RESIDUES AND TRACE ELEMENTS

Speciation and Determination of Dissolved Iodide and Iodine in Environmental Aqueous Samples by Inductively Coupled Plasma Atomic Emission Spectrometry

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Total dissolved iodide (I^-) and iodine (I_2) are determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using iodine vapor generation. I^- is determined directly after filtration. It is oxidized in situ to I_2 with potassium nitrite in sulfuric acid in a simplified continuous-flow manifold. A standard nebulizer separates I_2, which is quantitated by ICP-AES at 206.16 nm. The instrument detection limit for I^- is 0.04 μg/mL. Recoveries from seawater, saltwater, and freshwater standard reference materials ranged from 86.5 to 118.6%, averaging 98.2%. I_2 is analyzed by ICP-AES without the iodine vapor generation reagents. For samples containing both I_2 and I^-, total iodine is determined with oxidizing reagents, I_2 alone is determined without oxidizing reagents, and I^- is calculated from the difference. The analysis is specific for the 2 species (I^- and I_2). Stability of I_2 in environmental samples was briefly investigated. This method demonstrates good accuracy and precision for samples of environmental interest and is especially well suited to small samples. It requires no additional apparatus for iodine generation or sample introduction.

Historically, analyses by inductively coupled plasma atomic emission spectrometry (ICP-AES) have been routinely used for metals because of their specific properties. Metals emit in the visible spectral region, whereas nonmetals emit in the ultraviolet spectral region. Metals have lower excitation energies than nonmetals; the excited-state populations are low, and hence emission intensities are lower for nonmetals, that is, low sensitivity. Introduction of gaseous hydride samples into an ICP-AES is an increasingly common technique used to increase sensitivity (reduce detection limits and matrix effects) for poor emitter elements such as arsenic, selenium, and antimony (1–4). Sensitivity increases because the transport efficiency of the gaseous hydride to the plasma is higher. In addition, atomization and excitation of the gaseous hydride is very efficient because the process avoids the energy-consuming desolvation and vaporization phases associated with liquid samples.

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We have developed a method for iodide (I^-), based on these same principles that enhance sensitivity in hydride generation methods for ICP-AES. Iodine (I_2) is generated in situ by oxidizing the sample with sodium nitrite in sulfuric acid. The generated I_2 is volatile and swept into the ICP-AES sample introduction system. Like the hydride methods, sensitivity is vastly improved over what would be conventionally achievable through noniodine, nongaseous analysis. The same processes that increase sensitivity for hydride methods are functioning with the I_2 method described here. A conventional nebulizer/spray chamber separates the gaseous I_2 from the sample. The ICP-AES is run under normal operating conditions. This results in no downtime as typically found in the conversion between conventional and gaseous sample introduction systems.

Iodine production has steadily increased over the past decade; current world production of I_2 is 15 000 tons per year (5). Iodine may be recovered from natural brines, which may contain 50–100 μg/mL iodide: The brine is treated with chlorine to oxidize I^- to I_2. I_2 is blown out with a stream of air (because it is volatile; 5). There is no one dominant use of I_2. About 50% is used to produce organic compounds such as iodoform, CHI_3 (an antiseptic), and methyl iodide, CH_3I. Other uses include production of silver iodide, which is used in photographic films and for seeding clouds to produce rain. Iodine is required in the human diet in small amounts; therefore, traces (10 mg/kg) of NaI are added to table salt. In addition, I^- is a common additive in wheat flour destined for bread production. Potassium iodide is added to animal and poultry feed. Iodine is essential for animal nutrition, and NaI, KI, and/or iodate salts are often added to animal feeds; however, I_2 is toxic in large quantities.

Iodide method sensitivity requirements vary depending on the matrix. Dietary levels less than 0.2–0.5 μg/mL (ppm) are considered deficient for most animals (6), and levels above 50 μg/mL (ppm) of dietary I_2 are considered toxic. Seawater typically contains 0.05–0.1 μg/mL total iodine. Brines may contain anywhere from 1 to >100 μg/mL total iodine. The ratio and concentrations of I^- to I_2 in environmental waters are important tools in environmental waste identification and enforcement investigations (7).

Methods for I_2 determination in environmental water, seawater, and brine samples present complications and problems. Complications arise from both the variety of matrixes, which present many interferences, and the sensitivity requirements for each matrix. Methods routinely used include U.S. Environmental Protection Agency (EPA) methods 345.1 and 300.0 and AOAC Official Methods **925.56** and **920.204**. Each of these methods, except AOAC Method **925.56**, are for water samples only. Seawater, wastewater, and brine samples typically require more preparation. EPA method 345.1 is an I^- titrimetric method with a detection limit of only 2 μg/mL. This sensitivity is often insufficient for most environmental work. The method requires sample pretreatment and uses hazardous reagents such as bromine and phenylarsine. The method is labor intensive and cannot be automated readily. EPA method 300.0, an ion chromatography (IC) method, is not currently certified for I_2, although an IC method should be easily adaptable for I_2 analyses. AOAC Method **925.56**, an I^- titrimetric method, has the same shortcomings as the titrimetric method discussed above. AOAC Method **920.204**, a colorimetric procedure, is not very sensitive, with detection limits of 10–50 μg/mL. This method is semiquantitative and quite labor intensive, with multiple evaporations, filtrations, and resuspensions along with several quantitative transfers.

Other methods for I_2 analysis include liquid chromatography coupled with inductively coupled plasma mass spectrometry (LC-ICP-MS; 8). Good detection limits were achieved in this study (25 pg), and some speciation of iodide was possible (8). Although this method is excellent, the technique is limited to specialized laboratories with access to an LC-ICP-MS system. A continuous-flow method for I_2 by helium microwave-induced plasma atomic emission spectrometry (MIP-AES) has yielded good results (9–11). Detection limits for I_2 were 2–3 ng/mL. However, specialized gas–liquid separator equipment was used in continuous-flow I_2 generation. Adaptation of this equipment to MIP-AES limits this method to laboratories with access to MIP-AES and can monopolize the equipment for extended periods. This method results in potentially large amounts of downtime occurring in the conversion between conventional and gaseous sample introduction instrument setup. An I_2 method by ICP-AES with good detection limits (20 ng/mL) was reported for water samples (12). This method used direct optical viewing of an ICP-AES through a sampling orifice inserted directly into the plasma (12). The specialized equipment and setup may make this method less useful for laboratories involved in routine production analyses. A prior-oxidation I_2 procedure for ICP-AES with detection limits ranging from 0.09 to 0.6 μg/mL has been described (12). This sensitivity is often insufficient for most environmental work, and only I^- standards have been analyzed to date. Iodate determination by reversed-phase ion-pair chromatography with amperometric detection had good sensitivity, with a method detection limit of 3.6 μg/mL; total I^- samples were however not analyzed (13).

We used gaseous I_2 generation ICP-AES for determination of total dissolved I^- and I_2 in environmental water samples. Speciation determination of I^- and I_2 individually is also demonstrated. This method requires no additional apparatus and the ICP-AES operates under standard conditions (1, 2, 4). This results in no downtime as typically found in the conversion between conventional and gaseous sample introduction systems. ICP-AES analysis has many advantages over other methods: high sensitivity, ease of operation, can easily be automated, reliability, and freedom from many interferences commonly encountered with other techniques. The method uses modest sample sizes (5–10 mL), often a requirement in environmental work; needs infrequent supervision during analysis; and requires no labor-intensive extractions or quantitative transfers. Minimization of sample size also assists in pollution prevention by minimizing reagents used and subsequent waste generated; in addition, the reagents used are considerably less toxic than those used in other I^- methods.

METHOD

Reagents

(a) *Sulfuric acid solution.*—5M H_2SO_4 (reagent ACS grade; Fisher, Pittsburgh, PA). To 1000 mL volumetric flask filled with ca 500 mL water (18 MΩ/cm) add 278 mL 18M H_2SO_4 and dilute to final volume with water. *Note*: Always add acid to water.

(b) *Sodium nitrite.*—2.0M $NaNO_2$ (Fisher, reagent ACS grade). Add 13.822 g $NaNO_2$ to a 100 mL volumetric flask and dilute to volume with 18 MΩ/cm water.

(c) *5M H_2SO_4/0.1M $NaNO_2$ solution.*—Add 10 mL 2.0M $NaNO_2$ to 200 mL 5M H_2SO_4.

(d) *Oxalic acid.*—0.1M $H_2C_2O_4 \cdot 2H_2O$ (analyzed reagent, purity 100.0%; J.T. Baker Chemical Co., Phillipsburg, PA).

(e) *Iodide stock standard.*—Prepare 2.0, 1.0, and 0.50 μg/mL from a 10 000 μg/mL KI standard by taking serial dilutions of stock iodide standard. (KI was dried at 110°C and stored in a desiccator.) Prepare a 10 000 μg/mL iodide primary standard by adding 1.308 g KI (Fisher, certified ACS/99.3%) to a 100 mL volumetric flask and diluting to volume with 18 MΩ/cm water (or ASTM type 1 water). Prepare all secondary standards fresh daily.

(f) *Potassium iodate.*—10 000 μg/mL KIO_3 (Fisher, certified ACS). Weigh 1.69 g KIO_3 and dilute to 100 mL with type 1 water. Prepare secondary standards by appropriate serial dilutions.

(g) *Reference materials.*—APG Water 7878 and APG Water 7879 (Analytical Products Group, Belpre, OH).

(h) *Seawater reference material.*—Collected from Elliot Bay, Washington, and stored at 4°C in plastic bottles until use. Total holding time was less than 30 days.

(i) *Iodine standard.*—150 μg/mL iodine (Baker analyzed reagent, sublimed 100.0%). Prepared from neat standard by adding 15 mg iodine to 100 mL volumetric flask and diluting with type 1 water. Other iodine standards (2.0, 5.0, and 10.0 μg/mL) were prepared similarly.

(j) *Iodine spike.*—1.0 μg/mL; prepared from primary standard.

Apparatus

(a) *Inductively coupled argon plasma atomic emission spectrometer.*—Model Perkin-Elmer P-40 ICP-AES with AS-90 autosampler. Measurements were made for iodide (and iodine) at 206.16 nm. P-40 operating conditions: integration time, 2496 ms; window width, 0.50 nm; photomultiplier tube, 900 v, 45 s read/wash time delay. Samples with high iodine content require longer rinse times. Left background correction point at –0.034 nm from analytical line used.

(b) *Nebulizer.*—Meinhard high solids tip, 2 mL/min, 31 psi, type C (Precision Glassblowing, Englewood, CO).

(c) *Peristaltic tubing.*—Teflon tubing and a small polypropylene "T" piece connects each tubing to the other (Figure 1). Pump rates for 5M H_2SO_4/2M $NaNO_2$ solution and sample introduction are ca 6 mL/min. Use 0.022 in. id tubing to connect reservoirs containing sample and oxidizing reagents to the pump. From the pump to the "T" connection, use 0.056 in. id tubing for the sample and 0.035 in. id tubing for the oxidizing reagents. From the "T" connection to the nebulizer, use 0.022 in. id tubing. *Note*: there is no unacceptable pressure buildup, the sample flow is simply faster through the smaller diameter tubing.

Sample Preparation and Analysis

Filter water through a 0.45 μm filter. The recommended sample size is 5–10 mL, and 10 mL typically is used for analysis. Smaller sample sizes may be accommodated without compromise (down to 2 mL) and without dilution. Brine samples high in I^- were diluted so I^- concentrations would fall within our typical calibration curve. Samples containing more than 1% salt were diluted by a factor of 10. Samples were stored at 4°C until analysis.

Setup the ICP-AES as specified by the instrument manufacturer and as described above. Equilibrate ICP-AES torch prior to analysis, typically 15–20 min or as recommended by the manufacturer. Use a 0.1M oxalic acid solution in the rinse bath instead of water. Pump oxidizing reagents (H_2SO_4/$NaNO_2$) through the system for about 10–15 min prior to calibration and analysis (Figure 1). Typically, a calibration curve consists of 0.00, 0.50, 1.00, and 2.00 μg/mL standards (or 0.00, 1.00, 2.00, and 10.00 μg/mL). With this setup, I_2 and I^- will be determined as total I^-. To determine I_2 alone, no oxidizing reagents are used; otherwise, the analysis proceeds the same as above. The ICP-AES is setup without any modifications or in situ reactions, that is, direct analyses.

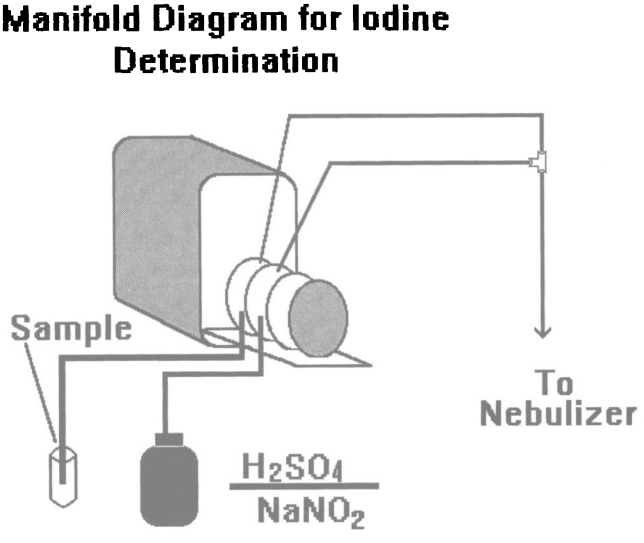

Figure 1. Total iodide instrument setup: ICP-AES peristaltic pump for in situ iodine generation.

Interference Study

Iodide standards of 1.0 and 5.0 μg/mL were prepared. Appropriate volumes of 10 000 μg/mL stock metal or element solutions were added to yield desired concentrations of potentially interfering ions. Interference study samples were prepared, calibrated, and analyzed. Elements tested in this way were Na, K, Ca, Mg, Mn, Fe, Co, Ni, Cu, Zn, Al, Pb, Cd, Se, As, P, and Cl. All species tested, except chloride, were at an original sample concentration of 0.1% (1000 μg/mL); chloride was at 1.8%. Groups of 5 elements were batched; if any signal enhancement or suppression occurred, each of the 5 elements would be isolated individually in a series of standards. For interfering elements, a study was performed to determine the concentrations at which the interferences became negligible.

Results and Discussion

Recoveries of I_2 and I^- at 206.16 nm from 12 water matrixes are listed in Tables 1 and 2. Over a 10-month period, they ranged from 86.5 to 118.6%; average recovery was 98.2% for the standard reference water samples. Iodide levels ranged from 0.05 to 10.0 μg/mL. Analytical conditions were constant during this 10-month data collection period. On the basis of recoveries of I_2 standards, 206.16 nm was found to be the optimum wavelength. Emission intensities for I_2 at 178.26 and 183.038 nm were lower or approximately the same as that at 206.16 nm. However, at 206.16 nm, a nitrogen or vacuum purge of the optics is not necessary, further simplifying the method. Atmospheric oxygen absorbs at wavelengths below 190 nm; therefore, vacuum or purged optics are required. Instrument detection limit was calculated as 3 times the standard deviation of the blank. Blanks were analyzed in more than 3 different analytical batches, with at least 10 blanks per run, each in replicates of 3. Instrument detection limit was 0.04 μg/mL. Dilution factors for water samples were eliminated by this method, which increases method detection limits.

The method is linear over 3 orders of magnitude, which minimizes analytical difficulties encountered with the relatively narrow concentration ranges of other methods. Standards at 0.00, 1.00, 10.00, 100.0, and 1000 μg/mL were analyzed to demonstrate linearity. Additional rinse times were required to prevent memory effects for high-concentration standards. Typically, a calibration curve consists of 0.00, 0.50, 1.00, and 2.00 μg/mL standards (or 0.00, 1.00, 2.00, and 10.0 μg/mL). Analysis of more than 25 analytical batches gave correlation coefficients (r) of 0.9942–1.000 (typically ≥0.9990).

Table 1. Iodide and Iodate recoveries from spiked aqueous environmental samples after in situ oxidation

Reference material	No. of determinations	Spike level, µg/mL	Recovery, µg/mL ± SD[a]	Average recovery, %	RSD, %
			Iodide (I^-)		
Water[b]	10	0.05	0.0593 ± 0.006	118.6	10.2
Water[b]	16	0.08	0.079 ± 0.005	98.8	5.35
Water[b]	26	0.10	0.928 ± 0.005	92.8	5.5
Water[b]	10	1.00	0.97 ± 0.01	97.5	1.06
APG 7879[c]	6	0.5	0.507 ± 0.026	101.4	3.9
APG 7879[c]	6	2.0	1.73 ± 0.025	86.5	0.74
APG 7879[c]	6	10.0	10.5 ± 0.22	105.0	2.25
Seawater[d]	6	0.5	0.499 ± 0.014	99.7	1.5
Seawater[d]	6	2.0	1.80 ± 0.025	89.8	1.93
Seawater[d]	6	10.0	9.99 ± 0.32	99.9	4.35
Simulated saltwater[e]	10	0.50	0.447 ± 0.006	89.3	1.34
			Iodate (IO_3^-)		
Water[b]	10	2.00	0.017 ± 0.003	0.8	19.1

[a] SD, standard deviation.
[b] Laboratory reagent water spiked with appropriate standard solutions, *see* Experimental section.
[c] Standard trace metals certified reference material spiked at different KI levels.
[d] Seawater from Elliot Bay, Washington, was collected and stored at 4°C, then spiked with KI standard solutions.
[e] Laboratory water spiked with 1% sodium chloride and iodide standard simulating saltwater/brine samples. *See* text about using dilutions to improve recoveries by an additional 5% (i.e., 95% recoveries).

Use of the Meinhard nebulizer as a gas–liquid separator is an accurate and efficient method of introducing sample into the ICP-AES instrument (1–4). The I_2 generation tubing setup (Figure 1) is simple, requires no additional apparatus, and is easily maintained for routine operation. Only an additional tubing line, which uses the peristaltic pump on the ICP-AES, is added. A 45 s read/wash delay for routine sample introduction is optimum. The wash is necessary to avoid memory effects. The read delay promotes consistent I_2 reaction time and allows for plasma stabilization after oxalic acid is introduced in the rinse wash cycle. Addition of oxalic acid to the wash facilitates rinsing of the tubing. Memory effects of I_2

Table 2. Speciation and time dependence studies of spiked aqueous environmental samples by direct analysis

Sample	No. of determinations	Spike level, µg/mL	Recovery, µg/mL ± SD[a]	Average recovery, %	RSD, %
			Iodine (I_2)[b]		
Water[c]	10	1.00	0.997 ± 0.07	99.7	7.5
Initial water[c,d]	12	5.00	4.59 ± 0.10	91.8	2.3
Initial water[c,d]	12	10.0	9.75 ± 0.12	97.5	1.3
24 hr water[c,d]	12	5.00	4.62 ± 0.04	92.4	1.0
24 hr water[c,d]	12	10.0	9.97 ± 0.18	99.7	1.8
48 hr water[c,d]	12	5.00	4.45 ± 0.07	89.0	1.7
48 hr water[c,d]	12	10.0	9.28 ± 0.20	92.8	2.1
1 wk water[c,d]	12	5.00	4.33 ± 0.13	86.6	3.0
1 wk water[c,d]	12	10.0	9.14 ± 0.19	91.4	2.1
2 wk water[c,d]	8	5.00	3.47 ± 0.12	69.4	3.4
2 wk water[c,d]	10	10.0	8.32 ± 0.28	83.2	3.3
			Iodate (IO_3^-)		
Water[c]	20	2.00	0.004 ± 0.001	0.002	50

[a] SD, standard deviation.
[b] Determined directly, without oxidizing reagents.
[c] Laboratory reagent water spiked with appropriate standard solutions.
[d] Iodine samples stored for various periods of time.

were substantially reduced when Teflon tubing and oxalic acid rinse are used.

Long-term performance under routine analytical conditions was tested by analyzing 4 water standard reference materials (SRMs) more than 125 times (Table 1). Correlation with expected values is excellent for all SRMs. In all cases, standard deviations are good, demonstrating the consistent reliability of the method (Tables 1 and 2). RSD for most of samples is about 5% or less. Iodide recovery and RSD for water sample spiked at 0.050 μg/mL were higher than typical (118.6 and 10.2%, respectively). compared with other spiked matrixes analyzed by the same method. However, this spike level is close to the detection limit (0.04 μg/mL) and may have more inherent variability associated with the recovery. Only modest increases in concentration, however, illustrate the sensitivity of the method; specifically, spike recoveries for 0.08 and 0.1 μg/mL I^- spikes are 98.2 and 92.8%, respectively.

Excellent results with seawater and simulated saltwater samples were obtained (Table 1). Average revovery from spiked seawater samples was 96.5%. Recovery of I^- from a simulated saltwater sample (1% NaCl) also was good (89.3%). Brine samples containing >1% salt yielded even better, more consistent results if a 1:10 dilution was used. After several initial experiments using nondiluted brine samples, including those listed in the Table 1, we found that recoveries could be improved with modest dilutions. Iodide recovery from brines improved from about 89–99% to a more consistent ≥95% when a 10-fold dilution was used. Therefore, samples with ≥1% total salt should be diluted 1:10 for better I^- recoveries, if sensitivity permits.

The method also allows speciation. Iodine can be determined directly by ICP-AES by omitting the oxidizing reagents. The method is extremely selective and no I^- is recovered without the in situ oxidizing reaction. When I^- were analyzed by the I_2 direct method, recoveries were 0%. To demonstrate method selectivity, 2.0, 5.0, and 10.0 μg/mL I_2 standards were prepared and analyzed by the direct method (without oxidizing reagents). Recoveries were within ± 10% of spiked levels, and average recovery was >96% (Table 2). When I_2 standards were spiked with 2 μg/mL I^- recovery by the I_2 method was the same, within ± 5% of the 2.00 μg/mL iodine spike value. Analyses of mixed I_2/I^- standards and the I^- (alone) standard demonstrated that no I^- is recovered when oxidizing reagents are not used. After I_2 is determined, the in situ oxidation can be setup, and total I_2 and I^- can be determined. This setup typically takes less than 5 min. Iodide concentration can be determined by subtracting the I_2 concentration from the total (I^- and I_2) concentration. The recoveries demonstrate the selectivity of the method for both I^- and I_2.

Iodate (IO_3–) does not interfere with either method as demonstrated by recovery studies of iodate samples, (Tables 1 and 2). Recoveries of iodate were <1% with the total I^- method (Table 1) and <0.01% with the I_2 direct method (Table 2). Therefore, iodate does not interfere with recovery of other iodine species.

No chemical interference wad observed from Na, K, Ca, Mg, Mn, Fe, Co, Ni, Cu, Zn, Al, Pb, Cd, Se, As, and P up to 0.1% and from Cl up to 1.8%, the highest levels tested. (An element does not interfere if recoveries of the 1.0 and 5.0 μg/mL iodide standards are within 10% of the spiked value.) Spectral interferences were observed for Cr at 0.1%, which enhanced the I^- signal by about 70%. Cr at 0.0025% gave no spectral interferences; that is, the 1.0 and 5.0 μg/mL standards were within 10% of their spiked values. Therefore, samples may be diluted to avoid this interference. Alternatively, analysis can be done at 183.038 nm. This analytical line is just as sensitive as 206.16 nm but does not suffer from Cr. The only drawback with using this wavelength is that vacuum or purged optics must be used. No interferences were seen with any of the above listed elements at this wavelength.

Iodide in the sample is oxidized to I_2 in situ when sodium nitrite is added, as described by the following reaction:

$$NO_2^- + I^- + 2H^+ \rightarrow NO + \tfrac{1}{2} I_2\uparrow + H_2O$$

In situ oxidation allows for optimum reaction time and yet eliminates the potential for I_2 losses, which occur with other oxidation methods. Other oxidizing agents were tested such as hydrogen peroxide, chlorine, and nitric acid. Sodium nitrite yielded the best I^- results; Nakahara (9–11) tested oxidizing agents for MIP-AES work and found sodium nitrite to be one of the more successful agents. Oxidation of KI standards by atmosphere oxygen will occur with time:

$$2H^+ + 2I^- + \tfrac{1}{2} O_2 \rightarrow I_2\uparrow + H_2O \ (\Delta G^\circ = -100 \text{ kJ/mol}).$$

Potential loss of I_2 through volatilization may occur; therefore all I^- standards should be prepared fresh daily.

We briefly investigated the stability of iodine-containing samples. Two I_2 samples were prepared, one at 5.0 mg/L and the other at 10.0 mg/L iodine. Samples were stored at 4°C to inhibit volatiliation and decomposition of I_2 in high density polyethylene bottles until analysis. A calibration curve and calibration standards were prepared fresh daily. Samples were analyzed after 0, 24, and 48 h, and after 1 and 2 weeks. Spikes and quality control samples were analyzed to verify the calibration curve and to ensure continuity of analysis throughout the 2-week study period. Check samples, spikes, and standard reference samples were within 6% of their true value in all stability studies. Results of this study are presented as part of Table 2. Although I_2 decreased slightly over the study duration, overall it was relatively persistent in environmental samples stored at 4°C. After 1 week, I_2 in both samples decreased by 5–6%. After 2 weeks, I_2 decreased by 20–30%. After 2 weeks, total iodide (I^- and I_2) was determined by both the direct iodine and the total iodide methods. Results were the same (3.4 mg/mL). Therefore, the samples contained no I^-. This result suggests that I_2 is most probably lost by volatilization or by decomposition to other I^- species.

Conclusions

This speciation method of iodine generation demonstrates good accuracy and precision and good recoveries of I^- and I_2 in freshwater, seawater, and saltwater. This method requires no additional apparatus for in situ I_2 generation or sample intro-

duction; the ICP-AES operates under standard conditions. Analysis procedures are fully amenable to programmed operation and autosampling. Analysis requires minimal sample, often a requirement in environmental work.

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