980895

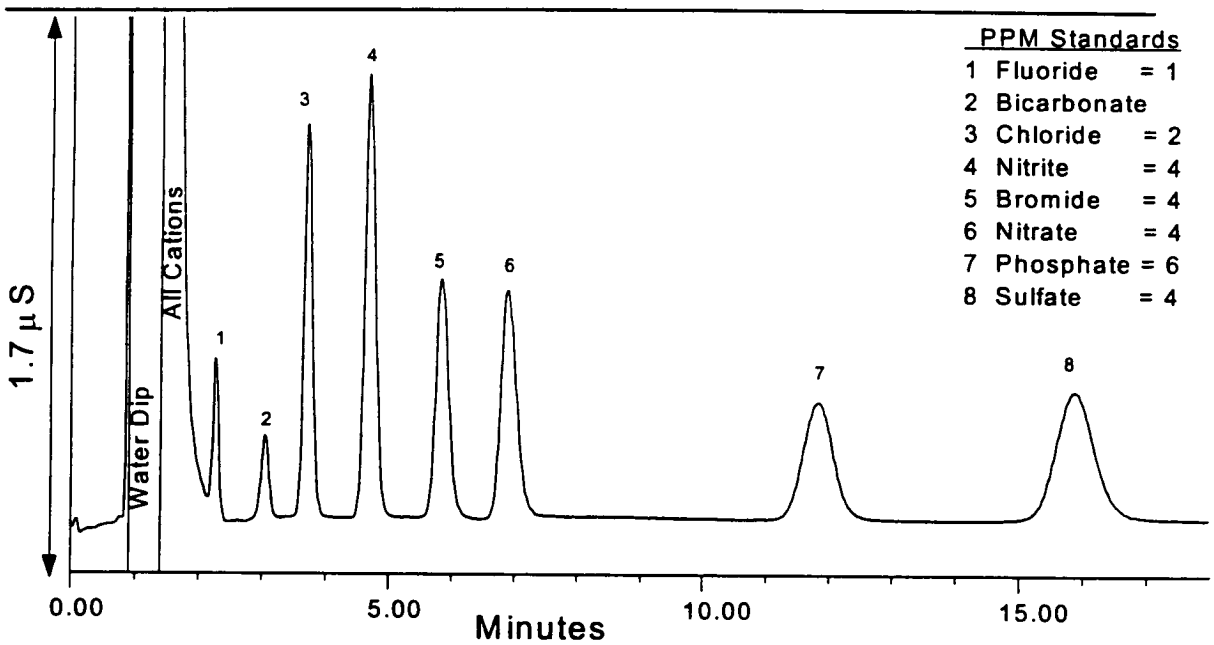
Waters®

Ion Chromatography Method

General Purpose Anion Analysis Using Conductivity and UV Detection 2000

Required Instrumentation:

	Part / Number
Alliance™, 2690 Separations Module (with Column Heater, Seal Wash, Degasser)	271013
432 Conductivity Detector	043061
Bus SAT/IN Module	073645
Millennium 32	Consult Waters
UV Detector (Optional)	Consult Waters



Analysis Conditions:

Column:	IC-Pak™ Anion HR (P/N 026765)
Eluent:	Borate / Gluconate containing 12% AcCN
Back Conductivity:	240 ± 20 µS
Degas:	Continuous
Flow Rate:	1 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:	Direct Conductivity
Base Range:	500
Attenuation:	50 µS / Volt Unattenuated
Polarity:	Positive

Eluent Preparation:

1) Into a 1 liter volumetric flask add
   -20 mL Lithium Borate/Gluconate concentrate
      (See Appendix for concentrate preparation)
   -120 mL of HPLC Grade Acetonitrile (AcCN)
2) Dilute to volume with DI Water
3) Natural pH is 8.2 ± 0.1
4) Vacuum degas through a 0.45 µm aqueous & solvent compatible membrane
5) Store in glass or plastic container at ambient temperature. Discard after 1 month.

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. This method is linear from 0.1 ppm to 100 ppm. 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.

If the sample contains high amounts of neutral organics, or is highly colored, then pass the diluted sample through a C_{18} 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 µm 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 Peal Apex for Retention Time

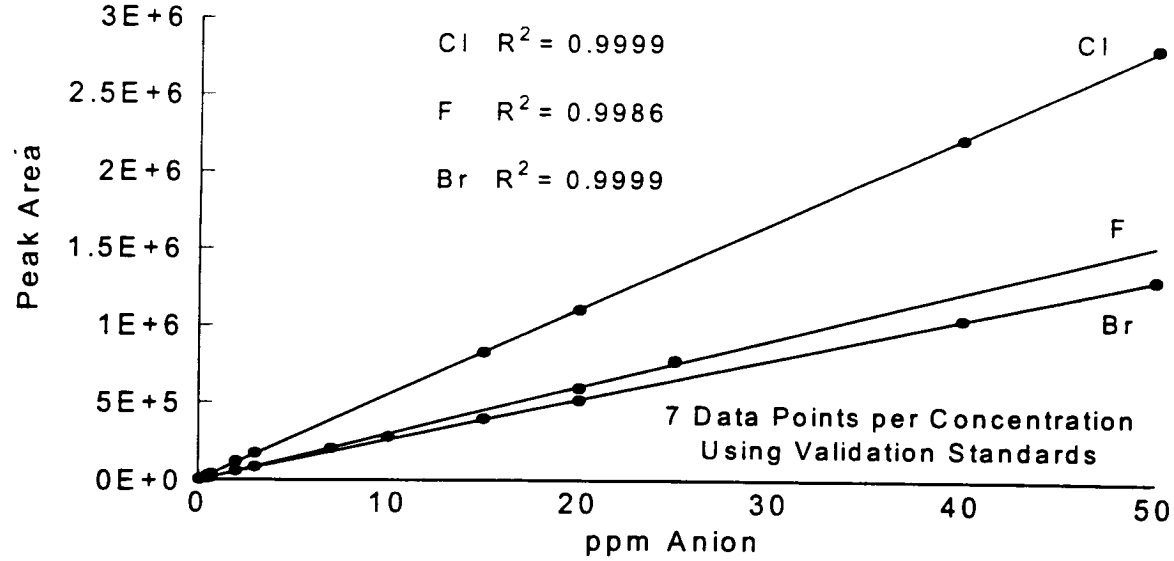
Integration	Peak Width	= 30.0	Threshold = 10--25
	Min Area	= 3000	Min Height = 150
	Inhibit Intg.	= 0 to 2 min	
Calibration	Averaging	= None	RT Window = 5%
	Update RT	= Never	
	Peak Match	= Closest	
	Quant By	= Peak Area	
	Fit Type	= Linear, for multi-point calibration or Linear Through Zero, for single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

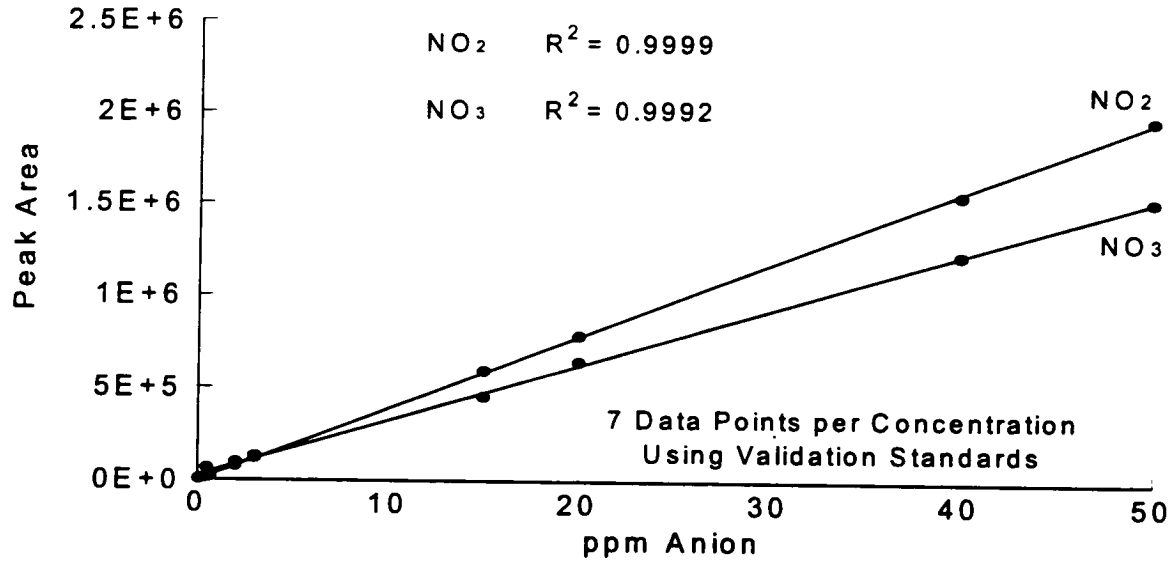
Method Validation: This validation design is abstracted from the ASTM/EPA validation for CIA. It has been used to validated all anion analysis methods. Many of the methods using this validation design are linear above 50 ppm.

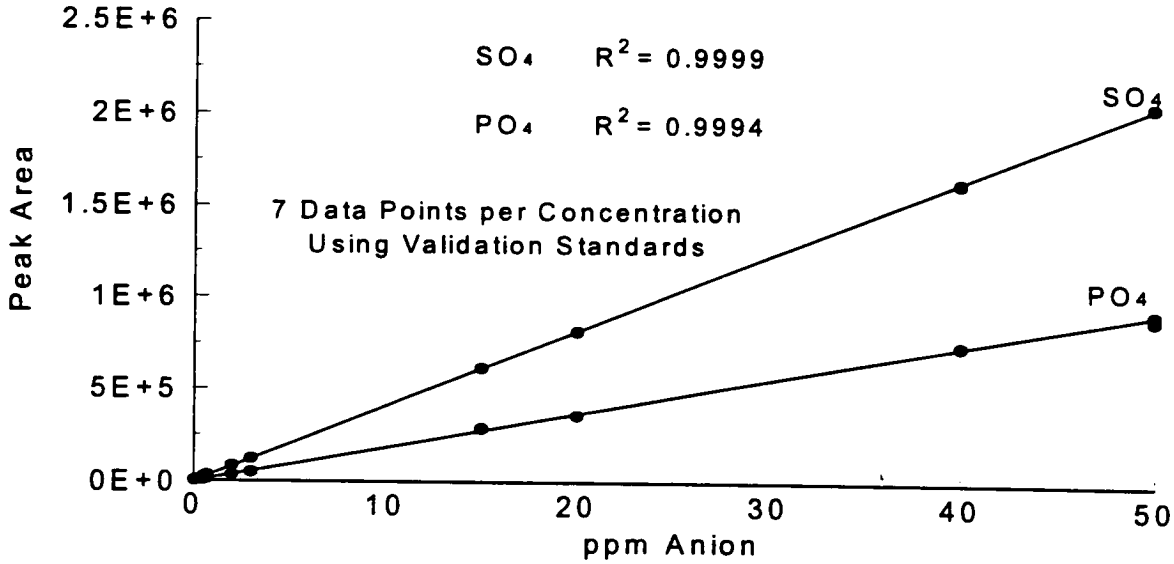
Individual Youden Pair Standard, in ppm

Analyte Anion	1	2	3	4	5	6	7	8
Cl	0.7	2.0	3.0	15.0	40.0	20.0	50.0	0.5
Br	2.0	3.0	15.0	40.0	20.0	50.0	0.7	0.5
NO_2	3.0	40.0	20.0	15.0	50.0	0.5	2.0	0.7
SO_4	40.0	50.0	0.5	0.7	2.0	3.0	15.0	20.0
NO_3	15.0	20.0	40.0	50.0	0.5	0.7	2.0	3.0
F	2.0	0.7	0.5	3.0	10.0	7.0	20.0	25.0
PO_4	50.0	40.0	20.0	0.5	3.0	2.0	0.7	15.0

Method Linearity:



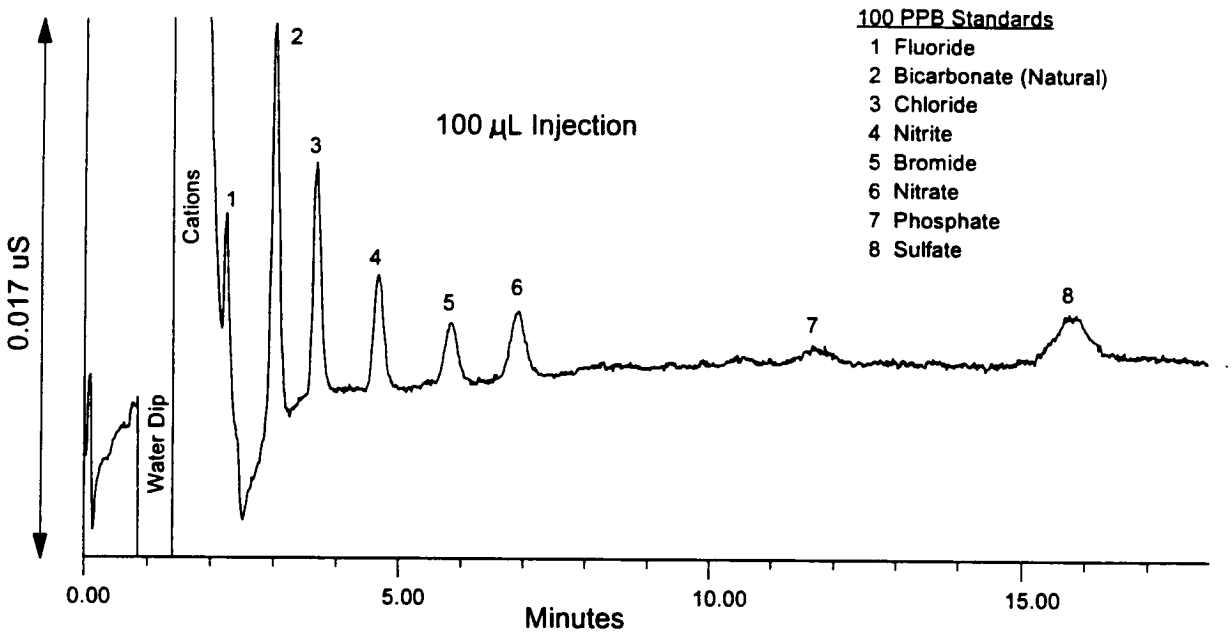




Quantitation Precision: % RSD of analyte peak area at each concentration. Data based upon 7 replicate injections of the validation standards.

Analyte		F	Cl	NO_2	Br	NO_3	PO_4	SO_4
ppm Concentration	0.5	0.95	1.11	3.44	5.17	0.32	12.98	7.62
	0.7	0.67	1.64	0.78	1.73	0.75	9.29	3.90
	2	0.17	0.18	0.56	1.14	0.91	2.91	1.07
	3	0.43	0.17	0.20	0.67	0.19	3.49	0.64
	15	0.44	0.05	0.28	0.11	0.16	0.50	0.32
	20	0.45	0.04	0.05	0.30	0.06	0.52	0.25
	40		0.05	0.04	0.03	0.08	0.37	0.26
	50		0.13	0.02	0.26	0.03	1.56	0.16

Method Detection Limits:



Based upon this representative chromatogram using a 100 µL injection, the estimated detection limits, as ppb, at 3 times signal to noise (S/N) are:

Fluoride = 50	Nitrite = 50	Nitrate = 75	Sulfate = 75
Chloride = 25	Bromide = 75	Phosphate = 125	

Quantitation below these detection limits is not advised.
Lower detection limits can be obtained by using a 250 µL injection.

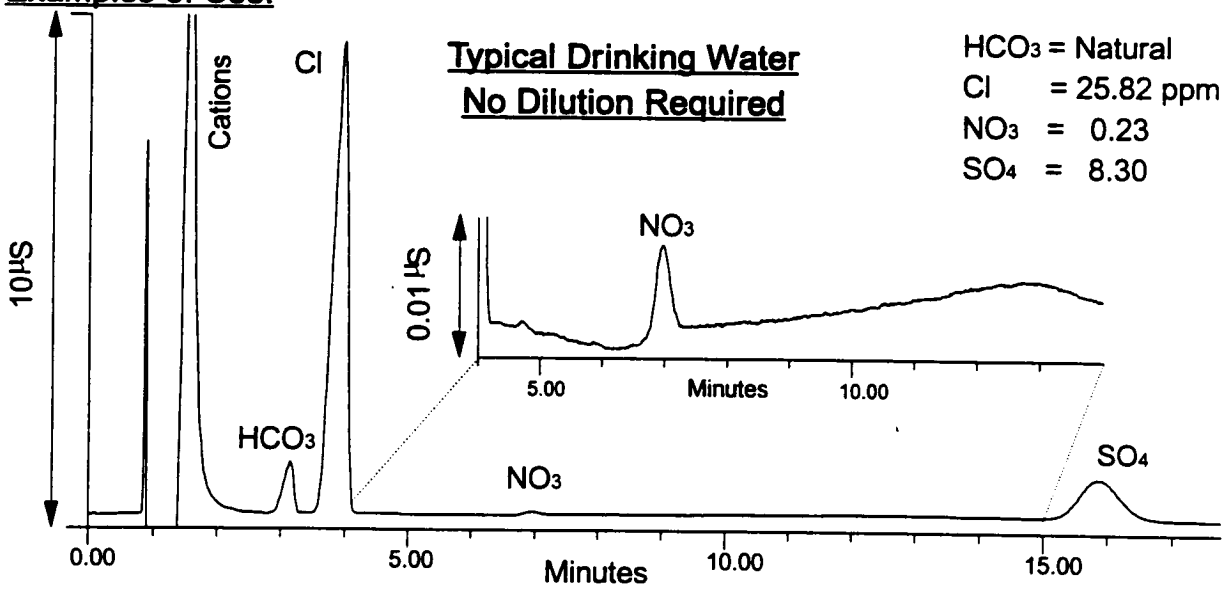
Quantitation Accuracy: Used a Certified Performance Evaluation Standard diluted 1:100 with DI Water. Amounts based upon multi-point calibration curve prepared from certified standards.

	Analyte	F	Cl	NO_2	NO_3	PO_4	SO_4
Performance Evaluation Standard	True Value in ppm	2.69	43.00	1.77	15.37	6.29	37.20
Official Anion Methods Wet Chem & IC	Measured Mean	2.75	43.30	1.77	15.42	6.38	37.00
	Measured Std Dev	0.26	3.09	0.07	1.15	0.21	2.24
IC Using Alliance IC Pak A/HR and B/G Eluent	Ave IC n=3	2.63 ± 0.05	43.87 ± 0.09	1.93 ± 0.01	15.04 ± 0.06	6.47 ± 0.09	37.03 ± 0.12
	IC/Mean	0.956	1.013	1.090	0.975	1.014	1.001
	IC/TrueValue	0.978	1.020	1.090	0.979	1.029	0.995

Analyte Recovery: The Certified Performance Evaluation Standards was diluted 1:100 with Typical Drinking Water. Amounts based upon multi-point calibration.

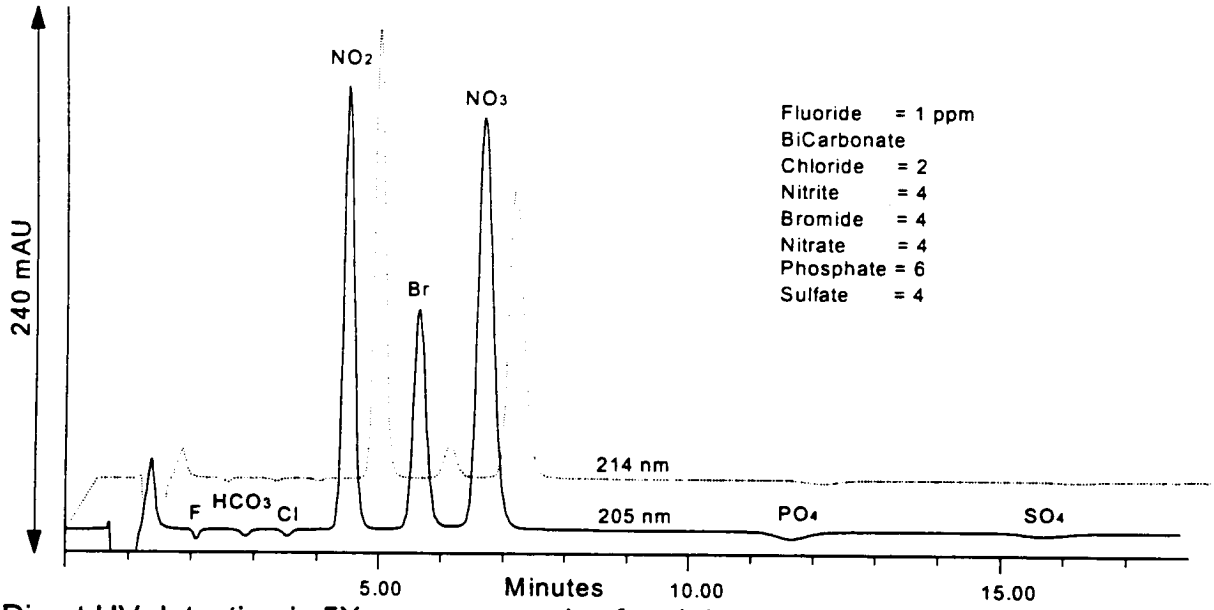
Analyte	F	Cl	NO_2	NO_3	PO_4	SO_4
Milford Drinking Water n=3, as ppm	Not Detected	25.82 ± 0.04	Not Detected	0.23 ± 0.002	Not Detected	8.30 ± 0.02
%RSD		0.16		0.92		0.27
Performance Evaluation Std	2.69	43.00	1.77	15.37	6.29	37.20
MDW + PES n=3; as ppm	2.46 ± 0.04	69.64 ± 0.08	1.82 ± 0.004	15.52 ± 0.02	5.35 + 0.05	46.46 ± 0.17
%RSD	1.51%	0.11%	0.21%	0.10%	0.92%	0.37%
% Recovery	91.4%	102.5%	102.8%	99.5%	85.1%	102.8%

Examples of Use:

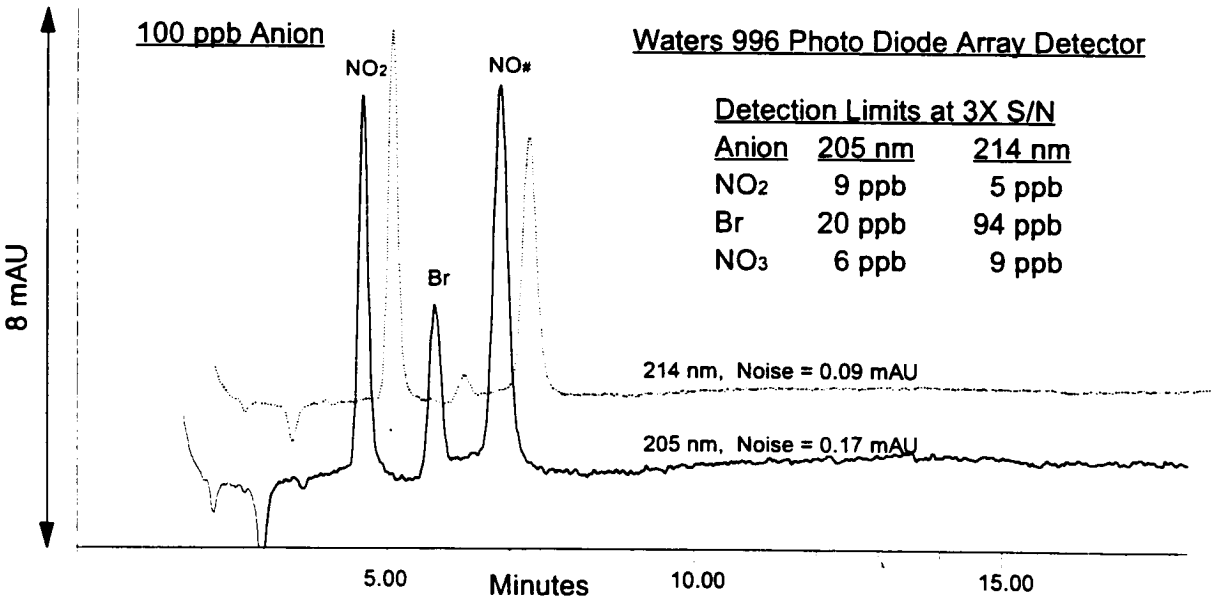


Use of Direct UV Detection:

Many anions are UV active in the range of 205 nm to 214 nm, such as NO_2, Br, and NO_3, and the use of direct UV detection provides a degree of detector selectivity. Below is the chromatogram of the anion standard that demonstrates this selectivity. Generally, the lower the wavelength of detection the greater is the response, as seen with the difference between 205 nm and 214 nm chromatograms. However, the borate gluconate eluent has some UV absorption which causes negatives peaks at the retention time of the UV transparent anion, such as F, Cl, PO_4, and SO_4, if present.



Direct UV detection is 5X more responsive for nitrite and nitrate than is conductivity detection and hence provides lower detection limits. The chromatogram below of 100 ppb anion standard demonstrates the improved sensitivity.



The borate gluconate eluent has some UV absorption. Use of eluents that are UV transparent, such as hydroxide and carbonate / bicarbonate, provide lower detection limits.

Appendix

Borate Gluconate 50X Stock Concentrate:

Using a 60 mL plastic syringe with 0.45 μm filter, add approx. 25 g of BioRad AG-50W-X12 strong cation exchange resin in the hydrogen form, or equivalent. Wash the resin with five 20 mL portions of DI water to remove any ionic impurities from the resin. Discard the washings.

Dissolve 9.06 g of sodium gluconate in approx. 20 mL of DI water. After dissolution, transfer this solution into the 60 mL syringe with resin. Slowly pass this solution into a 1 liter volumetric flask. Wash the resin with five 20 mL portion of DI water; add the washing to the volumetric flask. Discard the syringe and resin.

An alternative to the above procedure is to use commercially available 50% Gluconic Acid. However, it comes as a brown solution that when diluted gives a yellow tint to the eluent that may effect long term performance. The brown color can be removed by passing 5 mL of 50% gluconic acid through a C18 Sep Pak cartridges; requires total of 3 Sep Pak cartridge. Use 13.2 mL of 50% Gluconic Acid for the eluent concentrate.

Adjust the volume in the flask to approx. 500 mL with DI water and add a stirring bar. Add 7.2 g of lithium hydroxide monohydrate and 25.5 g of boric acid. With the aid of a magnetic stirrer, mix until all reagents are dissolved.

Add 94 mL of 95% Glycerol and mix. Remove the stirring bar and fill to the mark with DI water.

Store this B/G Concentrate in a plastic container and store at ambient temperature for up to 6 months. Can store in 4°C for up to 1 year, but warm to ambient temperature before use.

A white "string like" material is observed at the bottom of the container indicates significant microbiological growth. If present discard and re-prepare.

Borate Gluconate Eluent:

In a 1 liter volumetric flask, add 20 mL of the 50X B/G Concentrate and dissolve in 500 mL of DI water. Add 120 mL of HPLC grade Acetonitrile. Mix and fill to the mark with DI water.

Vacuum degas through a 0.45 μm aqueous / organic membrane.

The background conductivity of the B/G Eluent is between 220 and 270 μS.