Determination of Nitrite and Nitrate in Wastewater Using Capillary IC with UV Detection

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Environmental Water, Ion Chromatography, Suppressed Conductivity

Introduction

Ion chromatography (IC) with suppressed conductivity detection is an effective technique to simultaneously determine common inorganic anions in environmental water and drinking water. However in some samples such as mineral water, wastewater, and brine, accurate quantification of some anions present at low concentrations can be challenging due to the high ionic strength of the sample. Ion chromatography with UV detection provides an alternate approach for determining nitrite and nitrate without compromising sensitivity. By combining suppressed conductivity with UV detection, the suppressor reduces the background noise.[1]

In 1991, Thermo Scientific Dionex Application Update (AU) 132 was published to demonstrate that 0.010 and 0.015 mg/L nitrite and nitrate, respectively can be detected in drinking water by UV absorbance detection. The analysis was carried out on a Thermo Scientific™ Dionex™ IonPac™ AS9-SC 4 mm column using a manually prepared carbonate/bicarbonate eluent. Good linearity was observed from 0.015 to 50 mg/L and from 0.015 to 75 mg/L for nitrite and nitrate, respectively.

Over the past 20 years, advancements have improved IC performance, lowered the cost of ownership, and simplified the technique. Developments have been made in column chemistry to improve selectivity, capacity, and speed of separation. Thermo Scientific™ Dionex™ Reagent-Free IC (RFIC™) instruments were introduced and developed to improve performance and simplify IC by just requiring the addition of water to produce eluent. The eluent generator automatically produces hydroxide eluent from deionized water, providing a stable baseline and making gradient separations as easy as isocratic separations. Most recently, capillary IC was introduced to simplify the IC workflow and lower the overall cost of ownership. With the introduction of the Thermo Scientific™ Dionex™ ICS-5000 Capillary IC system fast turnaround analysis is achieved because the system can be left always on due to its low consumption of eluent.

The work shown here updates the previous determination of nitrite and nitrate using a state-of-the-art IC instrument and consumables. Inorganic anions were separated on a Thermo Scientific™ Dionex™ IonPac™ AS18-Fast Capillary Column using electrolytically generated potassium hydroxide at 15 µL/min. The Dionex IonPac AS18-Fast column is designed for fast determinations of common inorganic anions in different samples including drinking water, ground water, wastewater, process streams, and scrubber solutions.

Equipment

Dionex ICS-5000 Capillary IC system* including:

- DP Dual Pump module, capillary
- EG Eluent Generator module with capillary EG cartridge and continuously regenerated trap column
- DC Detector/Chromatography Compartment with Thermo Scientific™ Dionex™ IC Cube™ module and Capillary CD Conductivity Detector
- Thermo Scientific™ Dionex™ AS-AP Autosampler
- Dionex ICS-Series VWD Variable Wavelength Detector with PEEK capillary cell (P/N 076072)

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software

*A Thermo Scientific™ Dionex™ ICS-4000 HPIC™ system or Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system can be used for equivalent results

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Preparation of Reagents and Standards

Nitrite, 1000 mg/L
Nitrate, 1000 mg/L (Fisher Scientific P/N AS-NO3N9-2y)

Eluent

Potassium hydroxide (KOH), electrolytically generated by a Thermo Scientific™ Dionex™ EGC-KOH (Capillary) Eluent Generator Cartridge

Working Standards

Dilute the 1000 mg/L stock standards appropriately to the concentrations of interest prior to analysis.

Configuration

Configure the Dionex ICS-5000 IC system according to the Thermo Scientific Dionex ICS-5000 IC System Installation and VWD Operator's manuals.[2,3] Install the VWD in series after the CD Conductivity Detector. Remove the backpressure loop that is typically installed on the suppressor.

Conditions

Column:	Dionex IonPac AS18-Fast, 0.4 × 150 mm
Eluent:	33 mM KOH
Flow Rate:	15 µL/min
Inj. Volume:	0.4 µL
Detection:	A: Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle
	B: UV, 210 nm, capillary

Results and Discussion

Nitrite and nitrate in the standard and in municipal wastewater were separated on the Dionex IonPac AS18-Fast Capillary Column within 7 min using electrolytically generated KOH eluent at 15 µL/min and detected by UV absorbance and suppressed conductivity. The linear range, detection limit, and recoveries were investigated to determine the suitability of this method for determining nitrite and nitrate with a capillary UV detector.

Linearity Range and Detection Limit

Figure 1 shows the chromatogram of a standard solution containing 1.0 mg/L nitrite and nitrate. Calibration linearity for nitrite and nitrate was investigated separately by making five replicate injections of the standard solution at six different concentrations (Table 1). Good linearity was observed from 0.05 to 100 mg/L for nitrite and nitrate. The method detection limits (MDL) were estimated by multiplying the standard deviation of seven replicate injections of 0.015 mg/L nitrite or nitrate standard solution which are close to the detection limit with the single-sided Student's t value 3.14 for the 99% confidence level. The calculated values of MDL for nitrite and nitrate were 0.010 and 0.015 mg/L, respectively.

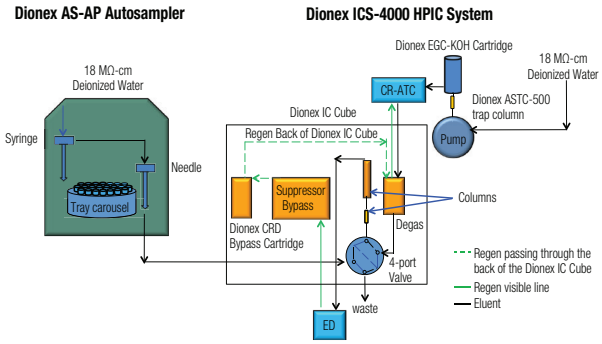

Figure 1. Separation of 1.0 mg/L nitrite and nitrate standard solution.

Table 1. Calibration and MDL results for nitrite and nitrate using the Dionex IonPac AS18-Fast column and UV detection

Analyte	Standard Concentrations (mg/L)	Coefficient of Determination (r^2)	Calculated MDL (mg/L)
Nitrite	0.05	0.9992	0.010
	0.1		
	1		
	10		
	50		
	100		
Nitrate	0.05	0.9994	0.015
	0.1		
	1		
	10		
	50		
	100		

Sample

The method was applied to a municipal wastewater sample. Nitrite was not present in the sample and the nitrate concentration was found to be 48.7 mg/L. To demonstrate the accuracy of the method, 0.030 mg/L nitrite (equal to the quantification limit of nitrite) and 5.0 mg/L nitrate standard were spiked into two separate sample solutions. Due to the high concentration of chloride in the matrix, the disparately smaller spiked nitrite was not detected by suppressed conductivity in this experiment (Figure 2, chromatogram A). However, the 0.030 mg/L nitrite was detected and well resolved from the chloride by UV detection (Figure 2, chromatogram B). The recovery of nitrite was determined to be 102% with 6.5% RSD. Alternately, the Dionex IonPac AS19 column can be used to separate small amounts of nitrite in wastewater with detection by suppressed conductivity. This column is designed for the analysis of trace nitrite and nitrate in high ionic strength matrices; however the run times are typically longer, around 30 min.[4]

A 104% recovery of spiked 5.0 mg/L nitrate was determined, indicating this method with UV detection is suitable for both nitrite and nitrate analysis in high ionic strength samples.

Conclusion

These experiments update nitrite and nitrate determinations by suppressed conductivity in series with UV detection using the latest capillary IC technology and consumables to achieve results comparable to those previously reported for nitrate and nitrite determinations in wastewater samples. The Dionex Capillary RFIC system delivers fast turnaround by reducing eluent preparation, system startup, and equilibration times. The capillary dimension reduces eluent usage to 10 µL/min, leading to an overall reduction in waste generated. Reducing from the 4 mm format to the capillary format also allows for higher mass sensitivity of the analytes of interest. The method is a solution for nitrite analysis when high concentrations of chloride can mask the presence of nitrite.

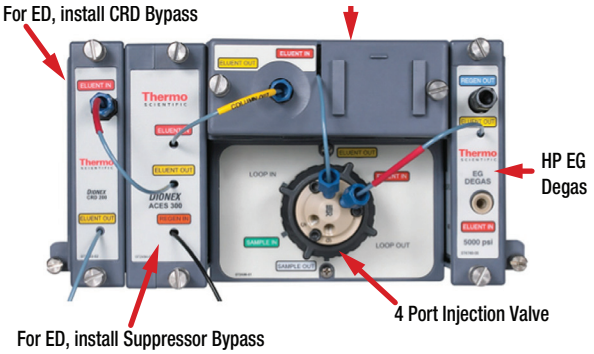

Figure 2. Separation of inorganic anions in a municipal wastewater sample spiked with 0.030 mg/L nitrite.

References

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