

Determination of Iodide in Seawater and Other Saline Matrices Using a Reagent-Free Ion Chromatography System with Suppressed Conductivity and UV Detections

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Introduction

Iodine is an essential nutrient found in seawater, seafood, and iodine-enriched food, such as iodized table salt. The most common forms of iodine in diet are iodide and iodate, with additional iodo-organic compounds providing a small fraction of bioavailable iodine. Iodine deficiency affects thyroid hormone production and leads to developmental diseases, goiter, and paralysis.¹ Table salt is routinely iodized to prevent such diseases and promote public health. Iodization levels vary by country and range from 5–100 mg iodine per kg of salt.² In the United States, Canada, and most northern European countries, potassium iodide is frequently used to iodize salt. In tropical countries, potassium iodate is preferred due to its greater stability under humid conditions.³

Because iodide is an essential source of iodine, there is need to determine iodide in a variety of matrices. Seawater is a large natural source of iodide, typically containing 50–60 µg/L iodide with a wide range of observed concentrations. For example, iodide amounts can range from less than 1 µg/L to greater than 60 µg/L, with the measured concentrations dependent on water depth, oxygen concentration, and the biological mediation of the iodide/iodate equilibrium.⁴ Determination of iodide in seawater and other saline matrices by ion chromatography is challenging due to high sample chloride concentrations. In seawater, the matrix is further complicated by high concentrations of carbonate and sulfate. This high ionic strength matrix makes direct analysis of samples containing iodide difficult.



In this application note (AN), a RFIC-EG system with UV detection is used to determine iodide in seawater, synthetic sea salt, and iodized table salt. Iodide is separated from other matrix anions on the Thermo Scientific™ Dionex™ IonPac™ AS20 column, which is a high-capacity column designed for the separation of polarizable anions. The unique selectivity of this column makes it ideal for separating hydrophobic anions in matrices with high concentrations of chloride, sulfate, and carbonate. The high capacity of the Dionex IonPac AS20 column allows the determination of iodide in saline matrices with no sample pretreatment. Furthermore, by detecting iodide by UV absorbance, other anions, such as chloride and carbonate, are not detected and do not interfere with iodide determination. This proposed method is further simplified by using a 2 mm column format and an in-line high-pressure hydroxide eluent generator requiring only the addition of deionized water for continuous operation. In this AN, the linearity, detection limits, precision, and recovery of iodide in saline matrices for the proposed method are demonstrated.

Equipment

Thermo Scientific™ Dionex™ ICS-3000 Reagent-Free™ Ion Chromatography (RFIC-EG) system* consisting of:

- SP Single Pump or DP Dual Pump module
- EG Eluent Generator module
- DC Detector/Chromatography module (single or dual temperature zone configuration)
- Thermo Scientific Dionex AS Autosampler
- Thermo Scientific Dionex ICS-3000 VWD UV-Vis Absorbance Detector (4 wavelength or single wavelength) with a PEEK semi-micro flow cell
- Thermo Scientific Dionex EGC II KOH cartridge
- Thermo Scientific Dionex CR-ATC II Continuously Regenerated Anion Trap Column
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) 6.8
- Polystyrene AutoSelect vials with caps and septa, 10 mL
- Thermo Scientific™ Nalgene™ 125 mL Narrow-Mouth HDPE Bottles
- Nalgene 250 mL Narrow-Mouth HDPE Bottles
- Thermo Scientific™ Nalgene™ Rapid-Flow™ 250 mL 0.2 um nylon filter unit
- Nalgene Rapid-Flow 1000 mL 0.2 um nylon filter unit

*Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ RFIC™ system.

Reagents and Standards

- Deionized water, Type I reagent grade, 18 MΩ-cm resistivity or better
- Sodium chloride
- Sodium sulfate
- Potassium chloride
- Sodium bicarbonate
- Potassium bromide
- Sodium fluoride
- Boric acid
- Potassium iodide

Conditions

Columns:	Dionex IonPac AG20, 2 × 50 mm Dionex IonPac AS20, 2 × 250 mm
Eluent:	13 mM KOH from 0–10 min, 13–45 mM KOH from 10–15 min, 45 mM KOH from 15–25 min*
Eluent Source:	Dionex EGC II KOH cartridge with Dionex CR-ATC column
Flow Rate:	0.25 mL/min
Temperature:	30 °C (column & detector compartment)
Inj. Volume:	10 µL
Detection:	A) Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating suppressor, 2 mm, external water mode, 28 mA suppressor current B) UV, 223 nm
Background Conductance:	<1 µS
Noise:	~0.5–1.0 nS (conductivity) ~0.05–0.10 mAU (UV)
System Backpressure:	~2600 psi

* The column equilibrates for 10 min at 13 mM KOH prior to injection.

Preparation of Solutions and Reagents

Eluent Solution

Generate the potassium hydroxide (KOH) eluent online by pumping high-quality, degassed, deionized water through the Dionex EGC II KOH cartridge. Chromeleon CDS software will track the amount of KOH used and calculate the remaining lifetime. To minimize the baseline shift and background noise, manual eluent preparation is not recommended.

Stock Standard Solution

A stock solution of 1000 mg/L of potassium iodide (KI) was prepared by dissolving 131 mg in 100 mL (100.00 g) of DI water. The solution was stored in Nalgene HDPE bottles at <6 °C.

Standard Solutions

Intermediate stock solutions of 1 mg/L were prepared gravimetrically by pipetting 0.100 mL (0.100 g) of a 1000 mg/L KI standard into a Nalgene 125 mL HDPE bottle and diluting to a total volume of 100 mL (100.0 g). Calibration standards between 10 µg/L and 250 µg/L were prepared by appropriate dilution of the intermediate stock solution with DI water. The standard solutions were stored at <6 °C when not in use.

Sample Preparation

Simulated Seawater

Simulated seawater was prepared by dissolving the salts listed in Table 1 into 1 L of DI water, following the method of Kester et al., with the exclusion of magnesium chloride, calcium chloride, and strontium chloride.⁵ These salts were not used in the simulated seawater because they add only a small amount of additional chloride to the matrix and require preparation by drying, dissolution, and volumetric addition to the other salts. This yields a solution with a salinity of approximately 3.5%.

Table 1. Salts added to form simulated seawater (1 L).

Reagent	Amount Added (mg)
Sodium Chloride	23900
Sodium Sulfate	400
Potassium Chloride	680
Sodium Bicarbonate	198
Potassium Bromide	95.4
Boric Acid	27.1
Sodium Fluoride	4.0

Synthetic Sea Salt

Commercially available synthetic sea salt was prepared by following package directions (1/2 cup of salt per gallon of deionized water) to prepare a solution of approximately 3.5% salinity. A 1 L portion was prepared with 30 g of aquarium salt. A sea salt density of approximately 2.2 g/cm³ was used to convert the preparation directions to metric units.⁶

Fresh Iodized Table Salt

Solutions of table salt were initially prepared at a salinity level similar to seawater. These solutions contained iodide in amounts that exceeded the standard curve and were further diluted to generate solutions of approximately 100 ppb iodide. This was done by serial dilution as follows: Dissolve 1.92 g of table salt in 100 mL of deionized water. Then, dilute 6.0 mL (6.0 g) of this solution in 57.5 g of DI water.

Seawater Collected at Half Moon Bay and Pacifica, CA

Surface seawater was collected in a Nalgene 250 mL HDPE bottle that had been cleaned prior to sample collection. The sample was stored on ice until it could be filter-sterilized through a Nalgene 250 mL, 0.2 µm nylon filter unit. After filtration the sample was stored at <6 °C. A 75 µg/L iodide standard was filtered by the same method and analyzed to determine iodide loss during the filtration step. The iodide concentration determined in the filtered standard was equivalent to an unfiltered standard, within the error of the method.

Precautions

Samples should be prepared for analysis within 24 h to prevent loss of iodide by oxidation. Additionally, all solutions should be stored at <6 °C and the autosampler should be thermostatically controlled to <10 °C.

The external water for regenerating the suppressor should be set to a flow rate of 2–2.5 mL/min. The recycle mode of suppressor regeneration is not feasible for this method due to the high salt concentrations that can dramatically shorten the working lifetime of the Dionex ASRS 300 suppressor and the Dionex CR-ATC column.

The method performance will critically depend on the noise observed in the UV detector. To reduce UV noise, the Dionex ASRS 300 suppressor performance must be optimized. This can be monitored by the observed noise in the conductivity detection channel. We recommend that the flow rate of the external water be confirmed daily to ensure that the Dionex ASRS 300 suppressor is consistently regenerated.

If conductivity detection is not used to analyze samples, the suppressor must still be in place to maintain an acceptable UV baseline. Without suppression, the hydroxide eluent will absorb in the UV and contribute to a high background, preventing detection of iodide.

Because these samples contain high concentrations of anions, carryover was observed when the syringe flush volume was less than 1000 µL. A syringe flush volume of 1000 µL or greater is strongly recommended between samples.

Results and Discussion

In preliminary experiments, the Dionex IonPac AS16, Dionex IonPac AS20, and Dionex IonPac AS24 columns were evaluated for the determination of iodide in seawater; however, the Dionex IonPac AS20 column was found to be superior for this application. This study found that while the capacity of the Dionex IonPac AS24 column is nearly double that of the Dionex IonPac AS20 column and more than three times that of the Dionex IonPac AS16 column, the retention time of iodide was 10 min longer on the Dionex IonPac AS24 column compared to the other columns. Compared to the Dionex IonPac AS16 column, the Dionex IonPac AS20 column has a higher capacity and better resolution between chloride, carbonate, sulfate, and iodide. The Dionex IonPac AS20 column provides a good compromise for shorter retention times, good sensitivity, and high capacity that allow the separation of iodide in a saline matrix without dilution.

Figure 1 shows the separation of an iodide standard spiked in simulated seawater. The high concentrations of chloride, sulfate, and carbonate in this matrix make quantification of iodide difficult by conductivity detection. As shown, the iodide peak is obscured by the carbonate and sulfate peaks (Figure 1A). Iodide absorbs in the UV at 223 nm while the other anions at high concentrations remain undetected. Iodide can easily be detected by UV absorbance without interference from sulfate or carbonate, as shown in Figure 1B.

Linear Range, Limit of Quantitation, Limit of Detection

To determine the linearity of the method, iodide calibration standards in deionized water were injected in triplicate, covering the average concentration range of iodide in seawater. Both detection methods showed similar linearity; 0.9967 and 0.9962 for conductivity and UV detection, respectively. The LOD and LOQ were confirmed by injections of iodide standards prepared at concentrations estimated to give peak heights that are 3 times and 10 times the noise, respectively. Table 2 summarizes the linearity, LOD, LOQ, retention time, and peak area precisions. The observed values will vary depending on the performance of the suppressor which affects the background and noise observed in the UV detector.

Column: Dionex IonPac AG20, Dionex IonPac AS20, 2 mm
 Eluent: Prior to injection 10 min of 13 mM KOH
 13 mM KOH for 0–10 min,
 13–45 mM KOH for 10–15 min,
 45 mM KOH for 15–25 min.
 Eluent Source: Dionex EGC II KOH cartridge with Dionex CR-ATC column
 Flow Rate: 0.25 mL/min
 Inj. Volume: 10 μ L
 Temperature: 30 $^{\circ}$ C
 Detection: A) Dionex ASRS 300 suppressor, 2 mm,
 external water mode, 28 mA
 B) UV, 223 nm

Sample: Iodide in simulated seawater

Peaks A): 1. Fluoride 1.80 mg/L (ppm)
 2. Chloride 14800
 3. Bromide 64.0
 4. Carbonate 141
 5. Sulfate 2700
 6. Iodide 0.269 (inset)

Peaks B): 1. Bromide 64.0
 2. Iodide 0.251

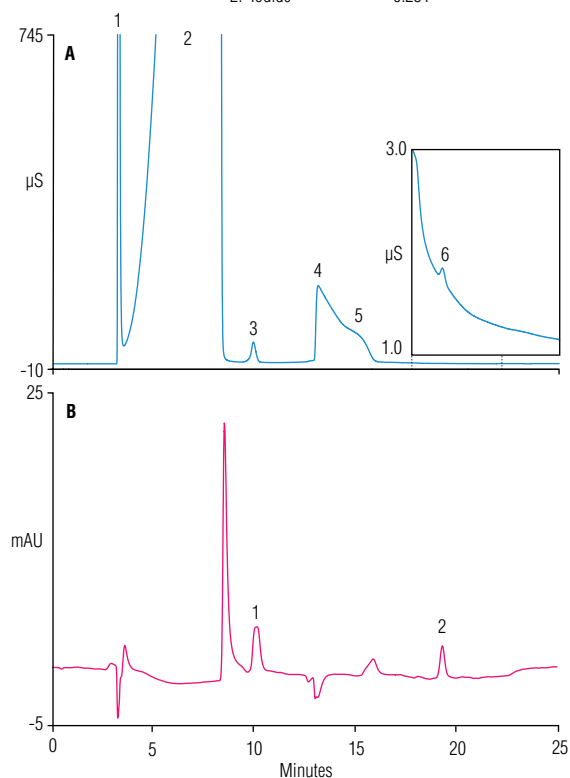


Figure 1. Determination of iodide in simulated seawater on the Dionex IonPac AS20 column.

Table 2. Linearity, LOD, LOQ, and precision for iodide determination by UV and CD detection methods.

Detection	Retention Time (min)	Range (μ g/L)	Correlation Coefficient (r^2)	LOD* (μ g/L)	LOQ* (μ g/L)	Retention Time Precision (RSD)**	Peak Area Precision (RSD)**
Conductivity	19.33	50–250	0.9967	15	50	0.013	1.67
UV	19.43	50–250	0.9962	15	50	0.032	1.34

* LOQ and LOD are highly dependent on the noise the day they are measured. The LOD and LOQ are concentrations that resulted in peaks during three days of testing that were an average of 3 \times and 10 \times the noise respectively.

** Seven injections of 100 μ g/L iodide standard.

Accuracy and Precision

The method performance was initially evaluated with seven replicate injections of a 100 µg/L iodide standard. The calculated retention time and peak area precisions were $\leq 0.03\%$ and $\leq 1.7\%$, respectively. Two samples were analyzed for iodide: a synthetic sea salt and an iodized table salt. Freshly prepared table salt contained 92.4 µg/L of iodide, or 46 µg/g of iodide in the dry salt. Figure 2 shows the determination of iodide in table salt using the Dionex IonPac AS20 column and conductivity and UV detections. The concentrations of chloride, carbonate, and sulfate in this sample are less than in the simulated seawater and, therefore, iodide is easily quantified using both conductivity and UV detections. The precision for triplicate injections of these samples was equivalent to or better than that observed for the standards (Table 3). Figure 3 shows the separation of iodide in a sample of synthetic sea salt. When prepared as described in the sample preparation section, synthetic sea salt contained 108 µg/L of iodide in solution, which is 3.6 µg/g of iodide in the dry salt. When compared to the table salt (Figure 2A), the iodide is difficult to determine using conductivity detection due to the high concentrations of sulfate and carbonate. However, the iodide peak is clearly resolved and easily quantified using UV detection (Figure 3B).

Table 3. Determination of iodide in saline samples with UV detection, triplicate injections.

Sample	Retention Time (min)	Retention Time Precision (RSD)	Peak Area Precision (RSD)	Amount Found (µg/L)	Amount in Dry Salt (µg/g)
Synthetic Sea Salt (30.4 mg/mL)	19.36	0.05	0.524	108 ± 0.6	3.6 ± 0.02
Table Salt (1.98 mg/mL)	19.43	<0.01	1.237	92.4 ± 1.2	46 ± 0.7

Column: Dionex IonPac AG20, Dionex IonPac AS20, 2 mm
 Eluent: Prior to injection 10 min of 13 mM KOH
 13 mM KOH for 0–10 min,
 13–45 mM KOH for 10–15 min,
 45 mM KOH for 15–25 min
 Eluent Source: Dionex EGC II KOH cartridge with Dionex CR-ATC column
 Temperature: 30 °C
 Flow Rate: 0.25 mL/min
 Inj. Volume: 10 µL
 Detection: (A) Dionex ASRS 300 suppressor, 2 mm,
 external water mode, 28 mA
 (B) UV, 223 nm

Sample: Iodide in iodized table salt, 1.7 mg/mL
 Peaks A): 1. Chloride – µg/L (ppb)
 2. Nitrate –
 3. Carbonate –
 4. Sulfate –
 5. Iodide 80.1

Peaks B): 1. Iodide 78.8

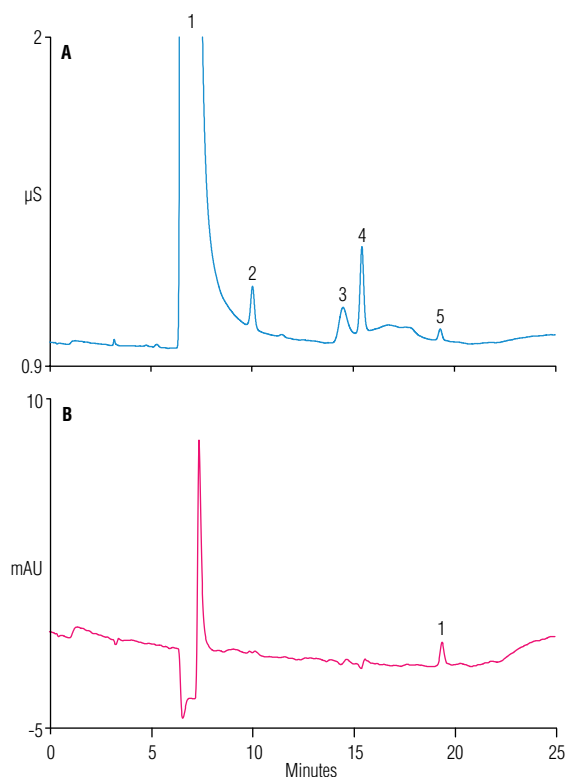


Figure 2. Determination of iodide in iodized table salt.

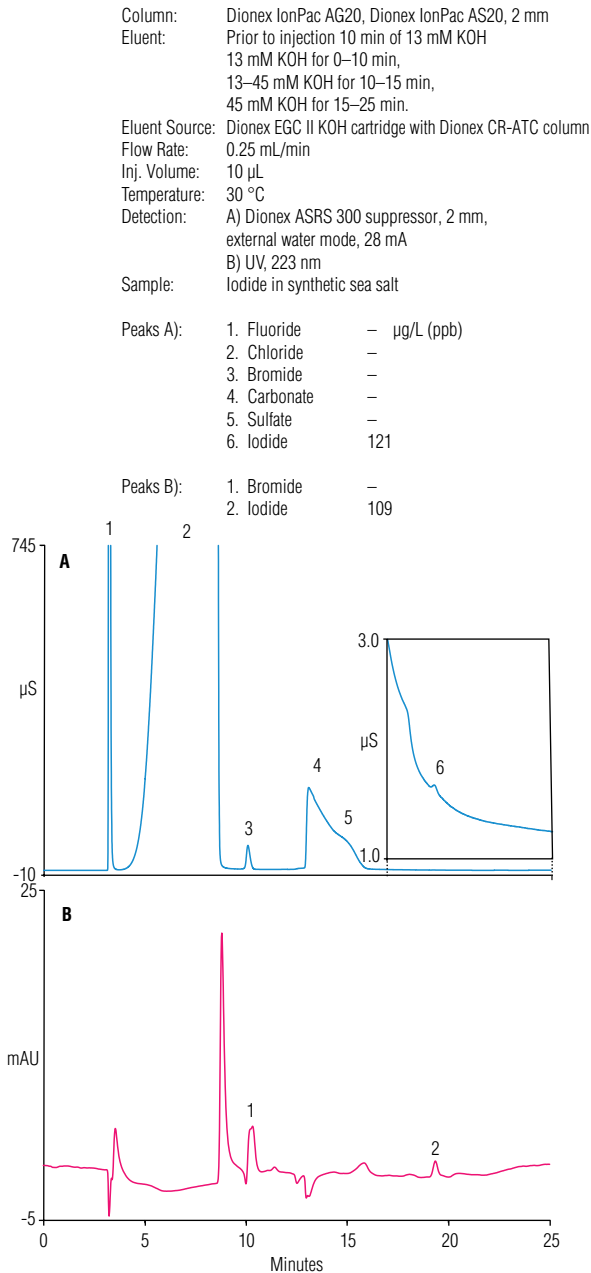


Figure 3. Determination of iodide in synthetic sea salt.

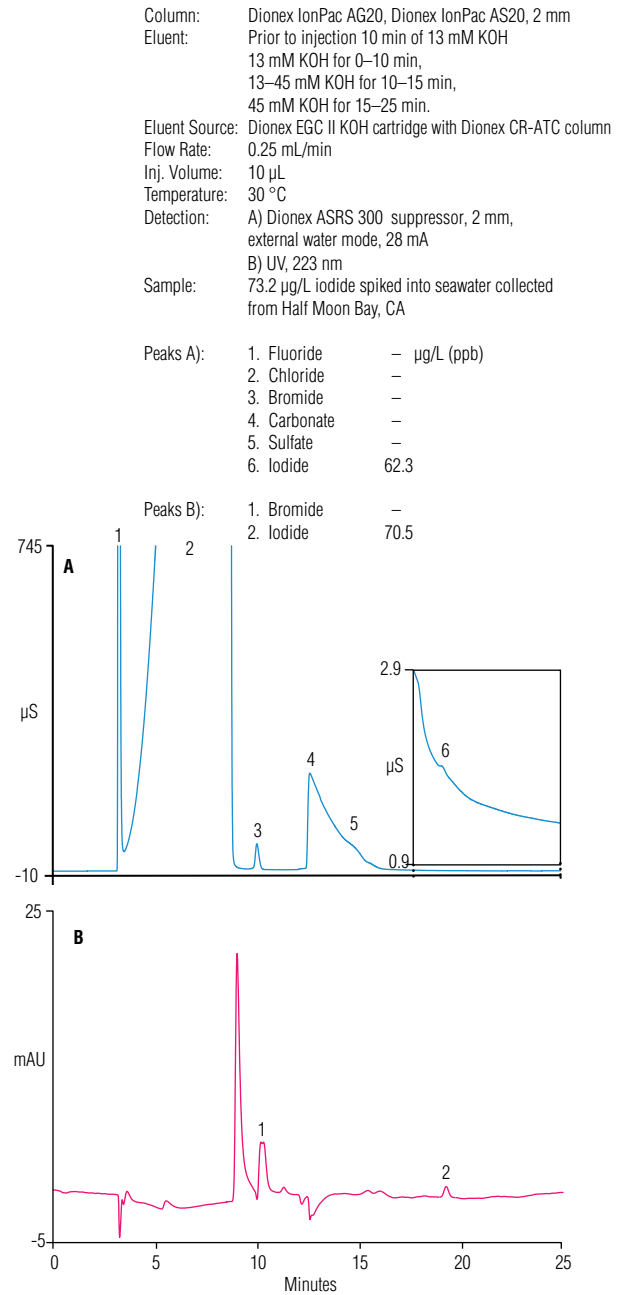


Figure 4. Determination of iodide in seawater collected at Half Moon Bay, CA.

To evaluate accuracy, recoveries were determined in five samples spiked with iodide. Recoveries using UV detection are excellent, ranging from 94–103% in saline matrices (Table 4). The salinity of the matrices is highly variable and these recoveries suggest that the method is accurate. Figures 4A and 5A show the separation of iodide spiked into natural seawater collected in Half Moon Bay, CA and Pacifica, CA, respectively. In both

samples, the iodide is very difficult to determine by conductivity detection and recoveries are low (77–85%). Sulfate and carbonate in the sample obscure iodide and make determination by suppressed conductivity difficult, leading to the observed poor recoveries. As shown in Figures 4B and 5B, iodide is easily determined by UV detection, resulting in improved recoveries.

Table 4. Recoveries of iodide from saline samples, UV detection.

Sample	Amount Found in Spiked Sample ($\mu\text{g/L}$)	Amount Added ($\mu\text{g/L}$)	Recovery (%) [*]
Synthetic Sea Water	48.2 ± 2.0	49.5	97 ± 4.1
	142 ± 1.2	141	101 ± 0.9
	252 ± 1.5	244	103 ± 0.6
Synthetic Sea Salt	201 ± 0.8	96.6	94 ± 0.4
Table Salt, Fresh	189 ± 1.0	99.1	99 ± 0.5
Seawater, Half Moon Bay, CA	70.5 ± 0.8	73.2	96 ± 1.2
Seawater, Pacifica, CA	72.4 ± 0.7	74.6	97 ± 1.0

^{*} Recovery of iodide was determined by triplicate spiked sample injections immediately following triplicate unspiked sample injections.

Conclusion

This application note describes the use of the Dionex IonPac AS20 column with electrolytically generated hydroxide eluent to determine iodide in saline matrices. The high capacity of the Dionex IonPac AS20 column allows sample analysis without dilution or sample pretreatment. The method was shown to be accurate by recovering iodide in a variety of samples including natural seawater and iodized table salt. UV detection simplifies integration of the iodide peak and improves specificity of the method in comparison to conductivity detection. The use of a RFIC-EG system allows continuous operation of the instrument with minimal maintenance. Only water for eluent generation and suppressor regeneration needs to be added to keep the instrument prepared for analyzing samples. Additionally, the 2 mm column format generates less waste and uses less eluent, saving both time and money.

Column: Dionex IonPac AG20, Dionex IonPac AS20, 2 mm
 Eluent: Prior to injection 10 min of 13 mM KOH
 13 mM KOH for 0–10 min, 13–45 mM KOH for 10–15 min, 45 mM KOH for 15–25 min
 Eluent Source: Dionex EGC II KOH cartridge with Dionex CR-ATC column
 Temperature: 30 °C
 Flow Rate: 0.25 mL/min
 Inj. Volume: 10 μL
 Detection: (A) Dionex ASRS 300 suppressor, 2 mm, external water mode, 28 mA
 (B) UV, 223 nm
 Sample: 74.6 $\mu\text{g/L}$ iodide spiked into seawater collected from Pacifica, CA

Peaks A): 1. Fluoride – $\mu\text{g/L}$ (ppb)
 2. Chloride –
 3. Bromide –
 4. Carbonate –
 5. Sulfate –
 6. Iodide 57.8

Peaks B): 1. Bromide –
 2. Iodide 72.8

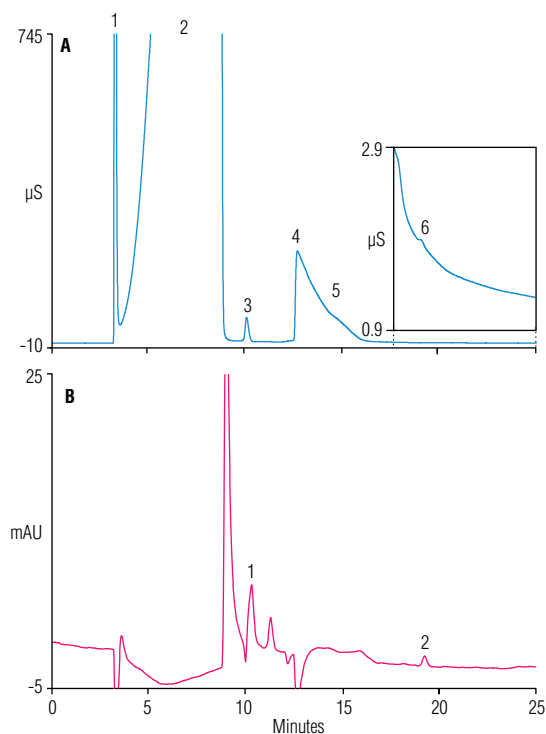


Figure 5. Determination of iodide in seawater collected at Pacifica, CA.

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