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Analysis of wastewater for anionic and cationic nutrients by ion chromatography in a single run with sequential flow injection analysis☆

Shreekant V. Karmarkar*

Zellweger Analytics, Lachat Instruments Division, 6645 West Mill Road, Milwaukee, WI 53218, USA

Abstract

To prevent nutrient enrichment and, hence the undesirable ecological impacts, the nutrients monitored in wastewater samples include two anionic species, i.e., nitrate and orthophosphate, and a cationic species, ammonium. Ion chromatography (IC) is one of the popularly used techniques for determinations of nitrate and phosphate in these samples, whereas determination of ammonium in wastewater samples is typically done using manual or automated wet chemistry, e.g., flow injection analysis (FIA). We have developed a sequential IC–FIA method, using Lachat's QC8000 IC system, which allows determinations of nitrate, phosphate and ammonia in a single injection. In this system, a QuikChem Small Suppressor cartridge is regenerated in between the samples. A sample is injected while leaving the suppressor off-line. Ammonium, a cation, elutes in the void volume of an anion-exchange column. The unsuppressed column effluent, exiting the conductivity flow cell, up to this point is used for FIA determination of ammonia. When ammonia exits the conductivity flow cell, a fully regenerated suppressor is brought in-line for conductometric detection of the anions. Analog data are simultaneously acquired from colorimetric and conductometric detectors, for the cationic and anionic nutrients, respectively. The method is accurate with spike recoveries in wastewater samples ranging from 91% for nitrate to 114% for chloride. It is precise with RSD values, for replicate analyses ($n=7$) of a mid-range standard, ranging from 0.4% for phosphate to 1% for nitrate.

Keywords: Water analysis; Environmental analysis; Inorganic anions; Inorganic cations

1. Introduction

Enrichment of aquatic areas with plant nutrients often results in growth of micro or macro algae, and these algal blooms lead to undesirable ecological impacts such as oxygen depletion, fish kills, loss of shellfish, declines in seagrasses and corals and toxic blooms [1]. To prevent enrichment of aquatic areas, the three key nutrients that are monitored in wastewater, influent and effluent samples, include two anionic species; nitrate and orthophosphate, and a cationic species, ammonium. The US Environmental Protection Agency (EPA) and several other regulatory agencies have set limits on concentrations of these nutrient species in influent and effluent samples, and have also approved methods for analyses of such samples.

One of the most popular regulatory methods is the EPA method 300.0 for ion chromatographic determination of anions in various waters [2]. This method covers determination of the two anionic nutrients,

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*Tel.: +1-414-358-4200; fax: +1-414-358-4206.
E-mail address: shree.karmarkar@zelana.com (S.V. Karmarkar)

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nitrate and phosphate, along with the other five anions; bromide, chloride, fluoride, nitrite, and sulfate. Regulatory analysis for the third nutrient, ammonia, is not commonly done using ion chromatography (IC) for several reasons. First, there is no EPA-approved IC method for cations in wastewater samples. Second, using the IC technique for ammonium only is not cost-justified. Third, separating a relatively small ammonium peak from a usually huge sodium peak is quite challenging. Determination of ammonium in wastewater samples is, therefore, typically done using manual or automated wet chemistry, e.g., flow injection analysis (FIA) employing a solute specific detector [3].

Recent advances in analytical instruments, based on a unique Shared Peripheral System (SPS), allow simultaneous operation of FIA and IC [4]. In the SPS, a multi-tasking Windows based software (Omnion) controls FIA and IC instruments and simultaneously acquires data from these two instruments. While a relatively slowly operating IC (~10 min per sample) is analyzing sample for the anions, the faster FIA (~50 s per sample) uses the peripherals such as autosampler and peristaltic pump to analyze samples for the non-IC type parameters, e.g., ammonia, total Kjeldahl nitrogen and phenol. The SPS type instrument, therefore, is seemingly a convincing route for regulatory-type determination of the three nutrient species. These instruments are, however, geared towards high-productivity laboratories, and may not appeal to small-scale laboratories with monetary constraints or to those laboratories where only a few samples are analyzed per day. To meet requirements of such laboratories, it is desirable to develop a simple, cost-effective IC method for simultaneous determination of anionic and cationic nutrient ions.

The present work describes IC determination of chloride and the two anionic nutrients, nitrate and phosphate with determination of the cationic nutrient, ammonium, by sequential FIA. The term sequential applies to serial determinations of ions using a combination of two different techniques. This method enables quantitation, in a single injection, of the two anionic nutrients using a bulk-property conductometric detector, and that of a cationic nutrient using a solute-specific colorimetric detector.

2. Experimental

2.1. Ion chromatography with sequential flow injection analysis

Lachat's QC8000 IC+ system (Zellweger Analytics, Milwaukee, WI, USA) was used. This system was equipped with an XYZ autosampler, an eluent delivery pump, a peristaltic pump, electronically actuated six-port sample valve and ten-port suppressor–regeneration valve, a QS-A5G guard column (20 mm×2.0 mm I.D.), a QS-A5 analytical column (150 mm×2.0 mm I.D.) packed with macroporous anion-exchange material, a QE-A1 suppressor cartridge (20 mm×4.6 mm I.D.) packed with high-capacity cation-exchange material in H^+ form, a temperature controlled conductivity detector (CM-100), a micro-gas diffusion block (Sialomed, Columbia, MD, USA, with a chamber volume of 20 μl) mounted with a PTFE membrane, a colorimetric detector with a 520 nm interference filter, and OmnionIC data station. The OmnionIC data station simultaneously acquired data from the conductivity and absorbance detectors. The schematic in Fig. 1 shows the fluidic path for IC determination of anions sequentially with FIA for ammonia.

The suppressor cartridge was reproducibly regenerated in between the samples using a using a ten-port valve as described in detail elsewhere [6]. Ammonia exists as a cation, ammonium, at the basic pH of the carbonate–hydrogencarbonate eluent, and it elutes in the column void volume. During method development, initially, ammonium was allowed to go through the suppressor cartridge (packed with high-capacity cation-exchange material) and the suppressed eluent stream was used for FIA determination of ammonium. Using this fluidic arrangement it was observed that the ammonium peak shape became severely distorted, and this could be attributed to poor efficiency of sodium, the counter-cation of the eluent, to elute out ammonium from a high-capacity cation-exchange material. Under the optimized conditions, therefore, ammonium was not allowed to go through the suppressor cartridge. Timed events for sample loading and suppressor regeneration valves are summarized in Table 1. In the events occurring, 3 s after sampling was started

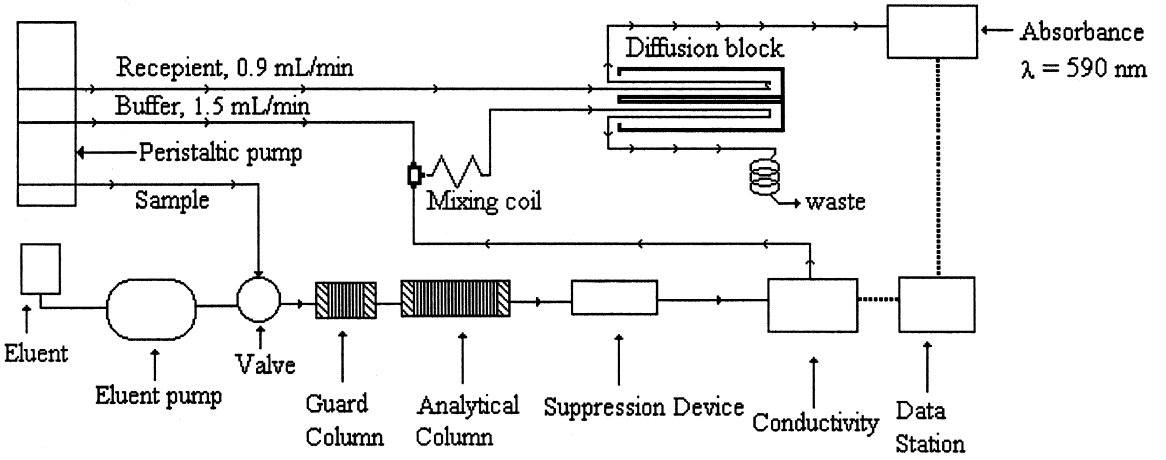

Fig. 1. Schematic illustrating IC with sequential FIA.

V1 and V2 were put to load states to fill a sample loop and to take the suppressor off-line for regeneration, respectively. The sample was injected onto the IC+ system while suppressor was being regenerated. Injected sample, containing ammonium cation, traveled through the analytical column, and bypassing the suppressor, entered the conductivity flow cell at 1.2 min. This non-suppressed eluent stream was then subjected to FIA ammonia. Mixing the stream with boric acid–EDTA buffer (pH 13) ensured formation of $NH_{3(g)}$ form. The mixed stream was then fed to a gas diffusion block in which the NH_3 gas diffused across a PTFE membrane and was trapped in a slightly acidic indicator solution. The resulting pH shift changed indicator solution color, and it was recorded at 590 nm. At 1.2 min, the fully regenerated suppressor was brought in-line to perform suppressed conductometric detection of the anions; chloride, nitrate, phosphate and sulfate.

Table 1
Timed events for sample loading and suppressor regeneration valves[a]

Event	Time (min)	V1	V2
Load sample and regenerate the suppressor	0.05	1	1
Inject sample	0.6	0	1
Start data acquisition	0.8	0	1
Regenerated suppressor brought in-line	1.2	0	0

[a] V1, six-port sample loading valve; V2, ten-port suppressor regeneration valve. The numbers 1 and 0 correspond to load and inject states, respectively. The valves were electronically actuated using OmnionIC software.

2.2. Reagents

Eluent consisting of 10 m*M* $NaHCO_3$ and 1 m*M* Na_2CO_3 and regenerant solution of 0.25 *M* H_2SO_4 was prepared from reagent grade chemicals. Eluent was filtered through a 0.22-μm filter and degassed.

The buffer solution was prepared by dissolving 30.0 g ethylenediaminotetraacetic acid, disodium salt in about 800 ml water, followed by dissolving 12.4 g boric acid, and adding 100 ml of 5 *M* sodium hydroxide. The solution was diluted to 1 l with deionized (DI) water. The pH of this solution was approximately 13 [7].

The stock mixed indicator solution consisted of 10 g bromocresol purple, sodium salt; 5 g bromothymol blue, sodium salt; 2.5 g cresol red, sodium salt; and 45 g potassium chloride, deionized water, 0.01 *M* sodium hydroxide and 10 ml ethanol. A working solution was degassed with helium and allowed to stand for 2 h before using. Prior to analysis, the pH was adjusted to 5.7. This solution can be stored at room temperature for two weeks in a glass bottle, and the pH checked prior to use [7].

Table 2
Summarized ranges for chloride, nitrite, bromide, nitrate, phosphate and sulfate in 16 influent and effluent wastewater samples[a]

Anion	Range (mg/l)
Chloride	100–394
Nitrite-N	0.01–0.5
Bromide	0.28–2.2
Nitrate-N	0.03–13.6
Phosphate-P	0.2–5
Sulfate	36–302

[a] Data summarized from Refs. [5] and [8].

2.3. Standards

Concentration values of anions, found in 16 wastewater samples, were used as guidelines in selecting calibration ranges for chloride, nitrate and phosphate. The upper calibration range for nitrate was kept at 10 mg N/l since at higher concentration values, nitrate peak shape was very asymmetric. The optimized IC conditions fully resolved bromide peak (0.28 to 2.2 mg/l) from nitrate peak (0.2 to 10 mg N/l). Samples for ammonia determination are typically preserved with eight drops of H_2SO_4 per liter, i.e., about 270 mg SO_4^{2-}/l. Considering the sulfate originally present (Table 2) and that added from preservation, the sulfate concentration was expected in the range of 306 to 572 mg SO_4/l. All the synthetic standards contained sulfate at 500 mg/l. The calibration ranges (in mg/l) used were chloride, 8 to 400; nitrate-N, 0.2 to 10; phosphate-P, 0.1 to 5; and ammonia-N, 0.2 to 10.

2.4. Samples

A quality control sample, lot 9977 from Environmental Resource Associates (ERA, Arvada, CO, USA) was prepared by diluting a 1.25 ml sample to 1 l with a solution containing eight drops of concentrated H_2SO_4 per liter. This sample was analyzed to check quality of data generated using the optimized sequential IC–FIA method.

Immediately after collection, wastewater influent and effluent samples were preserved with eight drops of concentrated H_2SO_4 per liter. These samples were filtered through a 0.45-μm filter, and analyzed using the optimized sequential IC–FIA method.

3. Results and discussion

3.1. Optimization of IC conditions for the determination of anions

The challenging tasks in IC separation were: (a) resolving small peaks for bromide, nitrate and phosphate (0.1 to 10 mg/l) in the presence of huge peaks for chloride (up to 400 mg/l) and sulfate (up to 800 mg/l), (b) achieving an isocratic separation, and (c) maintaining a short run time. Using an eluent made of 10 m*M* $NaHCO_3$+1 m*M* Na_2CO_3, the phosphate peak shifted to the left of the sulfate peak. Further optimization in separation was done using a higher capacity column, packed with 300H material, as shown in Table 3. Although data is not presented, this column also fully resolved bromide and nitrate

Table 3
Effect of anion-exchange capacity of columns on resolution values (R_s) between adjacent anions[a]

Column	Capacity, (mequiv./g)	Eluent conditions	R_s		
			Cl:NO_3	NO_3:HPO_4	HPO_4:SO_4
150×2.0 mm, packed with AN300	0.02	10 m*M* $NaHCO_3$+ 0.2 m*M* Na_2CO_3	3.4	2.7	1.1
150 mm×2.0, packed with 300H	0.04	10 m*M* $NaHCO_3$+ 1.0 m*M* Na_2CO_3	4.4	3.3	1.8

[a] For analytical conditions, see Fig. 2. Concentration of anions: chloride, 200 mg/l; nitrate, 5 mg N/l; phosphate, 5 mg P/l; and sulfate, 470 mg/l.

peaks. Fluoride, formate, and acetate peaks may not be fully resolved from chloride, although our preliminary results (data not presented) showed that these peaks eluted just at the injection disturbance which appears as a dip in Figs. 2 and 3. A 25-μl sample-loop provided ample sensitivity for quantitation of nutrient ions down to 0.1 to 0.2 mg/l. With these optimized conditions, isocratic separation of peaks in the expected concentrations was achieved with a run time of less than 9 min.

3.2. IC for anions with sequential FIA for ammonia

The simultaneous determinations of anionic and cationic nutrients is illustrated in Fig. 2 which shows a trace, on channel B, for FIA–ammonia and a chromatogram, on channel A, for the anions; chloride, nitrate, phosphate and sulfate. As the ammonia peak elutes out on channel B, the chloride peak starts rising up on channel A. Time delay for the ammonia peak to show up on channel B was estimated at 35 s. The valving arrangement allowed injecting a sample and feeding the non-suppressed eluent to FIA chemistry, while the suppressor was taken off-line for regeneration. The close proximity of the two detectors provided minimal dead volume for the FIA NH_3 chemistry.

The method calibrated well, for chloride (8 to 400 mg/l), nitrate (0.2 to 10 mg N/l), phosphate (0.1 to 5 mg P/l) and ammonia (0.2 to 10 mg N/l), as evident from the R^2 values of greater than 0.999 for the quadratic fits. The disturbance peak did not affect calibration for chloride in the range tested, however,

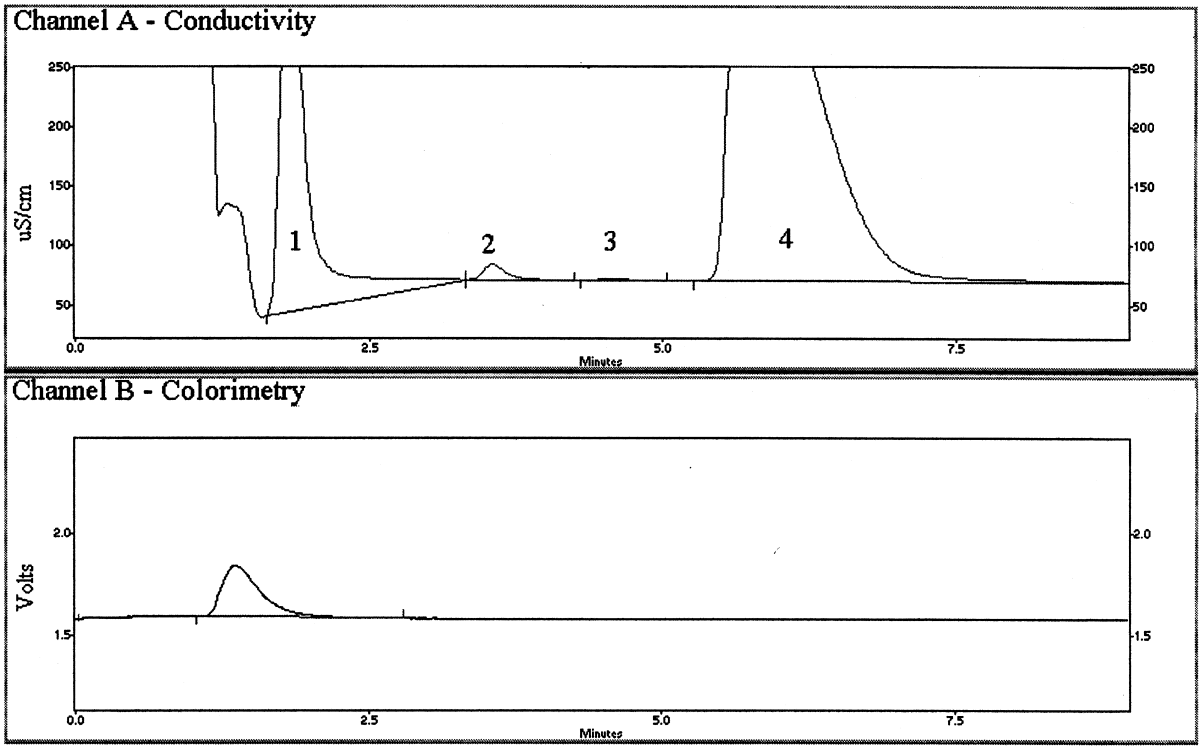

Fig. 2. Typical trace, on channel B, for FIA–ammonia (1 mg N/l) and ion chromatogram, on channel A, showing separation of 1; chloride at 200 mg/l, 2; nitrate at 1 mg N/l, 3; phosphate at 1 mg P/l, and 4; sulfate at 500 mg/l. Analytical conditions: eluent, 10 m*M* $NaHCO_3$+1 m*M* Na_2CO_3 at the rate of 0.6 ml/min; column, QS-A5 (150×2.0 mm); suppressor, QE-A1 regenerated with a 1-ml loop filled with 0.25 *M* H_2SO_4; 25-μl sample loop; FIA reagents as shown in Fig. 1.

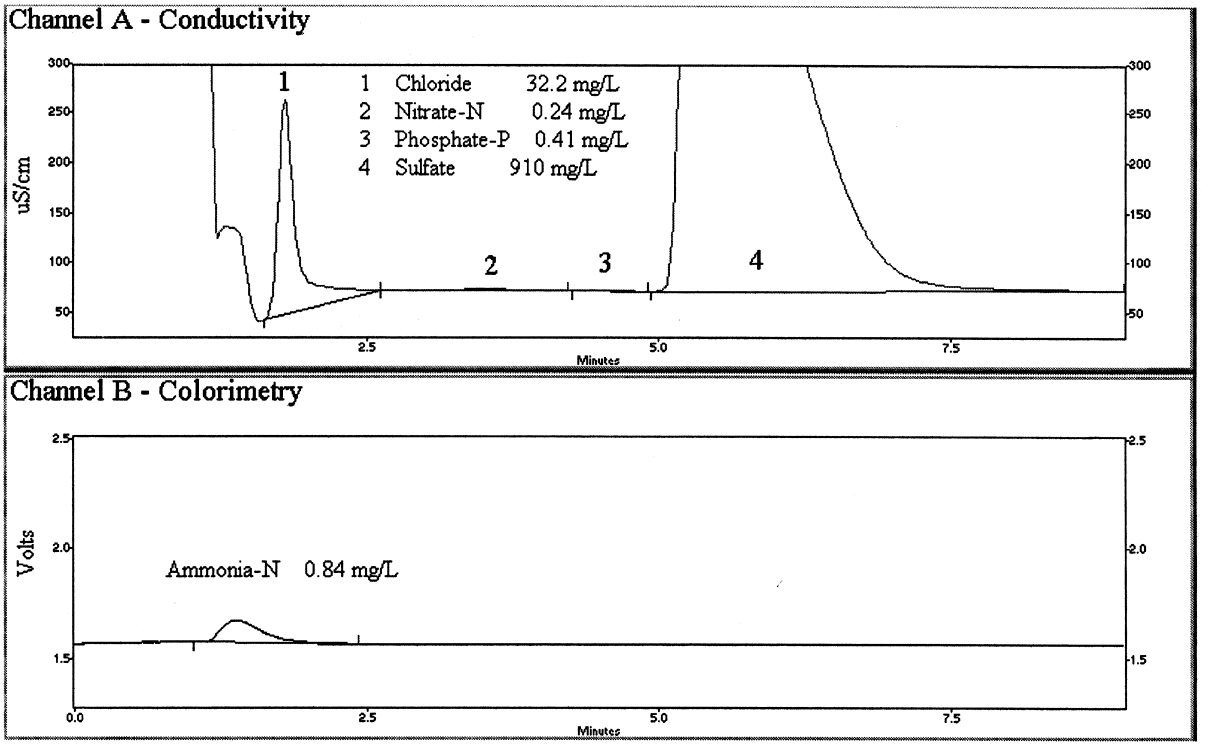

Fig. 3. Typical trace, on channel B, for FIA–ammonia and chromatogram, on channel A, showing separation of chloride, nitrate, phosphate and sulfate in a Lagoon discharge sample. Note the concentration ratio of 2220 between phosphate and sulfate. For analytical conditions, see Fig. 2.

the method may not provide accurate results for chloride when its concentration is less than 8 mg/l. The residual values were generally less than 10%. Method detection limits for the nutrient ions were 0.005 mg NO_3^- – N/l, 0.006 mg HPO_4^2 – P/l and 0.01 mg NH_3 – N/l.

In order to assess the data quality, a certified ERA standard was analyzed in duplicate. Compared with values given by ERA, the error in average determined values for the three nutrient ions was less than 6%. The method was precise since the relative standard deviation (RSD) values, for replicate analyses ($n=7$) of a mid-range standard, ranged from 0.4% for phosphate to 1% for nitrate.

The method was further applied to the determination of chloride and the nutrient ions in four influent and effluent wastewater samples (Table 4). Filtered samples, without any dilution, were analyzed using the sequential method. One of the samples, Lagoon discharge, contained phosphate at 0.41 mg P/l and sulfate at 910 mg/l, resulting in a concentration ratio of 2200 between sulfate and phosphate (Fig. 3). The IC method provided fully resolved phosphate and sulfate peaks even at this high concentration ratio.

In order to assess method accuracy in the sample matrix, each of the four samples (Table 4) and a reagent water sample were spiked with a standard containing Cl^-, 40 mg/l; and NO_3^--N, HPO_4^{2-}-P, and NH_3-N each at 0.5 mg/l. The spiked samples were then analyzed using the sequential method. The method was accurate, since the recovery values ranged from 91% for nitrate in effluent sample 2 to 111% for phosphate in reagent water.

4. Summary

The novel method, using isocratic IC with sequential FIA, enables accurate and precise analyses of

Table 4
Percentage recovery of spikes in reagent and wastewater samples[a]

Water sample		Chloride	Nitrate-N	Phosphate-P	Ammonia-N
Reagent	Unspiked (mg/l)	0	0	0	0
	Recovery (%)	110	107	111	98
Effluent sample, 1	Unspiked (mg/l)	132.3	0.21	3.2	2.1
	Recovery (%)	92	93	93	96
Lagoon discharge	Unspiked (mg/l)	32.2	0.24	0.41	0.84
	Recovery (%)	114	97	104	105
Influent sample, 1	Unspiked (mg/l)	51.4	0	1.8	4.1
	Recovery (%)	103	98	98	91.4
Effluent sample, 2	Unspiked (mg/l)	118	5.0	3.6	0.16
	Recovery (%)	98	91	95	93.2

[a] Unspiked samples were analyzed using the sequential method. A 10-ml water sample was then spiked with a standard containing Cl^-, 40 mg/l; and NO_3^--N, HPO_4^{2-}-P and NH_3-N each at 0.5 mg/l, and spiked sample was analyzed using the method.

wastewater samples for chloride, for the anionic nutrients nitrate and phosphate, and for cationic nutrient ammonia in a single injection. Further work is necessary to study the effects of fluoride, formate, acetate, and other organic acids on the quantitation of chloride. The method has a run time of less than 9 min. It enables determination of phosphate in the presence of disparate concentration levels of sulfate, to tolerate preservation of samples for ammonia with H_2SO_4, without any sample pretreatment for removal of sulfate.

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