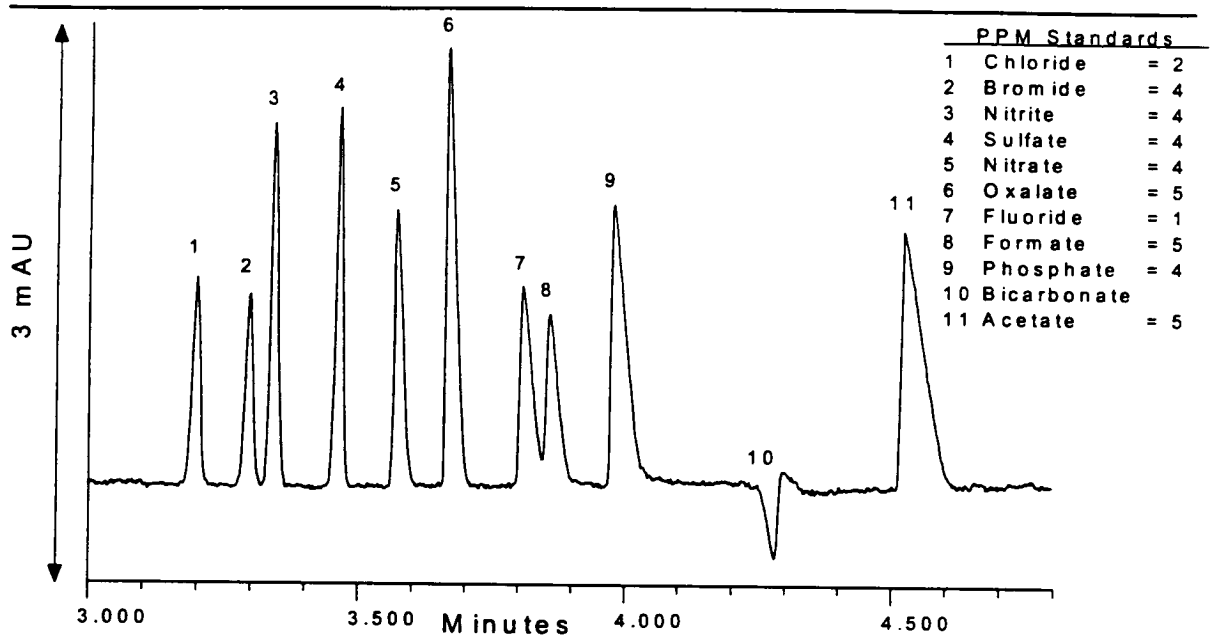
980899

Waters

Capillary Ion Analysis Method

General Inorganic Anion & Organic Acid Analysis with Indirect UV Detection
Basis for EPA Method 6500, ASTM, and Standard Methods 4140 2000

Required Instrumentation:	Part / Number
Capillary Ion Analyzer	251000
Bus SAT/IN Module	073645
Millennium 32	Consult Waters



Analysis Conditions:

Electrolyte:	IonSelect High Mobility Anion Electrolyte, P/N 49385
Capillary:	75 µm (id) x 375 µm (od) x 60 cm (length)
Temperature:	25°C (5°C Above Ambient)
Power Supply:	Negative
Voltage:	15 kV
Current:	14 ± 1 µA (Use Constant Current for Analysis)
Sampling:	Hydrostatic for 30 Seconds
Detection:	Indirect UV at 254 nm, Hg Lamp, 185 or 254 nm Window
Time Constant:	0.3 Seconds, or less
Sampling Rate:	20 Data Points per Second
Analyte MT:	Mid-Point of Analyte Peak Width at Baseline
Quantitation:	Time Corrected Peak Area (Peak Area / MT)

Electrolyte Preparation:
This electrolyte can be obtained preformulated from Waters (P/N 49385), or prepare as follows: See Reagents Section for Solution Preparation.

1) Into a 100 mL volumetric flask add
   -4.7 mL of 100 mM Sodium Chromate Solution
   -4 mL of 100 mM OFM-OH (available from Waters, P/N 49387)
   -10 mL of 100 mM CHES Buffer Solution
   -10 mL of 1 mM Calcium Gluconate Solution.
2) Dilute to volume with DI Water.
3) Natural pH is 9 ± 0.1.
4) Vacuum Degas through 0.45 µm aqueous compatible membrane.
5) Store any unused electrolyte in a plastic container at ambient temperature.
6) Allow to thermally equilibrate in the CIA Analyzer for 15 minutes before use.
7) Use fresh electrolyte daily; recalibrate with every change in electrolyte.

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.

The test mix available in the IonSelect High Mobility Electrolyte Kit should be used to evaluate electrolyte selectivity only. Do not use for accurate quantitation.

Prepare at least 3 mixed analyte standards within the expected range of sample analyte concentration. Add 5 ppm formate to all analyte calibration standards to aid in the correct identification of fluoride. Formate is a common anion in most samples.

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 future calibration.

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

Best quantitation is achieved when all analytes are baseline resolved. For 2 adjacent peaks reliable quantitation can be achieved when the concentration differential is less than 100:1. As the resolution between 2 analyte peaks increases so does the tolerated concentration differential.

If necessary, dilute the sample with DI water only. Analyte migration time reproducibility and peak shape improves with increased sample dilution.

Initially analyze in triplicate and evaluate resulting pherograms for analyte migration time reproducibility. Significant migration time change amongst the replicates indicates a change in EOF due to sample matrix effects at the capillary wall. Consider a 500 mM NaOH capillary rinse between samplings. If migration time reproducibility is less than 1% then no rinse is needed and the sample can be run in duplicate to ensure reproducibility.

CIA Analyzer Special Function Programming:

Use to program the CIA Analyzer as a stand alone system, without Millennium control. Use the same programming for the Millennium Instrument Method.

SF# and Description		Value
55	CIA	1 = CIA (Default)
88	Custom IMT	0, Enter 99 to activate SF# 58-60
89	SPS	1 = Constant Current (Enter in Sample Voltage)
90	C2C Mapping	0 = Off (Place electrolyte in position 1 only)
91	t°C Temperature	25 (set 5°C above ambient temperature)
92	r19, Rinse Vial	0 = Off, Enter Rinse Time in Minutes
93	r20, Rinse Vial	0 = Off, Enter Rinse Time in Minutes
94	Adjust Voltage	15 (in kV, use for manual voltage initiation only)
95	Carousel Type	20 = 20 Sample Position Carousel
96	Current Test	0 = Off (Must reset after power down)
97	Conductivity Test	0 = Off
98	Purge Time	1 (Time in Minutes)
99	CIA Version	3.0

Millennium Data Processing Method:

CIA Processing Method using Mid-Point of Peak Width for Migration Time

Integration	Peak Width = 2.25 - 3.00	Threshold = 100 ± 25
	Min Area = 100	Min Height = 50
	Inhibit Intg. = 0 to 3 min	
Calibration	Averaging = None	MT Window = 2%
	Update MT = Average Standards	
	Peak Match = First for Chloride	
	(Cl is always first in the pherogram, use as a ref peak)	
	Cl MT Window = 10%	
	Other Analytes = Closest	
	Quantitate By = Time Corrected Peak Area	
	Fit Type = Linear, for multi-point calibration	
	Linear Through Zero, for single point.	
Report	Analyte Name	
	Analyte Migration Time	
	Analyte Migration Time Ratio (respect to Cl Ref Peak)	
	Peak Area	
	Time Corrected Peak Area	
	Amounts	

Use fresh electrolyte daily; recalibrate with every change in electrolyte.
Clear previous calibration (in Quick Set Page) before recalibration.
Do Not use analyte peak height for quantitation due to asymmetrical peak shapes.

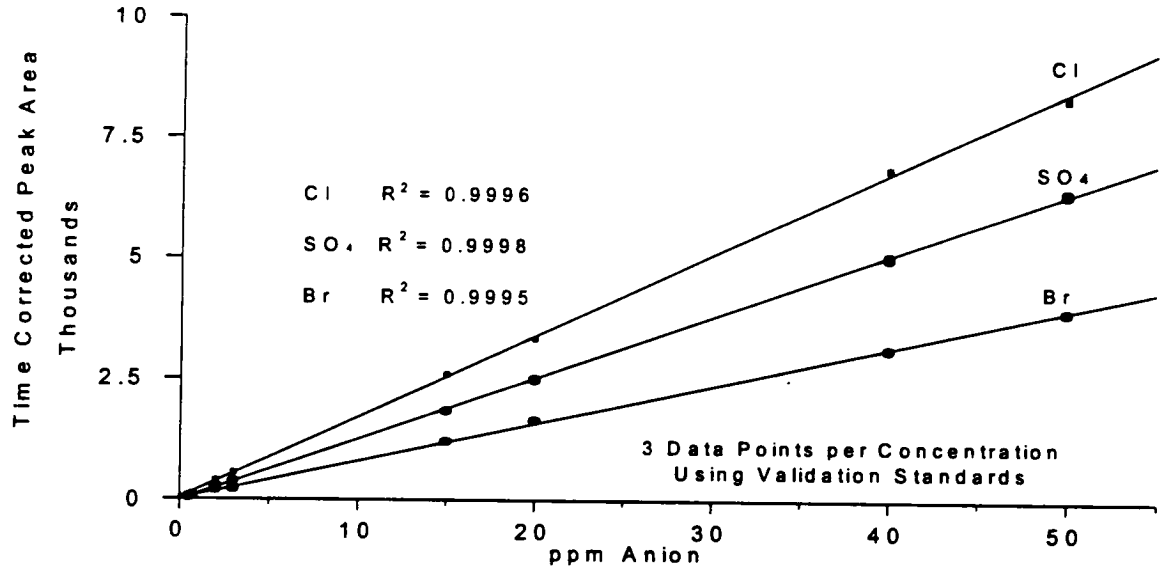
Method Validation:

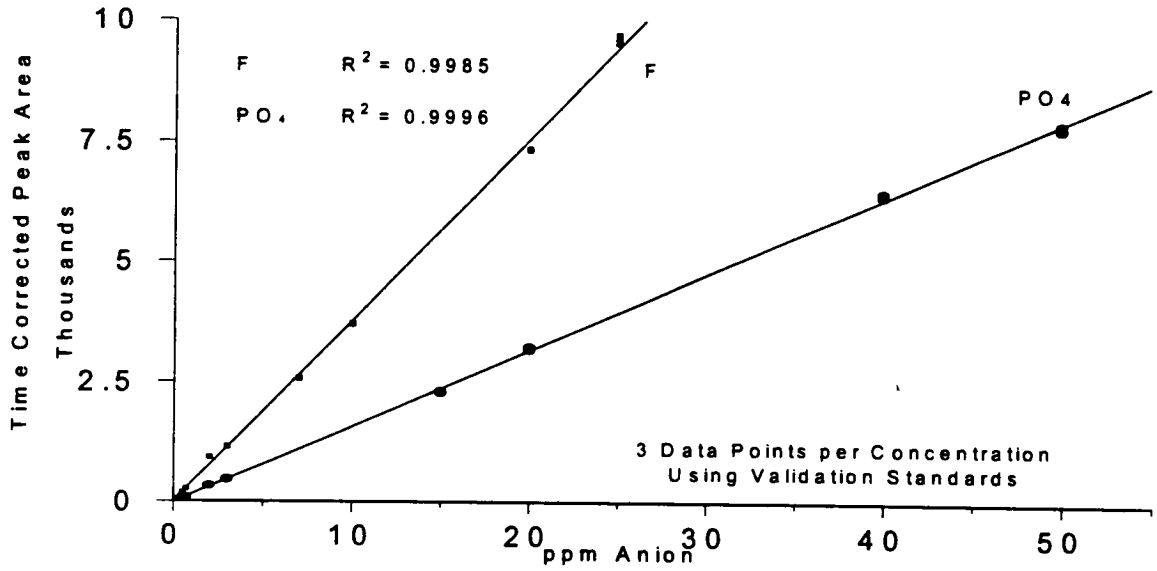
This validation design is abstracted from the ASTM/EPA validation of CIA. It has been used to validate all anion analysis methods.

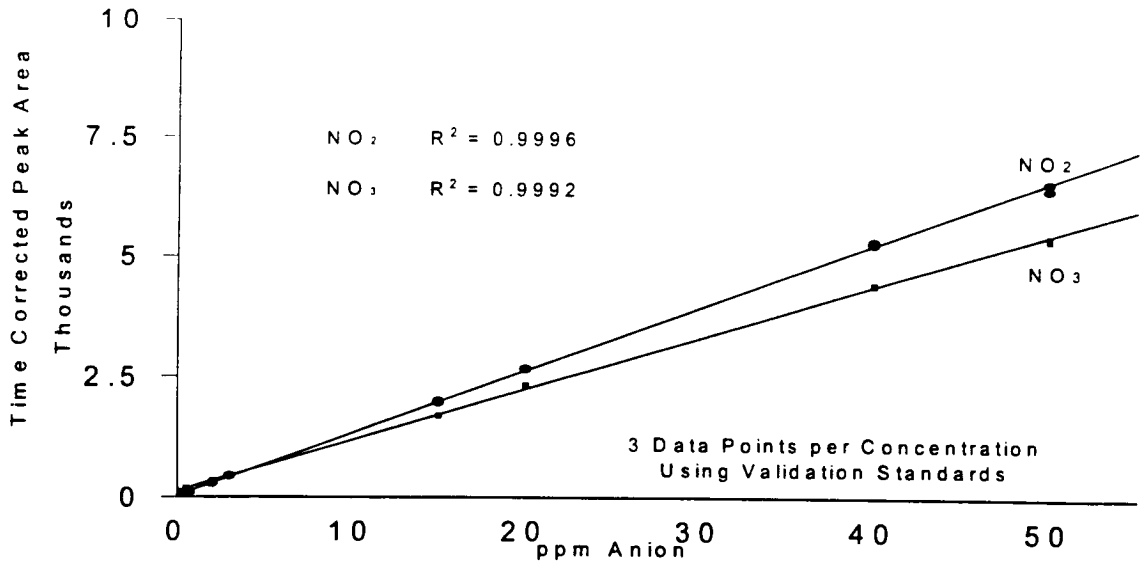
Individual Youden Pair Standard, in ppm

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

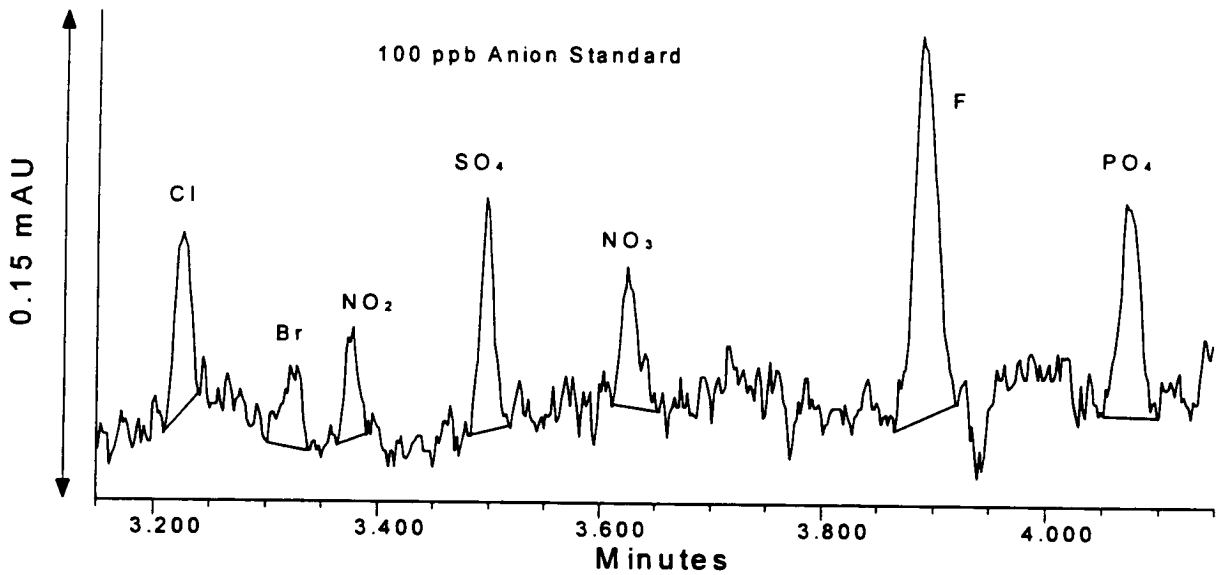
Method Linearity:







Method Detection Limits:



Seven replicates of the above 100 ppb anion standard were used to calculate time corrected peak area precision. Using EPA and Standard Methods protocols, the detection limits, as ppb, for these analytes are:

Chloride = 46	Bromide = 90	Nitrite = 72	Sulfate = 32
Nitrate = 84	Fluoride = 20	Phosphate = 41	

This method has been validated between 0.1 to 50 ppm. Quantitation below 0.1 ppm is not advised.

Migration Time Reproducibility:
Used mid-point of analyte peak width at the baseline as the analyte migration time determinant. Data given as average absolute migration time for each validation standard analyzed in triplicate.

Analyte	Cl	Br	NO_2	SO_4	NO_3	F	PO_4
Validation Standard 1	3.132	3.226	3.275	3.405	3.502	3.761	3.906
2	3.147	3.239	3.298	3.431	3.517	3.779	3.931
3	3.138	3.231	3.283	3.411	3.497	3.771	3.925
4	3.158	3.244	3.307	3.434	3.510	3.781	3.963
5	3.184	3.271	3.331	3.435	3.551	3.787	3.981
6	3.171	3.260	3.312	3.418	3.537	3.776	3.964
7	3.191	3.272	3.315	3.437	3.544	3.773	3.978
8	3.152	3.248	3.294	3.418	3.526	3.739	3.954
Std Dev	0.021	0.015	0.018	0.012	0.20	0.015	0.027
%RSD	0.67%	0.46%	0.55%	0.36%	0.56%	0.40%	0.68%

Average Standard Deviation = 0.018 min = 1.1 sec
Average %RSD of Analyte Migration Time = 0.53%

Quantitation Precision:
Time Corrected Peak Area Precision, given as %RSD, based upon 3 samplings per concentration.

Analyte	Cl	Br	NO_2	SO_4	NO_3	F	PO_4
ppm concentration 0.1	12.36	18.89	16.19	13.25	23.13	9.82	14.00
0.5	10.51	20.00	3.90	2.25	2.18	2.03	7.71
0.7	1.23	13.36	2.01	2.95	0.37	2.72	4.41
2	0.32	3.76	4.14	1.79	2.17	0.73	1.91
3	0.63	1.80	1.72	1.70	0.58	0.98	2.70
15	0.43	0.27	0.48	0.07	0.36	0.15	1.37
20	0.45	0.66	0.17	0.13	0.88	0.16	0.81
40	0.36	0.56	0.36	0.46	0.58		0.47
50	0.45	0.51	0.48	0.16	0.46		0.46

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.

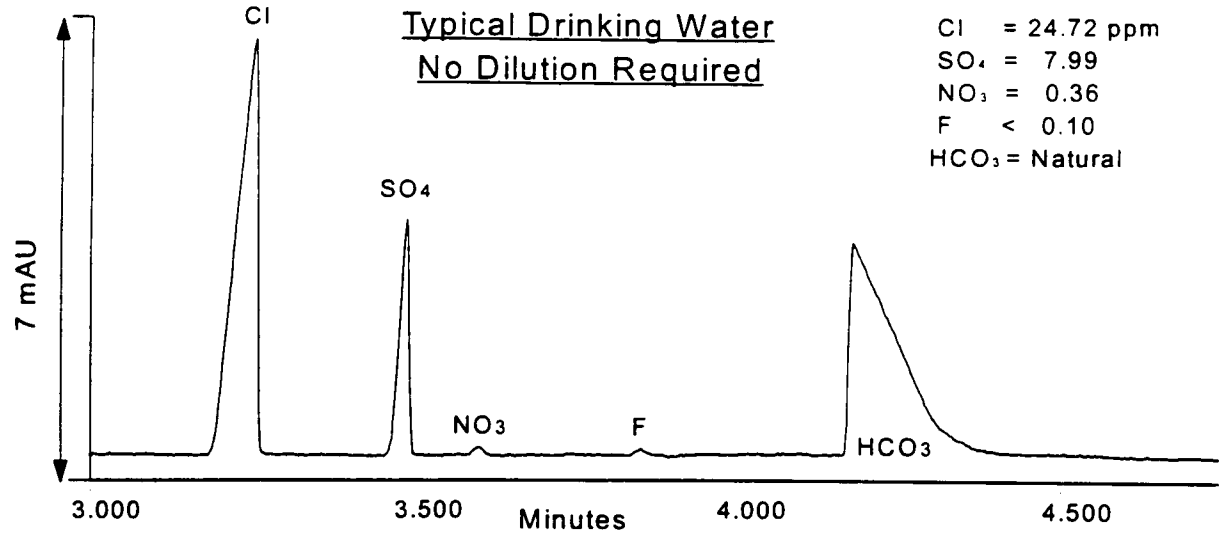
	Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Performance Evaluation Standard	True Value in ppm	43.00	1.77	37.20	15.37	2.69	6.29
Official Anion	Measured Mean	43.30	1.77	37.00	15.42	2.75	6.38
Methods Wet Chem & IC	Measured Std Dev	3.09	0.07	2.24	1.15	0.26	0.21
CIA Using Chromate	Ave CIA n=18	43.34	1.64	37.11	14.41	2.64	6.34
Electrolyte	CIA/Mean	1.003	0.927	1.003	0.935	0.959	0.993
	CIA/TrueValue	1.008	0.927	0.996	0.938	0.981	1.008

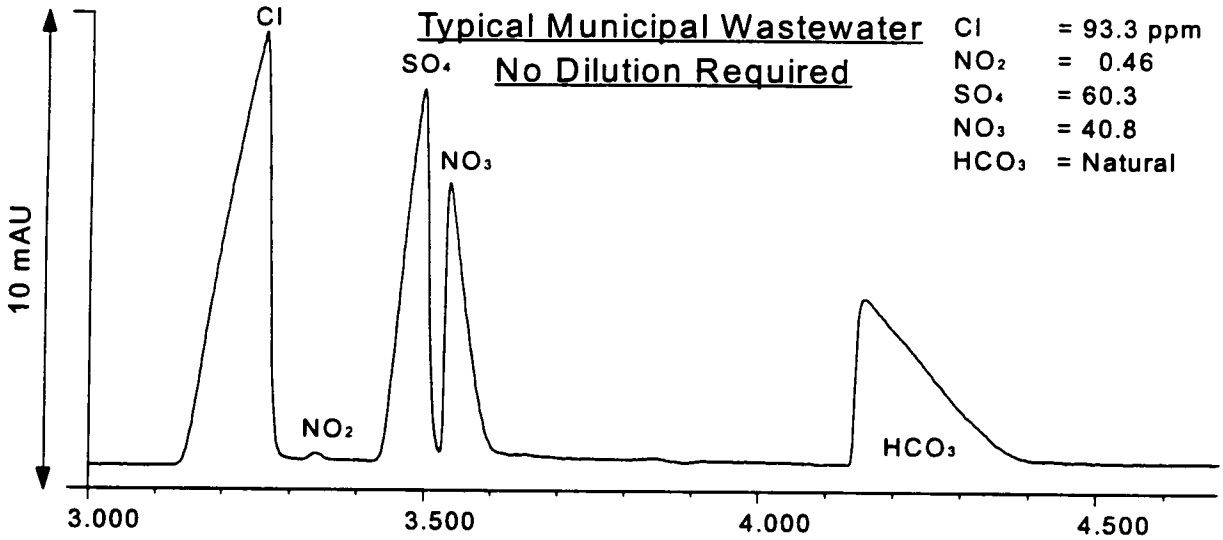
A CIA/True Value, or Mean = 1.000 indicates perfect agreement between CIA and official anion methods.

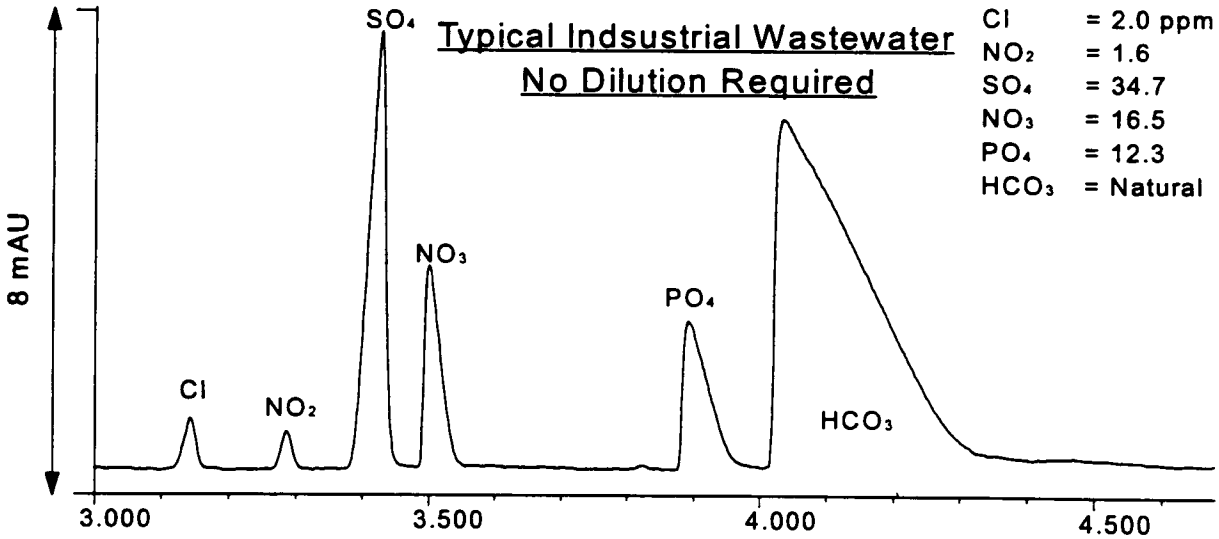
Method Recovery:
A Certified Performance Evaluation Standard (PES) was diluted 1:100 with Typical Drinking Water (DW). Amounts based upon multi-point calibration curve prepared from certified standards.

Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Drinking Water n=3, as ppm	24.72 ± 0.18	Not Detected	7.99 ± 0.07	0.36 ± 0.05	Not Detected	Not Detected
Amount %RSD	0.73%		0.91%	13.3%		
Performance Evaluation Std	43.00	1.77	37.20	15.37	2.69	6.29
DW + PES n=3; as ppm	66.57 ± 0.34	1.74 ± 0.03	45.19 ± 0.17	15.42 ± 0.12	2.62 ± 0.07	5.55 ± 0.31
Amount %RSD	0.51%	1.85%	0.38%	0.79%	2.69%	5.52%
% Recovery	97.9%	98.3%	100.2%	98.1%	97.4%	88.2%

Examples of Use:







Observations and Comments:

-Dissolved carbonate, detected as HCO_3^{-1}, is an anion present in all samples, especially alkaline samples. At less than 200 ppm, carbonate will not interfere with phosphate quantitation.

-Carbonate cannot be accurately quantitated with this method due to absorption of CO_2 from the air compromising response and standard accuracy.

-Phosphate quantitation in the sample may give low biased due to complexation with dissolved transition metals in the sample matrix.

-Chlorate (ClO_3) and divalent organic acids migrate shortly after phosphate and at greater than 10 ppm concentration may interfere with phosphate quantitation.

-Selectivity of this method can be changed by changing the concentration of the OFM-OH.

-Presence of negative peaks suggests an anion present in the electrolyte that is not present in the sample. Its identity corresponds to its migration time.

Stock Reagent Preparation:

100 mM Sodium Chromate Solution: Dissolve 23.41 g of sodium chromate tetrahydrate ($Na_2CrO_4 \cdot 4H_2O$) in a 1 liter volumetric flask with DI water, and fill to the mark with DI water. Store this solution in a capped plastic container for up to 1 year.

100 mM OFM-OH Solution: This tetradecyltrimethyl ammonium hydroxide (TTAOH) solution can be purchased from Waters Corp., P/N 49387, or can be prepared as needed as follows. Requires an anion exchange cartridge in the Hydroxide form, available from Alltech (as Maxi-Clean IC-OH Plus, P/N 30254; or equivalent) and a 20 mL plastic syringe.

Prepare a 100 mM OFM-Br Solution dissolve 3.365 g of tetradecyltrimethyl ammonium bromide (TTABr) in a 100 mL volumetric flask, and fill to the mark DI water. Convert only the require volume of OFM-Br to prepare the working electrolyte

Wash the anion exchange cartridge with 10 mL of 500 mM NaOH followed by 20 mL of DI water. Discard the washings. (Prepare sufficient volume for immediate use only, and use less than 10 mL per cartridge.)

Slowly pass the desired volume of TTABr through the cartridge into a volumetric flask used to prepare the final electrolyte. Rinse the cartridge with 20 mL of DI water, adding the washings to the volumetric flask.

100 mM CHES Buffer Solution:-- Dissolve 20.73 g of CHES (2-[N-CycloHexylamino]-Ethane Sulfonic Acid) in a 1 liter volumetric flask, and fill to the mark with DI water. Store this solution in a capped plastic container for up to 1 year.

1 mM Calcium Gluconate Solution: Dissolve 0.43 g of calcium gluconate in a 1 liter volumetric flask, and fill to the mark with DI water. Store this solution in a capped plastic container for up to 1 year.

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