

Waters

Ion Chromatography Method

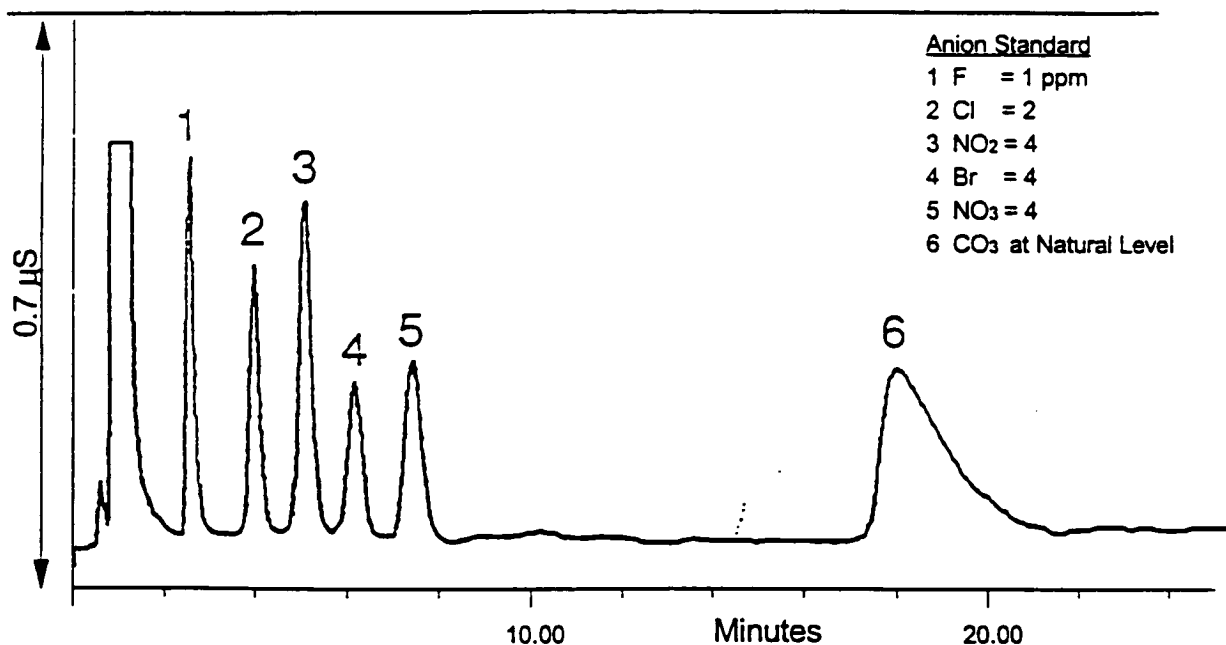
Anion Analysis Using Hydroxide Eluent and Indirect Conductivity Detection and EPA Method B-1011 for Nitrite and Nitrate Using UV Detection 2000

Required Instrumentation:

Alliance, 2690 Separations Module
(with Column Heater, Seal Wash, Degasser)
432 Conductivity Detector
UV Detector
Bus SAT/IN Module
Millennium 32

Part / Number

271013
043061
Consult Waters
073645
Consult Waters



Analysis Conditions:

Column: IC-Pak Anion HR (P/N 026765)
Eluent: 2.5 mM Lithium Hydroxide
Back Conductivity: 475 ± 20 μS
Degas: Continuous
Flow Rate: 1.2 mL / min
Back Pressure: 1200 ± 200 psi
Temperature: 30°C (Column Heater); 35°C (Detector)
Injection: 100 μL
Needle Wash: 12% AcCN in DI Water
Detection: Indirect Conductivity
Base Range: 500
Attenuation: 50 μS / Volt Unattenuated
Polarity: Negative

Eluent Preparation:

This eluent should be prepared fresh daily as follows,

- 1) In a 1 liter plastic volumetric flask, add 2.5 mL of 100 mM lithium hydroxide (LiOH), and dilute to the mark with freshly drawn DI water.
- 2) Vacuum degas through a 0.45 μ m aqueous compatible membrane.
- 3) Place into a plastic container, and protect from CO₂ absorption using an Ascarite trap, or helium sparging.
- 4) Discard after 2 days.

Standard Preparation:

It is recommended that certified 1000 ppm anion standards be used with this method. If unavailable, see Reagent Section for uncertified standard preparation.

Prepare at least 3 mixed analyte standards within the expected range of sample analyte concentration. After the multi-point calibration curve has been validated, a single point calibration within the expected analyte concentration range is appropriate for recalibration.

Sample Preparation:

Determine the expected range of analyte concentration and other anionic component in the sample matrix. The major analyte should be less than 100 ppm for best results.

If necessary dilute the sample with DI Water or eluent.

If the sample contains high amounts of neutral organics, or is highly colored, then pass the diluted sample through a C₁₈ Sep Pak Cartridge. Anions pass through unretained, but may note a loss of fluoride recovery.

Samples containing suspended solids should be filtered through a 0.45 μ m aqueous compatible disk prior to injection. Failure to filter solids results in the risk of increased column backpressure.

Sample pH should be within 3 to 11 for best results

Samples treated with a sample preparation disk in the H⁺ form, used to remove cations and neutralize high pH, will yield chromatograms similar to suppressed conductivity chromatograms.

Millennium Data Processing Method:

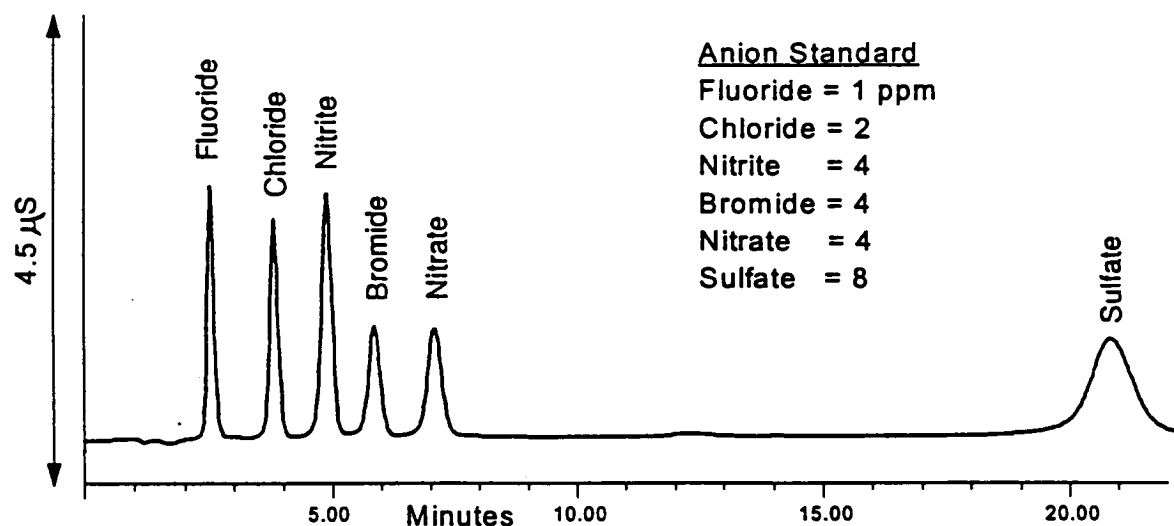
IC Processing Method using Peak Apex for Retention Time

<u>Integration</u>	Peak Width	= 30.0	Threshold	= 10--25
	Min Area	= 3000	Min Height	= 150
	Inhibit Intg.	= 0 to 2 min		
<u>Calibration</u>	Averaging	= None	RT Window	= 5%
	Update RT	= Never		
	Peak Match	= Closest		
	Quant By	= Peak Area		
	Fit Type	= Linear, for multi-point calibration or Linear Through Zero, for single point		

<u>Report</u>	Analyte Name
	Analyte Retention Time
	Peak Area
	Amounts

Chemical Suppression Conductivity Detection:

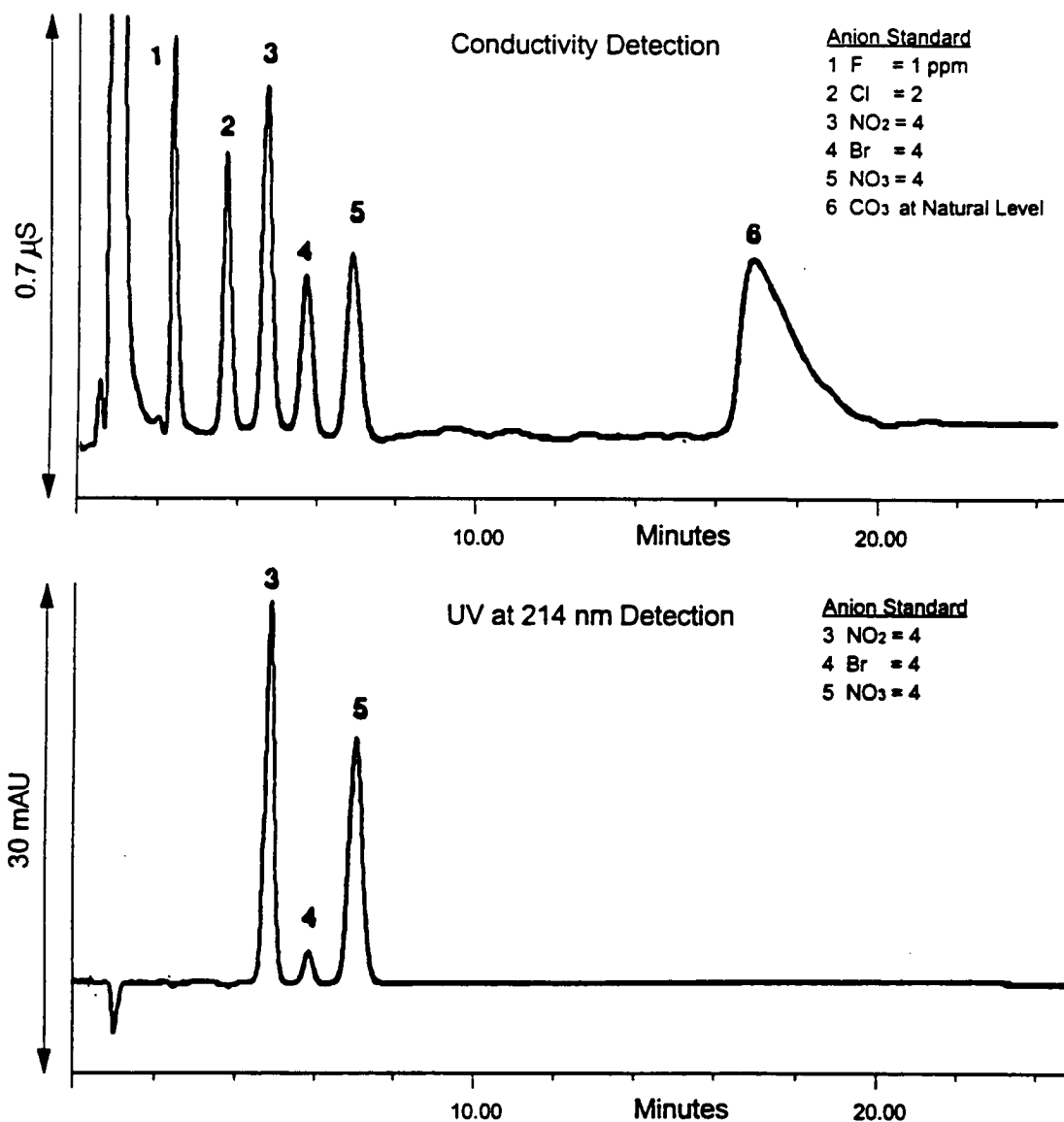
Hydroxide eluents can also be used with the Alltech ERIS 1000HP Autosuppressor to provide increased sensitivity as shown below. The hydroxide is converted to water which is non-conductive and decreases the background conductivity to 10 to 15 μS .



With chemical suppressed conductivity detection, carbonate and silicate will not be detected.

EPA Method B-1011 for Nitrite and Nitrate:

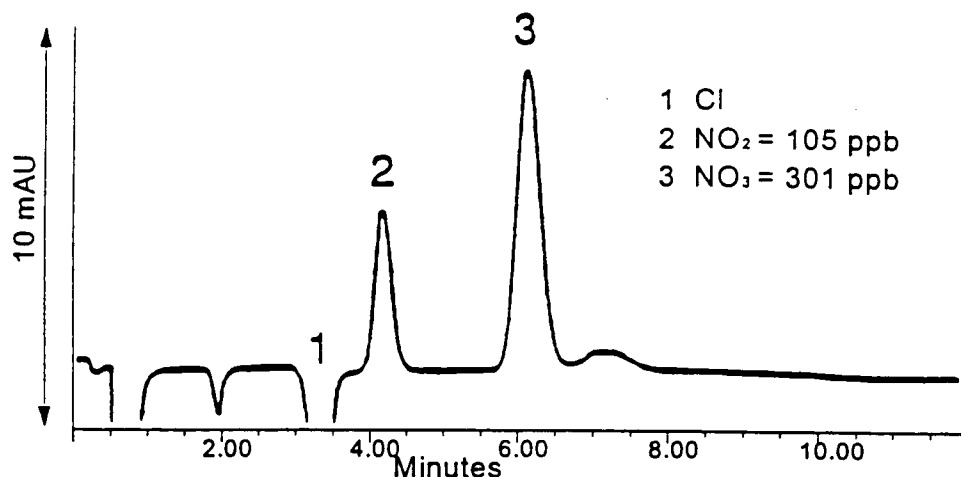
This methods utilizes the 2.5 mM LiOH eluent and the direct UV detection of NO_2 and NO_3 . Generally environmental water samples are preserved with sulfuric acid to minimize the degradation of NO_x and PO_4 by bacteria, and the high concentration of SO_4 will interfere with the conductivity detection of NO_3 . Analogously, high concentrations of Cl will interfere with ppb NO_2 detection. These detection problems are eliminated by using direct UV detection for NO_x , between 205 nm and 215 nm, where Cl and SO_4 are transparent.



The detection limits reported in the EPA B-1011 method using EPA detection limit protocol are 10 ppb for nitrite and 2 ppb for nitrate.

Hydroxide eluents are UV transparent, but contaminants in the DI water such as formate and acetate, and absorption of CO_2 give the eluent low UV activity. This may cause the appearance of negative peaks in the region corresponding to the retention time of transparent matrix analytes such as Cl .

An example of chlorinated drinking water abstracted from the EPA B-1011 method shows both phenomena.



Observations / Comments:

- Sodium hydroxide or potassium hydroxide can be substituted for lithium hydroxide.
- Hydroxide eluents will absorb CO₂ from the air to form carbonate. Carbonate is a stronger displacing anion than is hydroxide such that as carbonate levels increase anion retention times decrease. The head space in the eluent reservoir must be protected from CO₂ absorption. Use of an ascarite trap, a plastic 1 cm column packed with ascarite, placed onto the cap covering the eluent scrubs CO₂ from the air before contact with the eluent. Helium sparging can also be used under a continuous flow; He is lighter than CO₂. In line degas does not remove carbonate from the eluent and does not protect the eluent head space.
- Dissolved carbonate in the sample will be detected but does not interfere with anion analysis.
- Hydroxide concentrations can be increased to 5 mM to decrease SO₄ retention time to under 20 minutes. Phosphate, as PO₄³⁻ is strongly retained.
- Silicate (SiO₃⁻) can be analyzed with a 0.5 mM Hydroxide eluent. This eluent will resolve fluoride, acetate, and formate, which typically coelute with most IC eluents; Cl retention time is 10 minutes.

Stock Reagent Preparation:

100 mM Lithium Hydroxide— In a 100 mL plastic volumetric flask dissolve 0.24 g of lithium hydroxide in 50 mL of DI water. This is an exothermic dissolution. Fill to the mark with DI water. Store in a plastic container for up to 1 year.