Analysis of Inorganic Nitrogen and Related Anions in High Salinity Water Using Ion Chromatography with Tandem UV and Conductivity Detectors

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Abstract

Over 97% of the Earth's water is high salinity water in the form of gulfs, oceans, and salt lakes. There is an increasing concern for the quality of water in bays, gulfs, oceans, and other natural waters. These waters are affected by many different sources of contamination. The sources are, but not limited to, groundwater run-off of nitrogen containing fertilizer, pesticides, cleaning agents, solid wastes, industrial waters, and many more. The final destinations of these contaminants are rivers, lakes, and bayous that eventually will lead to bays, gulfs, and oceans. Many industries depend on the quality of these waters, such as the fishing industry. In addition to wild marine life, there are large aquariums and fish and shrimp farms that are required to know the quality of the water. However, the ability of these industries to monitor their processes is limited. Most analytical methods do not apply to the analysis of high salinity waters. They are dependent on wet chemistry techniques, spectrophotometers, and flow analyzers. These methods do not have the accuracy, precision, and sensitivity when compared to ion chromatography (IC). Since the inception of IC, it has become a standard practice for determining the content of many different water samples. Many IC methods are limited in the range of analytes that can be detected, as well as the numerous sample sources of which the methods are applicable. The main focus of current IC methods does not include high salinity waters. This research demonstrates an ion chromatographic method that has the ability to determine low level concentrations of inorganic nitrogen and related anions (nitrite-N, nitrate-N, phosphorous-P, sulfate, bromide, chloride, sulfide, fluoride, ammonia, calcium, and magnesium) in a single run using a combination of UV and conductivity detectors. This method is applicable to various waters, and uses both freshwater and high salinity water samples.

Introduction

There are several regulatory and consensus methods currently available for the analysis of inorganic nitrogen and related species in various waters. The U.S. Environmental Protection Agency (EPA) monitors the quality of the drinking water and wastewaters in the U.S. Two relevant U.S. EPA methods are EPA300.0 and EPA300.1. These two ion chromatography (IC) methods are designed to test for the quantity of anions and cations in drinking water. The American Society for Testing and Materials (ASTM) is recognized internationally for the testing of water methods used in industries. The relevant ASTM methods include ASTM D4327, D6508, and D6919. The U.S. Geological Survey (USGS) regulates the quality of natural waters within the U.S., such as groundwater, rivers, and lakes. Its relevant IC methods include I-2057 and I-2058 for the testing of common anions in natural water. The Association of Analytical Communities (AOAC) International is an international association dedicated to publishing methods for chemical and microbiological analysis. The corresponding AOAC method, AOAC 993.3, is mostly applied to the food industry. *Standard Methods*, a joint

Table I. Method Detection Limit of Existing IC Methods*							
Method	Source	NO_3^-–N	NO_2^-–N	$H_2PO_4^{2-}$–P	SO_4^{2-}	Br^-	Cl^-	F^-
300.0	EPA	2	4	3	20	10	20	10
300.1		8	1	19	19	15	4	9
317						1		
9056A		100	100	100	100	100	100	50
993.3	AOAC	300	300	300	2000	300	300	300
D4327	ASTM	420	36	690	2850	630	780	260
D5996		0.02		0.02	0		0.02	0.02
D6581					2.91			
I-2057	USGS	50	20	60	200	100	200	10
I-2058		10		10	10	10	10	10
4110C	Standard	17	15	40	75	75	20	40
4110B	Methods	2.7	3.7	14	18	14	4	2
4110D					75			

* Method detection limit by analyte (parts per billion)

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publication of American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environmental Federation (WEF), focuses on the testing of water and wastewater. It has Standard Methods 4110 is used as a means of testing anions in water and wastewater.

It should be noted that all of the previously mentioned methods utilizing IC do not apply to a seawater matrix because of the high concentration of chloride and other potentially interfering analytes. With all of these methods, a high concentration of chloride will result in a tailing of the chloride peak, which reduces the resolution with the nitrite peak eluted after chloride. In addition, a high concentration of chloride necessitates a large dilution of the sample so that the concentration measured will fall within an acceptable quantitative range. For other analytes of interest, this requires a much lower limits of detection (LOD) and limit of quantitation. Table I shows the methods and the LODs of each of the relevant analytes.

As shown in Table I, there are no current methods that are able to analyze all analytes of interest. There are no methods to date that have the capability to determine the concentrations in a single method when testing high salinity water samples. All of these IC methods utilize a conductivity detector for the analysis of water samples with low concentrations of chloride.

Apparatus, reagents and relative information

Standards were prepared using deionized (DI) water (18 MΩ) and pure reagent grade compounds. A list of reagents used is shown in Table II.

Table II. Required Reagents

Chemical Ion	Reagent Compound
NO_3^--N	Sodium Nitrate
NO_2^--N	Sodium Nitrite
$H_2PO_4^{2-}$-P	Potassium Di-Hydrogen Phosphate
SO_4^{2-}	Sodium Sulfate
S^{2-}	Sodium Sulfide
Br^-	Potassium Bromide
Cl^-	Sodium Chloride
F^-	Sodium Fluoride
NH_4^+-N	Ammonium Sulfate
Ca^{2+}	Calcium Nitrate
Mg^{2+}	Magnesium Chloride
Na^+	Sodium Chloride
K^+	Potassium Bromide

Table III. Anion Method Parameters

Column	Metrosep ASUPP7-250
Oven Temp.	45°C
Mobile Phase	3.5 mmol/L Sodium Carbonate
Flow Rate	0.7 mLs/min
UV wavelength	215 nm
Injection Volume	20 µL

Each sequence ran contained a DI water blank to demonstrate a lack of contamination due to the instrument or any of its components. A 5 ppm standard containing each of the analytes of interest was measured to show the accuracy of the current calibration. The percent recovery was within 10%. Each sample was spiked with a standard resulting in a 10 ppb spike of each of the analytes of interest. The spiked sample demonstrated a 10% recovery, when compared to the sample. (Note: the standard/spiked analytes may be divided into multiple standards for the injection on their relative columns.)

Instrumentation

The Metrohm USA IC system (Model #850 Professional IC AnCat version, Riverview, FL) consists of an auto-sampler (Model #858, Professional AS), dual injection valves (20-uL injection loops), dual metal-free pumps, a column oven, two conductivity detectors, and a UV detector. The method was run on two separate columns at the same time. A High-resolution anion exchange column focused on the anions (nitrate-N, nitrite-N, phosphorous, sulfate, sulfide, bromide, chloride, and fluoride), while the high-resolution cation exchange column focused on the cations (ammonia-N, sodium, potassium, calcium, and magnesium).

Table IV. Cation Method Parameters

Column	Metrosep C4-250
Oven Temp.	45°C
Mobile Phase	1.75 mmol/L Oxalic Acid + 0.75 mmol/L Di-Picolinic Acid
Flow Rate	0.9 mLs/min
Injection Volume	20 µL

Table V. Sample Locations (Random Order)

Tap Water Samples	Sea Water Samples (Bay)
Pearland Tap Water	Lower Galveston Bay
Friendswood Tap Water	Trinity Bay
Pasadena (TX) Tap Water	Clearlake Bay
Seabrook Tap Water	Upper Galveston Bay
Clearlake Tap Water	East Galveston Bay
Houston Tap Water	West Galveston Bay
	Galveston Jetties
Bottled Water Samples	
Ozarka Bottled Water	**Aquarium Samples**
Dasani Bottled Water	Coral Aquarium Downtown
Aquafina Bottled Water	South Pacific Aquarium Moody Gardens
Smart Bottled Water	Carribean Aquarium Moody Gardens
Deja Vue Bottled Water	Soft Coral Aquarium Moody Gardens
Evian Bottled Water	Pompano Aquarium Moody Gardens
	Coral Aquarium Kemah
Ground Water Samples	Shark Aquarium Downtown
League City Well Water	
Armand Bayou Park Pier	
Lake Livingston	
Swimming pool water	
Crossby TX well water	
Fresh water from Aquarium	

Table VI. Anion data–Calculated MDL*

	Conductivity Detection			UV detection		
Sample ID	Nitrite-N	Nitrate-N	Phosphate-P		Nitrite-N	Nitrate-N
MDL1-1	0.0103	0.0386	0.0613		0.0099	0.0345
MDL1-2	0.0101	0.0375	0.0612		0.0098	0.0331
MDL1-3	0.0113	0.0384	0.0635		0.0111	0.0322
MDL1-4	0.0119	0.0388	0.0657		0.0116	0.0329
MDL1-5	0.0109	0.0392	0.0623		0.0106	0.0328
MDL1-6	0.0121	0.0384	0.0655		0.0118	0.0324
MDL1-7	0.0117	0.0370	0.0656		0.0114	0.0325
Average	0.0112	0.0383	0.0636	Average	0.0109	0.0329
Std. Dev	0.00078	0.00076	0.00203	Std. Dev	0.00081	0.00076
C. MDL†	0.00246	0.00240	0.00638	C. MDL	0.00253	0.00240

* All measurements are parts per million.
† C. MDL = calculated method detection limit.

Table VII. Cation Data–Calculated MDL*

	Non Suppressed Conductivity Detection			
Sample ID	Ammonia-N	Potassium	Calcium	Magnesium
MDL -1-1	0.593	0.576	0.539	0.424
MDL -1-2	0.598	0.580	0.547	0.428
MDL -1-3	0.596	0.580	0.543	0.428
MDL -1-4	0.632	0.619	0.590	0.465
MDL -1-5	0.631	0.611	0.588	0.456
MDL -1-6	0.634	0.614	0.578	0.467
MDL -1-7	0.630	0.622	0.580	0.461
Average	0.616	0.600	0.566	0.447
Std. Dev	0.0194	0.0206	0.0224	0.0194
C. MDL	0.061	0.065	0.070	0.061

* All measurements in parts per million.

Table VIII. Anion QA/QC Data*

	Nitrite-N				Nitrate-N			
Sample ID	Sample Value	True Spike value	Recovered Value	% Spike Recovery	Sample Value	True Spike value	Recovered Value	% Spike Recovery
QA/QC Suppressed conductivity detection								
Tap Water-1†	0.06	0.20	0.27	101.50	0.36	1.50	1.87	101.00
Bottled water 2†	0.00	0.20	0.23	114.00	0.05	1.50	1.43	92.00
GW-1†	0.00	0.20	0.21	103.50	0.00	1.50	1.46	97.53
Seawater-1†	0.00	1.25	1.12	89.76	0.00	1.50	1.46	97.33
Aquarium-5†	0.00	1.25	1.16	92.56	0.12	1.50	1.43	87.47
QA/QC Tandem UV Detection								
Tap Water-1†	0.06	0.20	0.26	98.50	0.38	1.50	1.97	106.47
Bottled water-2†	0.00	0.20	0.19	93.50	0.05	1.50	1.49	95.73
GW-1†	0.00	0.20	0.22	107.50	0.00	1.50	1.52	101.40
Seawater-1†	0.00	1.25	1.12	89.52	0.00	1.50	1.50	100.20
Aquarium-5†	0.00	1.25	1.15	91.60	0.10	1.50	1.47	91.67

* All measurements in parts per million.
† spike ($n = 2$).

The anion side of the system utilized the auto-sampler, injection valve, pump, column, suppressor, conductivity detector, and UV detector in tandem. The method parameters are shown in Table III.

The cation side of the system utilizes the auto-sampler, injection valve, pump, column, and conductivity detector. The method parameters are shown in Table IV.

The saltwater samples were prepared by performing a 250-fold dilution and filtering through a 0.45-µm filter. Fresh water samples were injected directly after filtering them through a 0.45-µm syringe filter.

Sample collection

This method is not limited to the analysis of high salinity water samples. It is applicable to many different types of water sources, such as freshwater, groundwater, well water, and seawater. The sources that were analyzed are shown in Table V.

Galveston Bay and the surrounding Houston waters provided a great opportunity to test the robustness of this method. The Houston area has a very large population of industrial manufacturing facilities. Samples were collected during the months of May and June. Sample containers were cleaned per EPA cleaning procedures listed in the OSWER Directive 9240.0–05A: "Specifications and Guidance for Contaminant-Free Sample Containers." After collection, the samples were stored on ice in a cooler until reaching the lab. Once in the lab, the samples were stored in a refrigerator at 2–8°C until they were analyzed. Samples were analyzed within 48 h of collection.

Results and Discussion

Method detection limit study

A method detection limit (MDL) is the minimum concentration of a specified analyte that can be detected and quantified with a 95% confidence level. The MDL was determined by injecting seven replicates of known concentration near the expected LOD. The standard deviation was determined from the results and multiplied by the t-value. The t-value for seven replicates was 3.14 at a 95% confidence level. A calculated MDL study was performed for both the anions and cations side of the instrument.

Anions

The results of the calculated anion MDL study were as expected with the results in the low-ppb range. Table VI. shows the results of the calculated anion MDL study for both conductivity and UV detection.
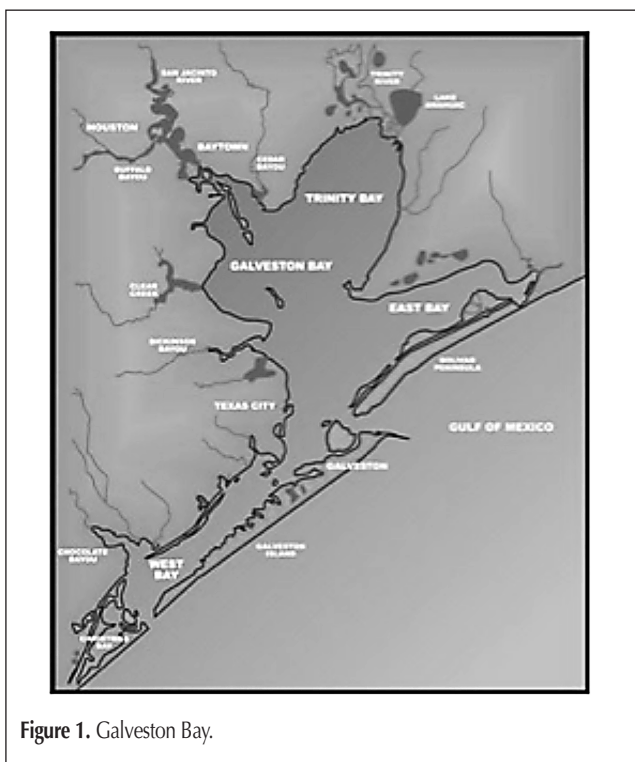
Figure 1. Galveston Bay.

Cations

The results of the calculated cation MDL study were as expected with results in the sub-ppm range. Table VII. shows the results of the calculated cation MDL study.

Calibration information

Anions

Figures 2 and 3 show an example chromatogram at calibration Level 1 for both conductivity and tandem UV detection. The chromatograms show excellent peak shape and resolution between analytes.

A 6-point calibration curve was prepared using an anion stock standard. A linear regression analysis was done to determine the correlation coefficient (r^2). Figures 4, 5, and 6 show the linearity of the calibration curve for nitrite-N, nitrate-N, and phosphate-P, respectively. Nitrite-N and nitrate-N have $r^2 > 0.999$, for both conductivity and UV detection. Phosphate-P also had a $r^2 > 0.999$ for conductivity detection. The relative standard deviation (RSD) for all the calibration curves was less than 3%.

Cations

A 5-point calibration curve was prepared using a cation stock standard. A linear regression analysis was done to determine r^2. Figure 7 shows the linearity of the calibration curve for
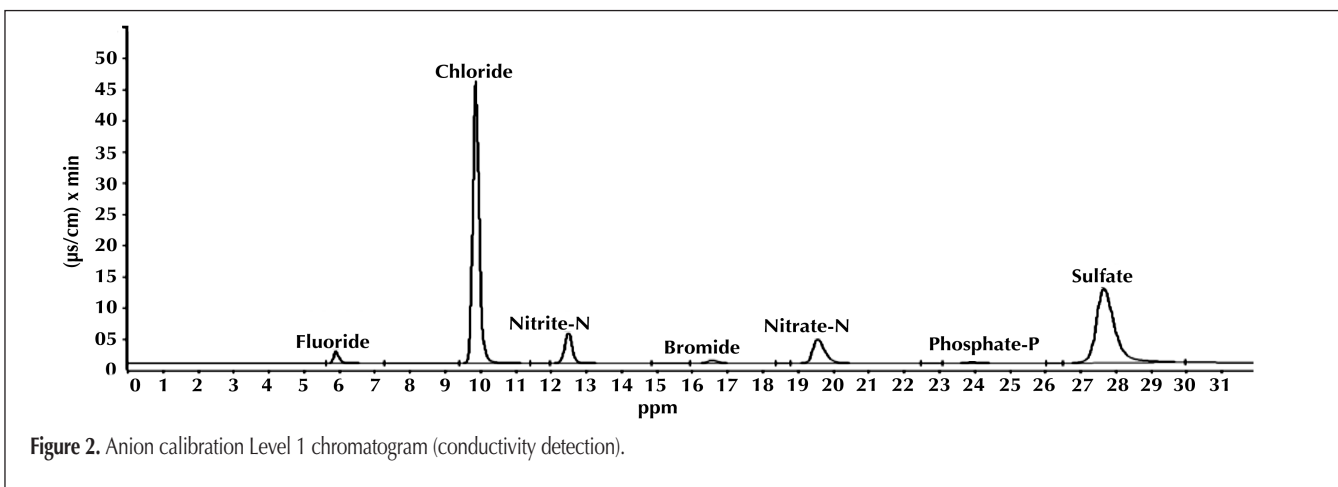

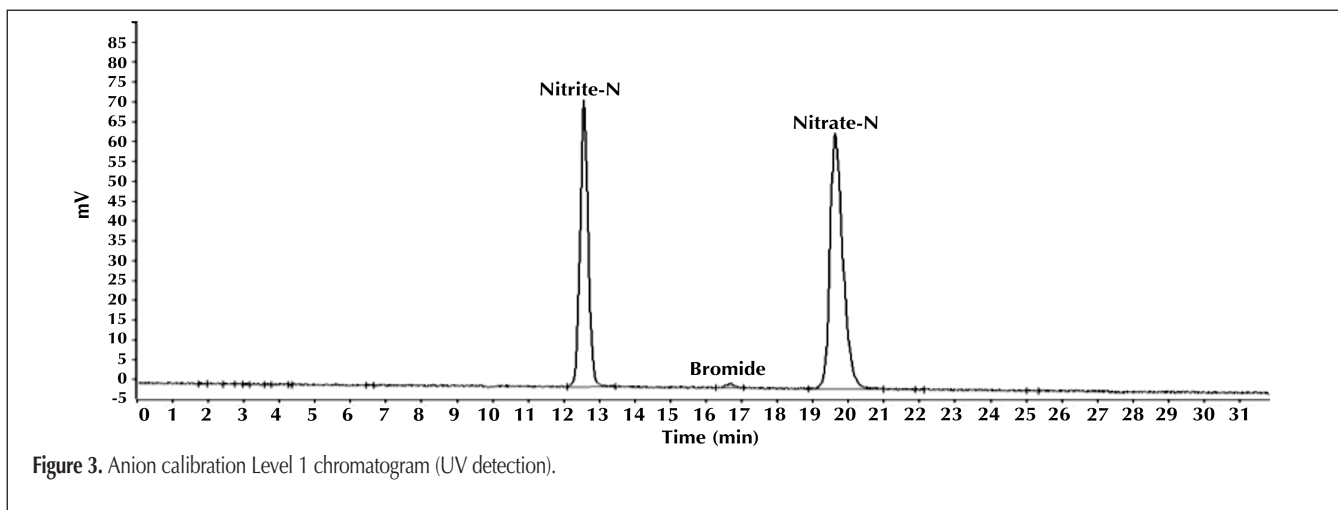**Figure 2.** Anion calibration Level 1 chromatogram (conductivity detection).

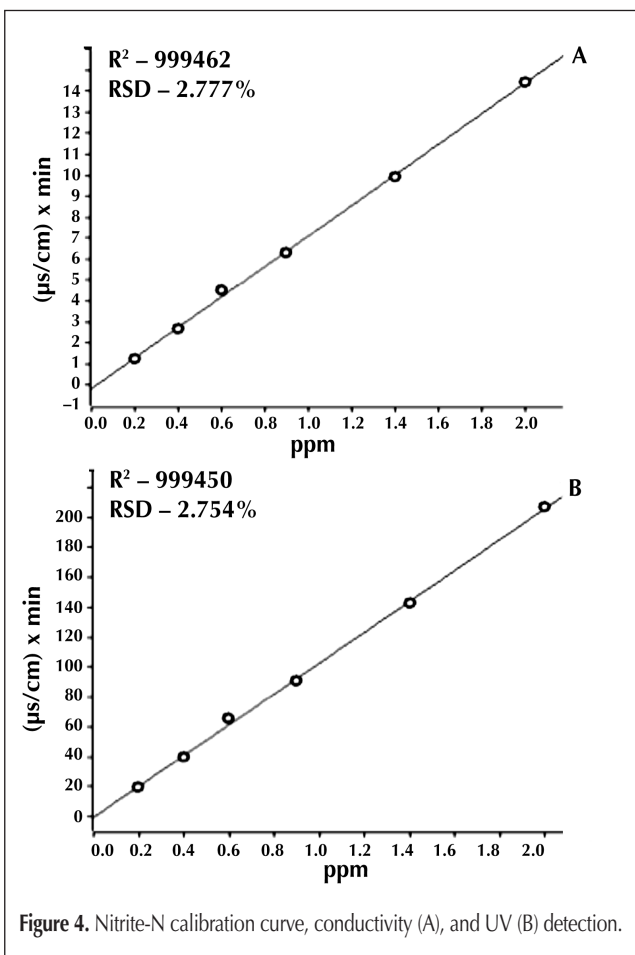**Figure 3.** Anion calibration Level 1 chromatogram (UV detection).

Figure 4. Nitrite-N calibration curve, conductivity (A), and UV (B) detection.

Figure 5. Nitrate-N calibration curve, conductivity (A), and UV (B) detection.

ammonia-N. Ammonia-N has a correlation coefficient of 0.999988. The RSD for ammonia-N was 0.548%.

Quality assurance/quality control information
Anions

Samples were chosen at random and spiked with the anion stock standard. Table VIII. shows the percent spike recovery for nitrite-N and nitrate-N. The spike recovery varies from 87.47–114.00%, with an average of 97.64% for both conductivity and UV detection.

Table IX. Cation QA/QC Data*

QA/QC Sample ID	Ammonia-N			
	Sample Value	True Spike value	Recovered Value	% Spike Recovery
Tap water-1[†]	0.04	2.50	2.44	95.84
Bottled water-2[†]	0.03	2.50	2.47	97.48
GW-1[†]	0.04	1.00	1.07	102.80
Seawater-1[†]	0.00	2.50	2.27	90.88
Aquarium-5[†]	0.00	1.00	1.09	108.50

* All measurements in parts per million.

[†] spike ($n = 2$).

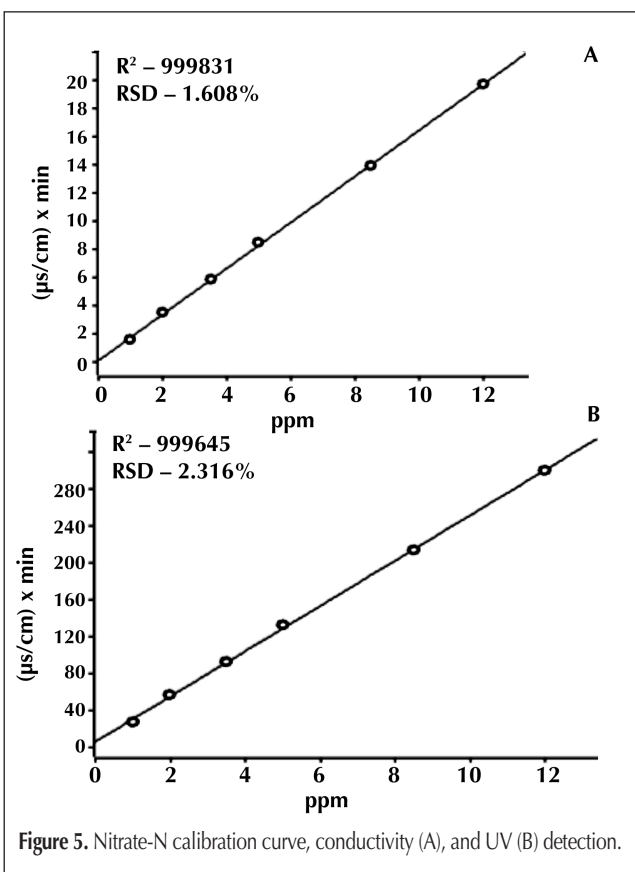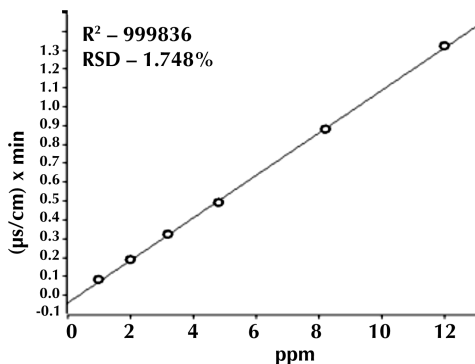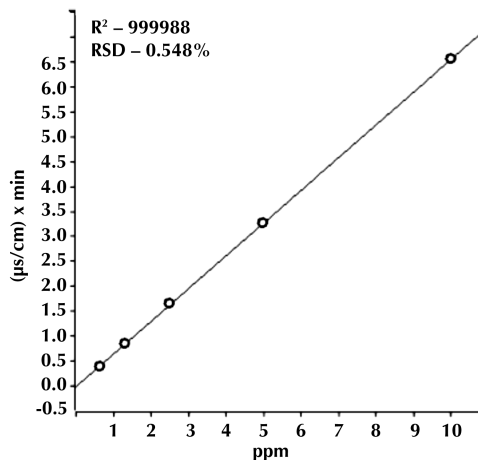**Figure 6.** Phosphate-P calibration curve, conductivity detection.

Figure 7. Ammonia-N calibration curve.

Cations

Samples were chosen at random and spiked with the cation stock standard. Table IX. shows the percent spike recovery for ammonia-N. The spike recovery varies from 90.88–108.50%, with an average of 99.10%.

Sample data

Anions

The anion sample data is compiled in Table X. Due to the low concentration of chlorine, the analysis of tap water samples demonstrates the continuity between the conductivity and tandem UV detection for nitrite-N and nitrate-N. The Aquarium-7 sample was the only high-salinity sample to show a detectable quantity of nitrite-N at 0.008 ppm. The nitrite-N for all other high salinity samples was below the LOD.

Cations

The Cation sample data is compiled in Table XI. Tap water samples are showing detectable levels of Ammonia-N even in presence of other cations. The high-salinity samples (Sea Water, Aquarium) show non-detectable levels for Ammonia-N.

Conclusions

An IC method was developed that has the ability to determine low levels of inorganic nitrogen and related anions and cations, including nitrite-N, nitrate-N, phosphate-P, and ammonia in a single run using a combination of UV and conductivity detectors. The method has applications in many different sample matrices. The LOD and recovery meets or exceeds previous methods. Comprehensive work is needed using total ion analysis, which

Table X. Anion Sample Data, Conductivity and UV Detection*

Sample ID	Conductivity Detection			UV detection	
	Nitrite-N	Nitrate-N	Phosphate-P	Nitrite-N	Nitrate-N
Tap water samples[†]					
Tap water-1	0.063	0.357	0.064	0.064	0.375
Tap water-2	0.015	0.203	n.d.*	0.013	0.187
Tap water-3	0.059	0.196	n.d.	0.058	0.209
Tap water-4	0.058	0.086	n.d.	0.056	0.085
Tap water-5	0.027	0.251	0.449	0.029	0.274
Tap water-6	n.d.	n.d.	n.d.	0.007	0.010
Bottled water samples[†]					
Bottled water-1	n.d.	n.d.	n.d.	n.d.	n.d.
Bottled water-2	n.d.	0.045	n.d.	n.d.	0.049
Bottled water-3	n.d.	0.035	n.d.	n.d.	0.037
Bottled water-4	n.d.	0.498	n.d.	n.d.	0.467
Bottled water-5	n.d.	n.d.	n.d.	n.d.	n.d.
Bottled water-6	n.d.	n.d.	n.d.	n.d.	n.d.
Ground water samples[†]					
GW-1	n.d.	n.d.	0.467	n.d.	n.d.
GW-2	n.d.	n.d.	3.296	n.d.	n.d.
GW-3	n.d.	n.d.	1.096	0.008	0.012
GW-4	n.d.	n.d.	n.d.	0.006	0.020
GW-5	n.d.	n.d.	0.749	0.008	0.027
GW-6	n.d.	0.049	0.546	n.d.	0.055
Seawater samples (Bay)[†]					
Seawater-1	n.d.	n.d.	n.d.	n.d.	n.d.
Seawater-2	n.d.	n.d.	n.d.	n.d.	n.d.
Seawater-3	n.d.	n.d.	n.d.	n.d.	n.d.
Seawater-4	n.d.	n.d.	n.d.	n.d.	n.d.
Seawater-5	n.d.	n.d.	n.d.	n.d.	n.d.
Seawater-6	n.d.	n.d.	n.d.	n.d.	n.d.
Aquarium samples[†]					
Aquarium-1	n.d.	0.040	n.d.	n.d.	0.058
Aquarium-2	n.d.	0.026	0.401	n.d.	0.021
Aquarium-3	n.d.	n.d.	n.d.	n.d.	n.d.
Aquarium-4	n.d.	0.105	n.d.	n.d.	0.111
Aquarium-5	n.d.	0.118	n.d.	n.d.	0.098
Aquarium-6	n.d.	0.041	n.d.	n.d.	0.040
Aquarium-7	n.d.	0.027	n.d.	0.008	0.031
Aquarium-8	n.d.	n.d.	n.d.	n.d.	n.d.

* All measurements in parts per million.

(*n* = 2).

Table XI. Cation Sample Data*

Sample ID[†]	Non Suppressed Conductivity Detection			
	Ammonia-N	Potassium	Calcium	Magnesium
Tap water-1	0.04	2.71	25.29	2.28
Tap water-2	0.04	2.14	25.60	2.32
Tap water-3	0.12	2.28	25.03	2.16
Tap water-4	0.06	0.87	8.27	0.55
Tap water-5	0.39	2.16	25.87	2.15
Tap water-6	0.39	2.11	24.36	2.56
Bottled water-1	n.d.[‡]	1.75	2.35	0.96
Bottled water-2	0.03	n.d.	n.d.	n.d.
Bottled water-3	n.d.	0.50	42.44	15.15
Bottled water-4	n.d.	0.50	n.d.	0.35
Bottled water-5	n.d.	1.50	n.d.	1.63
Bottled water-6	0.04	0.02	n.d.	n.d.
GW-1	0.04	0.24	1.81	0.06
GW-2	n.d.	10.07	92.45	10.92
GW-3	0.18	2.31	9.15	3.39
GW-4	0.17	2.42	12.31	4.54
GW-5	0.03	2.20	22.34	2.45
GW-6	n.d.	3.92	69.72	2.32
Seawater-1	n.d.	7.20	75.57	254.89
Seawater-2	n.d.	8.19	86.33	297.05
Seawater-3	n.d.	12.95	135.63	506.97
Seawater-4	n.d.	16.92	152.72	631.91
Seawater-5	n.d.	8.12	80.19	287.23
Seawater-6	n.d.	13.74	149.90	533.41
Aquarium-1	n.d.	166.1	189.8	686.1
Aquarium-2	n.d.	150.9	219.8	599.3
Aquarium-3	n.d.	163.1	159.5	733.0
Aquarium-4	n.d.	178.0	159.9	598.4
Aquarium-5	n.d.	144.6	168.7	569.8
Aquarium-6	n.d.	187.9	290.4	725.2
Aquarium-7	n.d.	162.9	212.4	664.6
Aquarium-8	n.d.	169.7	182.3	679.8

* All measurements in parts per million.

[†] (*n* = 2).   [‡] n.d. = Non detect.

allows a mass balance of ions with related total dissolved solids, alkalinity, and pH. A detailed sample analysis of the "dead zone" in the Gulf of Mexico is needed.

References

1. 300.0. Determination of Inorganic Anions by Ion Chromatography, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency. Rev. 2.1. 1993.
2. 300.1. Determination of Inorganic Anions in Drinking Water by Ion Chromatography, National Exposure Research Laboratory, U.S. Environmental Protection Agency. Rev. 1.0. 1993.
3. 317.0. Determination of Inorganic Oxyhalide Disinfection by-Products in Drinking Water Using Ion Chromatography with the Addition of a Post-column Reagent for Trace Bromate Analysis, National Exposure Research Laboratory, U.S. Environmental Protection Agency. Rev. 1.0. 2000.
4. 4110 A(B). Determination of Anions by Ion Chromatography, Standard Methods. 1990.
5. 9056A. Determination of Inorganic Anions by Ion Chromatography, U.S. Environmental Protection Agency. Rev 1. 2000.
6. 980896, Anion Analysis Using Hydroxide Eluent and Indirect Conductivity Detection and EPA Method B-1011 for Nitrite and Nitrate Using UV Detection, Ion Chromatography Method, Water, Inc. 2000. 993.30. Inorganic Anions in Water, AOAC Official Method. 1997.
7. AW CH6-0841-062005, Determination of nitrite, nitrate and phosphate in seawater of a shrimp farm, IC Application Work, Metrohm Peak, Inc.
8. AW CH6-0848-082005, LODs of nitrite in ultra pure – and sea water with ELCD, IC Application Work, Metrohm AG.
9. AW IN6-0701-012007, Nitrite and Nitrate in Sea Water, IC Application Work, Metrohm AG.
10. AW US6-0090-012005, Determination of Low Level Nitrate, Sulfate, Sulfide, Thiosulfate, Acetate, Formate, Lactate in Sea Water by Suppressed Conductivity and Direct UV Detection, IC Application Work, Metrohm Peak, Inc.
11. I-2057-85. Anions, ion-exchange Chromatographic, Automated, U.S. Geological Survey. 1985.
12. I-2058-85. Anions, ion-exchange Chromatographic, Low Ionic-Strength Water, Automated, U.S. Geological Survey. 1985.
13. Asopuru A. Okemgbo, Herbert H. Hill, and William F. Siems. Reverse polarity capillary zone electrophoretic analysis of nitrate and nitrite in natural water samples. *Anal. Chem.* **71:** 2725–2731 (1999).
14. Claudia Eith, Maximilian Kolb, Achim Rumi, Andreas Seubert, and Kai Henning Viehweger. Practical Ion Chromatography, An Introduction, 2nd Ed. Metrohm AG. 2007.
15. David Jenkins. The Differentiation, analysis, and preservation of nitrogen and phosphorus forms in natural waters, trace inorganics in water. *Adv. in Chem.* **73(16):** 265–280 (1968).
16. Donald Scavia and Kristina A. Donnely, Reassessing Hypoxia Forecasts for the Gulf of Mexico, Environ. Sci. Technol. 2007, 41, 8111–8117. http://www.seafriends.org.nz/oceano/seawater.htm
17. Hie-Joon Kim and Young-Kyung Kim. Determination of nitrite in drinking water and environmental samples by ion exclusion chromatography with electrochemical detection. *Anal. Chem.* **61(14):** 1485–1489 (1989).
18. Hong Yu, Hongjing Ai, and Qian Chen. Rapid analysis of nitrate and nitrite by ion-interaction chromatography on a monolithic column. *Chromatographia.* **70:** 1017–1022 (2009).
19. Hyun-Mee Park, Young-Man Kim, Dai Woon Lee, Su-won Lee, and Kang-Bong Lee. Ion chromatographic determination of inorganic anions in environmental samples of Korea. *Anal. Sci.* **18:** 343–346 (2002).
20. Jason B. Sylvan, Quay Dortch, David M. Nelson, Alisa F. Maier Brown, Wendy Morrison, and James W. Ammerman. Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation. *Environ. Sci. Technol.* **40(24):** 7548–7553 (2006).
21. Kang Tian, Purnendu K. Dasgupta, and Todd A. Anderson. Determination of trace perchlorate in high-salinity water samples by ion chromatography with on-line preconcentration and preelution. *Anal. Chem.* **75:** 701–706 (2003).
22. Kazuaki Ito, Yasunobu Ariyoshi, Fumio Tanabiki, and Hirshi Sunahara. Anion chromatography using octadecylsilane reversed-phase columns coated with cetyltrimethylammonium and its application to nitrite and nitrate in seawater. *Anal. Chem.* **63:** 273–276 (1991).
23. Lakshmy M.Nair and Raaidah Saari-Nordhaus. Use of a conventional HPLC system for performing U.S. EPA method 300.0, determination of inorganic anions by ion chromatography. *Am. Lab.* **29(4):** 33FF–33MM (1997).
24. M.C. Gennaro, C. Abrigo, D, Giacosa, and G. Saini. Determination of nitrite, nitrate, iodide, bromide, chloride, sulfate, in Venice lagoon-water by reversed-phase ion-interaction HPLC. *J. Enviorn. Sci. Health A.* **A30(3):** 675–687 (1995).
25. Peter A. Bruttel and Nadine Seifert. Analysis of Water Samples and Water Constituents with Metrohm Instruments, Metrohm AG. 2007.
26. Peter E. Jackson, Dave Thomas, and Kirk Chassaniol. Environmental Analysis of Inorganic Anions and Perchlorate by Ion Chromatography, ACS Symposium Series, American Chemical Society, 2003.