the attached dispenser 10 seconds before the scheduled time, emptying the aliquot into brucine at exactly the time desired, and allowing 10 seconds for reproducible drainage of the dispenser. Normally, aliquots were taken every 2 minutes until four had been quenched.

The absorptivities of the quenched aliquots were then measured (in the same order in which they were taken) in the spectrophotometer at 440 $m\mu$, with a slit width of 0.04 mm. and a distilled water comparison cell. After the reaction had gone to essential completion and no ceric ion coloration remained in the mixture, a fifth aliquot was removed which, when quenched with brucine, was measured in the spectrophotometer; the reading thus obtained was subtracted from the readings obtained with the previous aliquots as a reagent blank correction.

The corrected absorptivities of the quenched aliquot portions were substituted into the first-order reaction rate constant equation to obtain a numerical estimate of the reaction rate constant of the sample. The absorptivities of the 1- and 5-minute aliquots and the 2- and 6-minute aliquots were used separately to obtain two individual values for the rate constant of one sample. Where the two rate constants differed by more than 5%, the absorptivities were plotted against time on

semilog graph paper, the best fit line was drawn through any three of the four points, and the rate constant was calculated graphically.

Calibration. Known amounts of iodine were added to sea water, which had been diluted to 15 ‰ Cl, to obtain a calibration curve of reaction rate against iodine content (Figure 3). As a check on the linearity of the calibration curve at iodine contents below that of the sea water used for calibration, an artificial iodine-free sea water was prepared from purified salts and adjusted to 15 ‰ Cl; then various known amounts of iodine were added. This curve is also shown in Figure 3. Both curves were straight and parallel, justifying the extrapolation of the sea water calibration curve in the direction of lower iodine concentrations. Bromide was added to artificial, iodine-free sea water to produce another calibration curve.

A least-squares treatment of all the calibration data resulted in the following linear equation, applicable to sea water diluted to 15 ‰ Cl, with the reagents and methods given above:

$$k = 0.013 \text{ min.}^{-1} + 3.6 \times 10^{-4} \frac{\text{min.}^{-1}}{\text{mg. Br/liter}} + 3.70 \frac{\text{min.}^{-1}}{\text{mg. I/liter}}$$

where the term 0.013 min.^{-1} was the rate constant due to the reagents in either redistilled water or artificial sea water. The bromide term in the equation can be considered a constant, 0.019 min.^{-1} , because the Br/Cl ratio for sea water was shown to be constant by Thompson and Karpi (18). Their data showed a mean value for the ratio Br/Cl of 0.00347 with a range of 0.00344 to 0.0351, so that 52 mg. per liter of bromide should be present in 15 ‰ Cl sea water. This amount of bromide has a catalytic effect equivalent to the effect of 0.005 mg. I per liter (5 γ per liter), so that even 100% variation in the bromide concentration would produce an error in the iodine determination in sea water of only 10%. The equation for computing the iodine concentration from a determination of the rate constant is therefore:

$$I(\gamma/\text{liter}) = \frac{k - 0.032}{3.70} \times 10^3 = \frac{10\%}{3.70} - 8.6$$

As an additional check on the validity of the calibration, the iodine content of the sea water used for calibration was determined by means of the amperometric method; an iodine value of 48.3 γ per liter was obtained for the original sample at 16.82 ‰ Cl, so that 43 γ per liter were present in the sample when diluted to 15 ‰ Cl. This value

Table II. Iodine Determinations by the Amperometric and Catalytic Methods

Station	Nominal Depth, Meters	Chlorinity, ‰	Total Inorganic Iodine Found, γ /Liter		Difference, γ /Liter
			Catalytic method	Amperometric method	
Station A 52°06'N, 167°39'W, Aug. 2, 1957					
	0	18.06	58	57.8	0.2
	10	18.06	61	58.6	2.4
	25	18.06	58	56.0	2.0
	40	18.07	58	54.9	3.1
	80	18.18	59	63.5	-4.5
	120	18.50	59	58.5	0.5
	175	18.75	65	61.0	4.0
	300	18.84	65	67.8	-2.8
	400	18.90	67	63.0	4.0
	600	18.98	62	64.5	-2.5
	800	19.02	64	65.0	-1.0
	1000	19.04	64	63.2	0.8
	1200	19.08	65	66.0	-1.0
	1800	19.14	61	58.8	2.2
Station B 48°35'N, 122°51'W, May 25, 1957					
	5	14.97	41	39.0	2.0
	20	16.49	46	48.5	-2.5
	45	16.91	47	46.7	0.3

Table III. Total Iodine and Iodate Iodine Found in Sea-Water Samples

Station	Depth, Meters	Chlorinity, ‰	Total Iodine, ^a γ /Liter	Iodate-Iodine, ^b γ /Liter
Station A 52°06'N, 167°39'W, Aug. 2, 1957				
	60	18.10	57	30.2
	100	18.30	58	25.6
	150	18.68	58	28.0
	200	18.77	68	32.5
	300	18.86	63	26.0
	500	18.94	61	29.7
	700	19.00	63	21.4
	900	19.04	65	27.0
	1100	19.07	62	30.3
Station B 48°35'N, 122°51'W, May 25, 1957				
	10	15.92	42	20.5
	30	16.77	46	26.8

^a Catalytic determination.
^b Amperometric determination.

agrees with that obtained in the catalytic procedure.

Iodide, elemental iodine, iodate, and periodate produced identical results with the method as given, where the sample was allowed to react with the arsenous acid for 30 minutes before the reaction was initiated. If, however, the ceric and arsenous reagents were added together or the ceric reagent was added first, iodate failed to catalyze the reaction for the first few minutes, after which the reaction rate began to increase until finally the reaction rate constant approached the value to be expected for the iodine present in the sample. This suggests that iodate per se does not act as a catalyst but must first be reduced to a lower oxidation state by reaction with arsenous acid.

Figure 4 shows the progress of a typical catalytic reaction in sea water. The rapid initial removal of ceric ion was always observed but varied in extent from sample to sample and was attributed to the removal of ceric ion by

small amounts of interfering material of unknown composition. After about 30 seconds the reaction proceeds with apparent first-order kinetics at a rate dependent only on iodine concentration when the other variables are controlled. Using the initial ceric ion concentration and only one subsequent point on the curve produces an erroneous value for the reaction rate constant. Thus, the first aliquot of the reaction mixture was not removed until 1 minute after the reaction had been initiated. The 4-minute sampling interval used in computations was chosen to ensure a minimum of error, because this is the approximate time required in most samples for the ceric ion concentration to decrease by two thirds.

RESULTS

The amperometric method was usable in the determination of iodine in sea water in concentrations down to 5 γ per liter, with a standard deviation of

2.1 γ per liter. The determination of iodate in sea water samples could be performed directly, thus minimizing the chances of iodine loss or contamination of the sample. Ferric and cupric ions in concentrations up to 280 γ iron per liter and 320 γ copper per liter (5 γ atoms per liter in each case) do not interfere. The determination of the total iodine content of sea water samples could also be done amperometrically, but the preliminary oxidation of the sample with bromine is time-consuming and introduces the possibility of contamination or iodine loss. However, the standard deviation of the total iodine determination was found to be the same as that for the iodate determination, and the values obtained agreed well with those from the catalytic method. The principal contribution of the amperometric method is that it provides a rapid means for determining the form in which iodine occurs in sea water samples.

The catalytic method for the determination of iodine in sea water was usable for minimum iodine concentrations of about 5 γ per liter, with a standard deviation of 1.3 γ per liter. The determination is direct, with no interferences present in sea water except the other halides, whose concentrations can be easily controlled. It is the most direct and rapid method for total inorganic iodine determinations in the range of concentrations encountered in sea water samples.

The catalytic and the amperometric methods for iodate and total iodine were

checked for accuracy from time to time during determinations on sea water samples by adding internal standards to duplicates of samples which had already been analyzed. Iodate or iodide standards were added at random but in fixed amounts which increased the concentrations by 40 γ per liter. For the amperometric determinations, the error was less than two standard deviations on over 90% of the determinations; for the catalytic determinations the error was greater but within three standard deviations for 90% of the samples. The increased error in the catalytic method was attributed to the marked increase in reaction rate, which made measurement difficult.

Table II gives results obtained by the two methods in total iodine on samples of sea water from various depths at two stations, one in the northeast Pacific Ocean and the other in an embayment north of Puget Sound. Table III shows data obtained on samples from the same stations analyzed for total chemically combined iodine and for the iodine in the form of iodate.

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