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- (17) Ono, N.; Yamada, T.; Saito, T.; Tanaka, K.; Kaji, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2401-2404.
- (18) Reference 10, Chapter 4.
- (19) Klelland, *Science (Washington, DC)* **1937**, *59*, 1675.
- (20) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; Chapman and Hall: London, 1974.
- (21) "IUPAC Recommendation for Nomenclature of Ion-Selective Electrodes"; *Pure Appl. Chem.* **1976**, *48*, 129-132.
- (22) Moody, G. J.; Thomas, J. D. R. *Selective Ion Sensitive Electrodes*; Merrow: Herts, England, 1971; Chapter 2.
- (23) Pioda, L. A. R.; Wipf, H. K.; Simon, W. *Chimia* **1968**, *22*, 189-191.
- (24) Ohki, M.; Takebayashi, Y.; Muto, G. *Chemical Data Book*; Baifukan: Tokyo, 1970; p 12.
- (25) Liu, C.-M.; Hermann, T. E. *J. Biol. Chem.* **1978**, *253*, 5892-5894.
- (26) Johnson, S. M.; Herrin, J.; Liu, S. J.; Paul, I. C. *J. Am. Chem. Soc.* **1970**, *92*, 4428-4435.
- (27) Maier, C. A.; Paul, I. C. *J. Chem. Soc., Chem. Commun.* **1971**, 181-182.
- (28) Kinashi, H.; Otake, N.; Yonehara, H.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 2411-2415.
- (29) Choy, E. M.; Evans, D. F.; Cussler, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 7085-7090.
- (30) Pioda, L. A. R.; Simon, W.; *Chimia* **1969**, *23*, 72-73.
- (31) Scholer, R.; Simon, W. *Helv. Chim. Acta* **1972**, *55*, 1801-1809.
- (32) Levins, R. J. *Anal. Chem.* **1971**, *43*, 1045-1047.
- (33) Schefer, U.; Ammann, D.; Pretsch, E.; Oesch, U.; Simon, W. *Anal. Chem.* **1986**, *58*, 2282-2285.
- (34) Lindner, E.; Tóth, K.; Pungor, E.; Behm, F.; Oggenfuss, P.; Welti, D. H.; Ammann, D.; Morf, W. E.; Pretsch, E.; Simon, W. *Anal. Chem.* **1984**, *56*, 1127-1131.
- (35) Tohda, K. M. Science Thesis, Keio University, 1987.
- (36) Erne, D.; Stojanac, N.; Ammann, D.; Hofstetter, P.; Pretsch, E.; Simon, W. *Helv. Chim. Acta* **1980**, *63*, 2271-2279.
- (37) Morf, W. E. *The Principles of Ion-Selective Electrodes and Membrane Transport*; Elsevier: New York, 1981; Chapter 14.
- (38) Kellner, R.; Fischböck, G.; Götzinger, G.; Pungor, E.; Tóth, K.; Polos, L.; Lindner, E. *Fresenius' Z. Anal. Chem.* **1985**, *322*, 151-156.

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Direct Determination of Iodide in Seawater by Cathodic Stripping Square Wave Voltammetry

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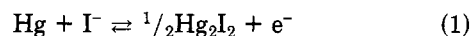
A procedure for the direct determination of iodide in seawater is described. By use of cathodic stripping square wave voltammetry, it is possible to determine low and subnanomolar levels of iodide in seawater, freshwater, and brackish water. Precision is typically $\pm 5\%$ (1σ). The minimum detection limit is 0.1–0.2 nM (12 parts per trillion) at a 180-s deposition time. Data obtained on Atlantic Ocean samples show similar trends to previously reported iodine speciation data. This method is more sensitive than previous methods by 1–2 orders of magnitude. Triton X-100 added to the sample enhances the mercury electrode's sensitivity to iodide.

Iodate and iodide are the two principal forms of iodine in seawater (1). To date, the principal methods for determining iodine speciation in marine waters have centered on the analysis of the five-electron irreversible wave of iodate using differential pulse polarography (2, 3) or the colorimetric determination of IO_3^- after conversion to I_3^- in acidic solution (4, 5). In each method iodate is determined directly on a sample. Total iodine is determined by converting iodide and organic iodine compounds to iodate via chemical (3, 5) or photochemical means (2). Thus, iodide and organic iodine are determined by difference. The minimum detectable limit of iodate obtained by using the differential pulse polarography method is near 20 nM. For the colorimetric method, the minimum detectable limit (MDL) is 30–50 nM in seawater. However, in freshwater and estuarine water, the MDL is higher due to UV absorption by naturally occurring organic matter at the wavelength for I_3^- detection (350 nm).

Total iodine concentration in seawater (35‰) is approximately 470 nM (2, 4–7). In surface ocean waters, iodate concentrations are near 300–400 nM and iodide concentrations can approach 100–200 nM (2, 4). At depth, iodate is the only

form that can be easily distinguished by these methods. Low levels of iodide (<20 nM for polarography and <70 nM for colorimetry) cannot be determined precisely. The determination of iodide by difference leaves in doubt the existence of a significant organic iodine fraction in the water column. The previously reported data are consistent with the fact that iodate is the thermodynamically stable form of iodine (8, 9) in oxygenated seawater and that iodine speciation is biologically mediated (7) in surface waters. The analytical difficulties have made it difficult to evaluate the nature of iodine reactions and the degree of iodine reactivity away from the most productive surface zone of marine waters.

To date, we are unaware of any reports analyzing iodide directly in seawater by polarographic methods. Turner et al. (10) have shown that iodide reacts with mercury in an one-electron process according to eq 1.



Propst (11) and Holak (12) have determined total iodine by converting all forms of iodine to iodide under acidic and reducing conditions and then determining iodide by cathodic stripping using normal pulse and differential pulse polarography, respectively. Although these methods are reliable for total iodine, they have not been explored for use in marine systems at seawater pH (near 8). We report on the direct determination of iodide at the pH of seawater using cathodic stripping square wave voltammetry. The method is fast and precise ($\pm 5\%$ relative standard deviation). Minimum detectable limits approach 0.1–0.2 nM. This method coupled with the direct determination of iodate allows for the speciation of iodine into its major inorganic forms.

EXPERIMENTAL SECTION

Apparatus. A Princeton Applied Research Model 384B-4 polarographic analyzer system, with a Model 303A static mercury drop electrode (SMDE) in the hanging mercury drop electrode

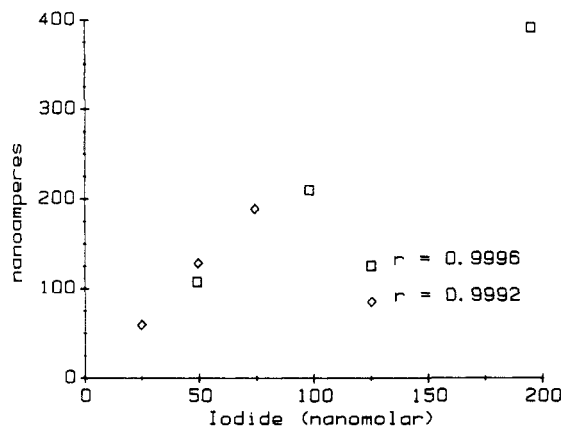


Figure 1. Standard addition curves of iodide in sodium chloride-sodium bicarbonate solution (\square) and an Atlantic Ocean surface seawater sample (\diamond): 30-s deposit; -0.10 V deposition; 20 mV pulse height; 100 Hz.

(HMDE) mode, was used for all square wave stripping work. Onboard ship we use the medium drop size because larger drops occasionally dislodge. A platinum wire served as the auxiliary electrode and a standard calomel electrode (SCE) was used as the reference electrode as described by Luther et al. (13). Briefly, the SCE makes contact with the solution via a salt bridge, which is placed in the opening on the right side of the plastic cell block of the SMDE. The Ag/AgCl reference electrode supplied with the instrument was not used in order to avoid reaction of iodide with the Ag. The Ag wire was sealed in a glass tube to prevent contact with the solution. Glass cells had a small hole drilled near the top for making standard additions to the cell. All potentials are reported vs the SCE.

Chemicals. The iodide stock solution was prepared in deionized water from potassium iodide (Fisher). The sensitivity of the method was increased dramatically by the addition of a small amount of surfactant to the cell. Good reproducible results were obtained by adding 50 μ L of a 0.2% Triton X-100 solution to each 10 mL of sample. Total Triton X-100 in the sample is thus 0.001%. The Triton X-100 solution was prepared in deionized water from the concentrated solution (Fisher). Sodium chloride (G. Frederick Smith) solutions were prepared for voltammetric parameter determinations. Typically 0.565 M sodium chloride was used because this is near the concentration of these ions in seawater. In these sodium chloride solutions, a small iodide peak was noticed consistently at a 180-s deposition time on the addition of Triton X-100 but not at 30-s deposition times.

Procedure. Samples were collected in GoFlo bottles and filtered from these bottles through 0.2- or 0.4- μ m Nuclepore filters into polypropylene bottles immediately upon collection. Some polypropylene bottles were trace metal cleaned and rinsed whereas other bottles were only thoroughly rinsed with deionized water before use. No adsorption or contamination effects have been observed with these bottles. A 10-mL aliquot of sample was added to the cell following the addition of the Triton X-100 and a small magnetic stirring bar. Samples were purged for 4 min with argon gas; a positive pressure of argon remained in the cell throughout the analysis, preventing oxygen from becoming redissolved in the sample. The scan was typically from -0.10 to -0.90 V under the following conditions: deposition potential, -0.10 V vs SCE; deposition time, 30 or 180 s; equilibration time, 5 s; scan rate, 200 mV/s; pulse height, 0.020 V; frequency, 100 Hz; mode, square wave; drop size, medium. Iodide was quantified by the method of standard additions to the seawater sample. All determinations were made in triplicate.

Sample Storage. Because very little sample preparation was required, the method was ideal for shipboard analysis. Samples that were not run immediately after collection were refrigerated or frozen for subsequent analysis.

RESULTS AND DISCUSSION

Because of our interest in determining iodine speciation, minimum sample preparation was performed. We specifically did not desire to change the pH of the seawater sample. It

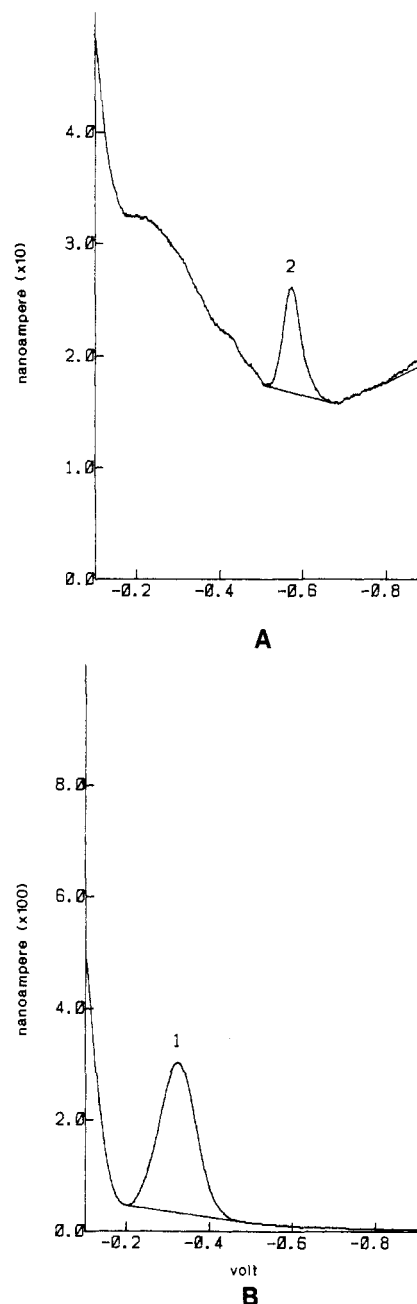


Figure 2. Voltammograms showing the iodide peak in a surface seawater sample before (A) and after (B) the addition of Triton X-100.

is well-known that acidification of solutions containing iodate can lead to some conversion of iodate to iodide. Thus, our work differs from that of Propst (11) and Holak (12) because they were interested in measuring total iodine as iodide.

Method Optimization. The voltammetric parameters chosen for analyses were determined by varying the square wave frequency or pulse height in a 0.565 M sodium chloride solution containing 4 mM sodium bicarbonate with Triton X-100. Either -0.05 or -0.10 V deposition potentials were employed. Generally we chose -0.10 V so that there would be negligible interference effects from the chloride and bromide ion peaks that have half-wave potentials near 0.16 and 0.02 V, respectively (14). Deposition time was 30 s for iodide solutions ranging from 10 to 240 nM. At a 20-mV pulse height the slopes of standard curves are typically 0.50 (25 Hz square wave frequency), 0.84 (50 Hz frequency) and 1.97 nA/nM (100 Hz frequency). Higher pulse heights increase the slope. However, the higher pulse height also gave a

Table I. Effect of Triton X-100 (0.2% (v/v)) on Peak Height for a 99.0 nM Solution of KI in 0.565 M NaCl

current, nA	Triton X-100, μ L	$E_{1/2}$, V
10.46	0	-0.174
260.7	25	-0.334
287.3	50	-0.324
295.5	75	-0.320
304.8	100	-0.316

broader wave. From these studies, we chose a pulse height of 20 mV and a square wave frequency of 100 Hz. Figure 1 shows a typical standard curve of potassium iodide in a 0.565 M sodium chloride solution containing 4 mM sodium bicarbonate using these parameters. We estimate a minimum detectable limit of 1 nM with a 30-s deposition time.

Triton X-100 Effects. We found a significant increase in sensitivity for the iodide peak with the addition of 0.2% Triton X-100. Table I shows the increase in current on addition of Triton X-100 to sodium chloride solutions containing 99 nM iodide (pulse height, 20 mV; frequency 100 Hz; 30-s deposition at -0.10 V). The increase in sensitivity levels off quickly. Figure 2 shows voltammograms of a seawater sample containing about 100 nM iodide before and after addition of Triton X-100. Figure 2A shows a broad iodide peak (not integrated) near -0.2 V in the untreated sample whereas Figure 2B shows a normal peak at -0.322 V in the treated sample. (The peak at -0.572 V in Figure 2A is due to sulfide (15).) This enhancement effect is reproducible in all seawater, brine, and sodium chloride solutions studied. To date we have analyzed approximately 120 samples: 50 from the Northwest Atlantic Ocean, 30 from the Mediterranean Sea, and 40 from the Chesapeake Bay. Standard addition curves in these samples of varying salinity are reproducible with slopes in seawater samples typically ranging from 2.2 to 2.6 nA/nM. It is unlikely that naturally occurring organic matter in the ocean interferes in an uncontrollable manner.

The reason for the increase in iodide sensitivity at the mercury electrode with addition of Triton X-100 is likely due to two reasons. First, the iodide wave shifts to more negative potentials (from -0.18 to -0.33 V). Thus, the deposition potential is further removed from the iodide half-wave potential and deposition is more efficient. Colovos et al. (14) have also noted similar peak height variations for the stripping of chloride and bromide from the mercury electrode on changing the deposition potential. A second and more important effect relates to the dynamics of the electrode process.

Colovos et al. (14) suggested that mercurous ions could be desorbed from the mercury electrode, diffuse into solution, and thus be unavailable for film formation at the mercury electrode. If mercurous halide formation occurs in the bulk solution rather than at the mercury electrode, then small peak heights should result. Because Triton X-100 adsorbs well to the mercury electrode surface, we suggest that mercurous ions are not able to diffuse readily into the bulk solution and that mercurous halide formation occurs preferentially at the electrode surface rather than in the bulk solution. Also, mercurous halide salts formed at the electrode should not be able to dissolve and to diffuse into the bulk solution. Thus, larger peak heights for iodide and other species forming mercurous salts (e.g. Cl^- and Br^-) should be observed with the addition of Triton X-100. Because Cl^- and Br^- concentrations are 0.565 M and 0.87 mM, respectively, in seawater and thus higher than the amount of Triton X-100 added, we did not investigate the effect of Triton X-100 on the peaks of these halides. Phenolphthalein additions to sodium chloride solutions also increase the iodide peak sensitivity, but the increase is not as great as Triton X-100 perhaps because the iodide peak is only shifted to -0.25 V.

Seawater Analyses. Seawater samples were analyzed by the method of standard additions. Figure 1 shows that there is a significant increase in sensitivity for the iodide peak in seawater samples compared to that in sodium chloride solutions. The current value for the sample has been subtracted out for comparison purposes. The slope of the standard curve for this sample is 2.62 nA/nM in seawater versus 1.93 nA/nM in 0.565 M sodium chloride. This data is for 30-s depositions that are used for samples containing 10 nM or greater concentrations of iodide in seawater. Standard addition curves obtained for 180-s depositions give slopes of about 8.0 nA/nM. Deposition times of 180 s are used when nanomolar (<10) to subnanomolar levels of iodide are to be determined. We estimate the minimum detectable limit to be 0.1–0.2 nM with a 180-s deposition at -0.10 V. We did not notice any adsorption of iodide onto the cell walls at these low concentrations during the course of the experiments.

Table II shows typical iodide data obtained on six samples (GF 19 and GF 20) taken from the Northwest Atlantic Ocean during July 1987. Our iodide measurements were calibrated by two methods. First, total iodine is conservative with salinity in the ocean (2–5, 7). For ocean waters, total iodine is about 470 nM at a salinity of 35.0‰ giving a constant ratio of about 13.4 nM/‰. Thus, total iodine ($I_{\text{predicted}}$) will increase or decrease with salinity according to this ratio. Second for three

Table II. Iodine Data Determined from Northwest Atlantic Ocean Samples GF19 (35.54.05 North; 74.00.53 West) and GF20 (35.59.23 North; 74.08.15 West) and Low Salinity Water Samples (CB6, CD5, CD6) from Northern Chesapeake Bay

Atlantic Ocean Samples							
sample no.	depth, m	concentration, nM					salinity, ‰
		I^-	IO_3^-	$\text{I}^- + \text{IO}_3^-$	I_{total}	$I_{\text{predicted}}$	
GF 19	9	135.5 \pm 2.79	336.3	471.8	455.7 \pm 4.16	471.6	35.117
GF 19	30	110.0 \pm 8.64	356.7	466.7	not analyzed	486.6	36.230
GF 19	245	3.09 \pm 0.264	501.0	504.1	not analyzed	478.4	35.620
GF 20	3	106.6 \pm 1.01	326.4	433.0	425.7 \pm 16.6	444.4	33.088
GF 20	59	61.3 \pm 3.09	421.2	482.5	464.4 \pm 9.67	487.5	36.303
GF 20	241	2.26 \pm 0.070	502.1	504.3	not analyzed	473.8	35.281
Northern Chesapeake Bay Samples							
sample no.	depth, m	location		$[\text{I}^-]$, nM	salinity, ‰		
		latitude (N)	longitude (W)				
CB 6	1	39.30.38	75.59.57	7.95 \pm 0.506	0.105		
CD 5	1	39.28.26	75.57.13	27.4 \pm 1.12	0.968		
CD 6	1	39.26.23	75.59.45	17.8 \pm 0.458	0.920		

of the samples given in Table II, we compared total iodine (I_{total}) determined by the total oxidation method of Takayanagi and Wong (3) to the addition of iodide plus iodate which were experimentally determined. The total iodine expected and experimentally determined compares within 5–6% of the experimentally determined sum of iodide and iodate. Our results show that the existence of a significant dissolved organic iodine fraction in the ocean is unlikely. The decrease in iodide from the surface to 240 m is consistent with iodate concentrations increasing with depth. The trend of this data is similar to that reported by Herring and Liss (2) and Wong et al. (6). They determined iodate by differential pulse polarography and iodide after chemical oxidation of the sample. Minimum detectable limit for iodide by difference techniques is about 15–20 nM.

For freshwater or low brackish water, we added about 0.5 mL of 0.565 M sodium chloride as a matrix modifier or supporting electrolyte. Standard addition curves in these solutions gave slightly higher slopes near 3.0 nA/nM compared to seawater or 0.565 M sodium chloride solutions. Table II also shows data from low salinity water samples taken at the confluence of the Chesapeake Bay and the Susquehanna River (CB6) and in the Chesapeake Bay–Delaware Bay canal (CD5 and 6).

The only interference that we have noted in marine samples analyzed to date is hydrogen sulfide. Sulfide has been noted as such by other workers (11, 12). However, on acidification with aliquots of 1 N hydrochloric acid and purging, it is possible to remove the sulfide and determine the iodide content of the sample. Standard addition curves in acidified samples give similar slopes as nonacidified samples.

CONCLUSIONS

Our results show that cathodic stripping square wave voltammetry is a fast and reliable method for the determination of iodide. Iodide in freshwater, brackish water, and seawater samples can be determined at the nanomolar level with a typical precision of better than 5% (1σ) and with minimum sample preparation or modification. The detection

limit of iodide in these environmental samples approaches 0.1 nM and is 1 to 2 orders of magnitude lower than previous reports obtained by using differential pulse polarographic difference methods (2, 6) and recently developed ion chromatographic methods (16).

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LITERATURE CITED

- (1) Barkley, R. A.; Thompson, T. G. *Deep Sea Res.* **1960**, *7*, 24–34.
- (2) Herring, J. R.; Liss, P. S. *Deep Sea Res.* **1974**, *21*, 777–783.
- (3) Takayanagi, K.; Wong, G. T. F. *Talanta* **1986**, *33*, 451–454.
- (4) Wong, G. T. F.; Brewer, P. G. *J. Mar. Res.* **1974**, *32*, 25–36.
- (5) Truesdale, V. W. *Mar. Chem.* **1978**, *6*, 253–273.
- (6) Wong, G. T. F.; Takayanagi, K.; Todd, J. F. *Mar. Chem.* **1985**, *17*, 177–183.
- (7) Elderfield, H.; Truesdale, V. W. *Earth Planet. Sci. Lett.* **1980**, *50*, 105–114.
- (8) Sillen, L. G. *Oceanography*; Sears, M., Ed.; American Association for the Advancement of Science: Washington, DC, 1961; pp 549–581.
- (9) Wong, G. T. F. *Mar. Chem.* **1980**, *9*, 13–24.
- (10) Turner, J. A.; Abel, R. H.; Osteryoung, R. A. *Anal. Chem.* **1975**, *47*, 1343–1347.
- (11) Propst, R. C. *Anal. Chem.* **1977**, *49*, 1199–1205.
- (12) Holak, W. *Anal. Chem.* **1987**, *59*, 2218–2221.
- (13) Luther, G. W., III; Giblin, A. E.; Varsolona, R. *Limnol. Oceanogr.* **1985**, *30*, 727–736.
- (14) Colovos, G.; Wilson, G. S.; Moyers, J. L. *Anal. Chem.* **1974**, *46*, 1045–1050.
- (15) Luther, G. W., III; Swartz, C. B. *EOS* **1987**, *68*, 1763.
- (16) Han, K.; Koch, W. F.; Pratt, K. *Anal. Chem.* **1987**, *59*, 731–736.

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