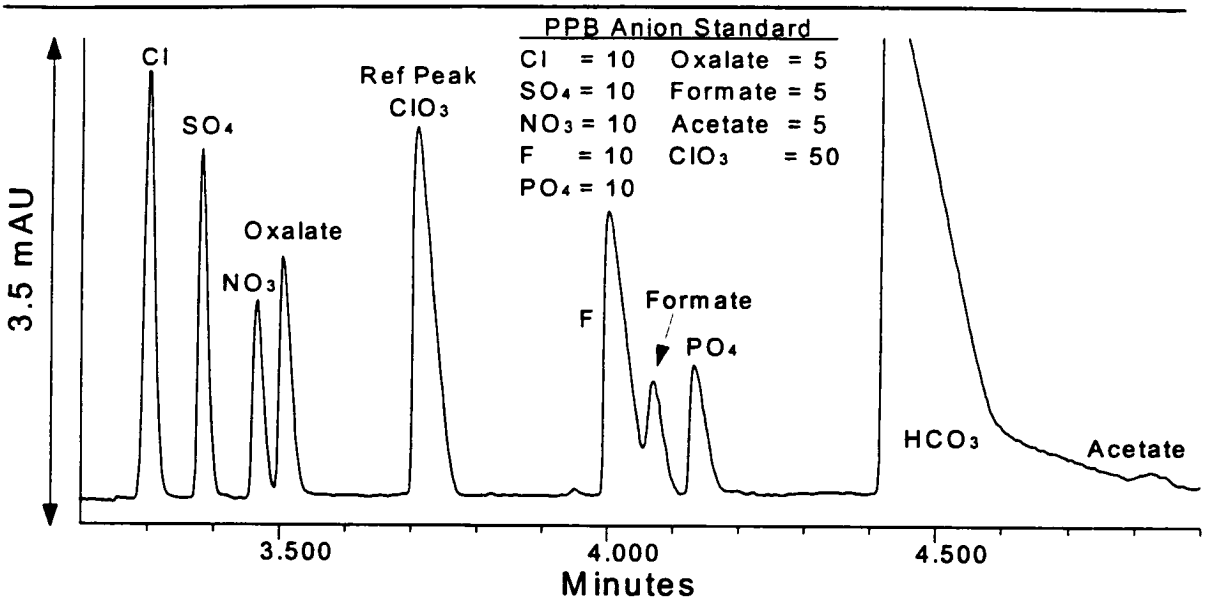
980902

# Waters

# Capillary Ion Analysis Method

**PPB Inorganic Anion and Organic Acid Analysis with Indirect UV Detection**
**High Purity Process Water Containing less than 100 ppb of All Analytes 2000**

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




**Analysis Conditions:**

| | |
|---|---|
| Electrolyte: | 5 mM Chromate / 0.5 mM OFM-OH / 6 mM Boric Acid, pH 8 |
| 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: | Constant 15 ± 1 µA (Use Constant Current for Analysis) |
| Carousel: | 6 Position Carousel with 4 mL Sample Vials |
| Sampling: | Electromigration, 5 kV for 45 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 Point per Second |
| Analyte MT: | Mid-Point of Analyte Peak Width at Baseline |
| Quantitation: | Time Corrected Peak Area (Peak Area / MT), and Internal Standard with respect to a Ref. Peak |

**Electrolyte Preparation:**
This electrolyte can be prepare as follows: See Reagents Section for Solution Preparation

1) Into a 100 mL volumetric flask add
   -5 mL of 100 mM Sodium Chromate Solution
   -0.5 mL of 100 mM OFM-OH (available from Waters, P/N 49387)
   -1.0 mL of 600 mM Boric Acid Buffer Solution
   -Dilute to volume with DI Water.
2) Natural pH is 8.1 ± 0.1.
3) Vacuum Degas through 0.45 µm Aqueous Compatible Membrane.
4) Store any used electrolyte in a plastic container at ambient temperature.
5) Allow to thermally equilibrate in the CIA Analyzer for 15 minutes before use.
6) Use fresh electrolyte daily; recalibrate with every change in electrolyte.

**Technique:**
The linearity and accuracy of this method is related to the quality of the DI Water used to prepare the electrolyte and standards, and to risk of environmental contamination. Use dedicated plasticware. Thoroughly rinse all flasks, pipette tips, sample analysis vials, and sample collection vials with DI water before use to minimize contamination. The most common contaminants are chloride, sulfate, and formate.

DI Water and purification systems containing high levels of TOC (Total Organic Carbon) and/or bacterial contamination will adversely effect performance. This is the source of organic acid contamination.

It is suggested that non-talc latex gloves be worn to minimize the risk of contamination.

**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 Anion Kit should be used to evaluate electrolyte selectivity only. Dilute original test mix 1:100 for ppm analysis; make a second 1:100 dilution for ppb evaluation. Do not use for accurate quantitation. Refer to pertinent information for example pherogram of anion standards using this electrolyte.

Prepare at least 3 mixed analyte standards, using 100 mL volumetric flasks, within the expected ppb range of sample analyte concentration, using a 1 ppm mixed analyte standard as an intermediate dilution solution. Add 100 µL of the Ref. Peak Additive solution per 100 mL to each ppb mixed analyte standard.

Prepare a Reagent Blank containing 100 µL of Ref. Peak Additive solution per 100 mL of DI water used for standard preparation. This solution will contain ppb level impurities which must be accounted for in the final calibration. Any impurities from the DI water, such as chloride, formate, and acetate will be detected.

After the multi-point calibration curve has been validated a single point calibration within the expected analyte concentration range is appropriate for recalibration.

Analyze in duplicate and evaluate resulting pherograms for analyte migration time reproducibility and peak shape. If the Cl and $SO_4$ peaks show indications of a doublet, disregard the analysis and repeat with fresh standard.

Run only one analysis per vial. For duplicate analysis place the same standard or sample into 2 consecutive vial positions.

**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 ppb for best results. High concentrations of a single analyte, including carbonate and hydroxide, will bias electromigration concentration and analyte quantitation.

If necessary, dilute the sample with DI water in a 100 mL volumetric flask. Analyte migration time reproducibility improves with increased sample dilution.

Add 100 µL of Ref. Peak Additive Solution per 100 mL of sample. Mix.

Analyze in duplicate and evaluate resulting pherograms for analyte migration time reproducibility and peak shape. If the Cl and $SO_4$ peaks show indications of a doublet, disregard the analysis and repeat with fresh standard.

**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 |
| 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) |
| 95 | Carousel Type | 6 = 6 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 |
| | Set Sample Mode to Electromigration | |

Use 4 mL HDPP vials in the 6 position carousel. They can be purchased from SunBrokers, Inc., 1-800/LAB-VIAL, P/N 500-160. Rinse and soak in DI water before use to minimize contamination.

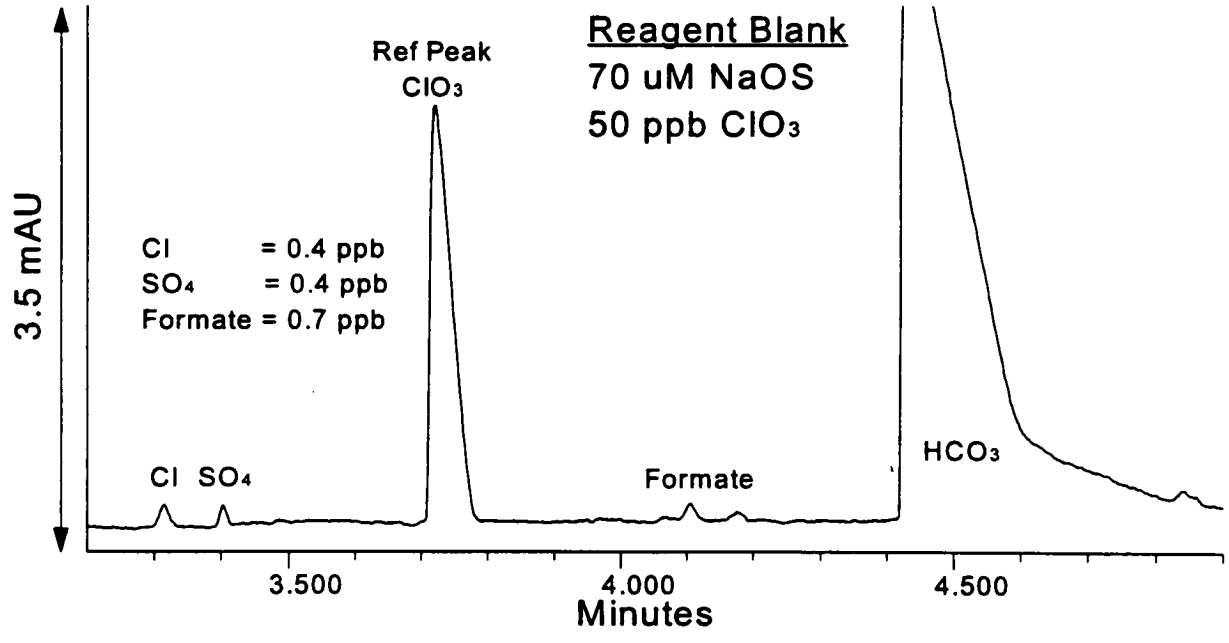
**Millennium Data Processing Method:**

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 = Closest |
| | Use $ClO_3$ as the reference peak for both MT Ref and as Internal Standard |
| | Ref MT Window = 5% |
| | Other Analytes = Closest |
| | Quant By = Time Corrected Peak Area, and Internal Standard using the $ClO_3$ reference peak |
| | 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 Ref Peak) |
| | Peak Area |
| | Time Corrected Peak Area |
| | Response ($TCPA_{Analyte}$ / $TCPA_{Ref\ Peak}$) |
| | Amounts |

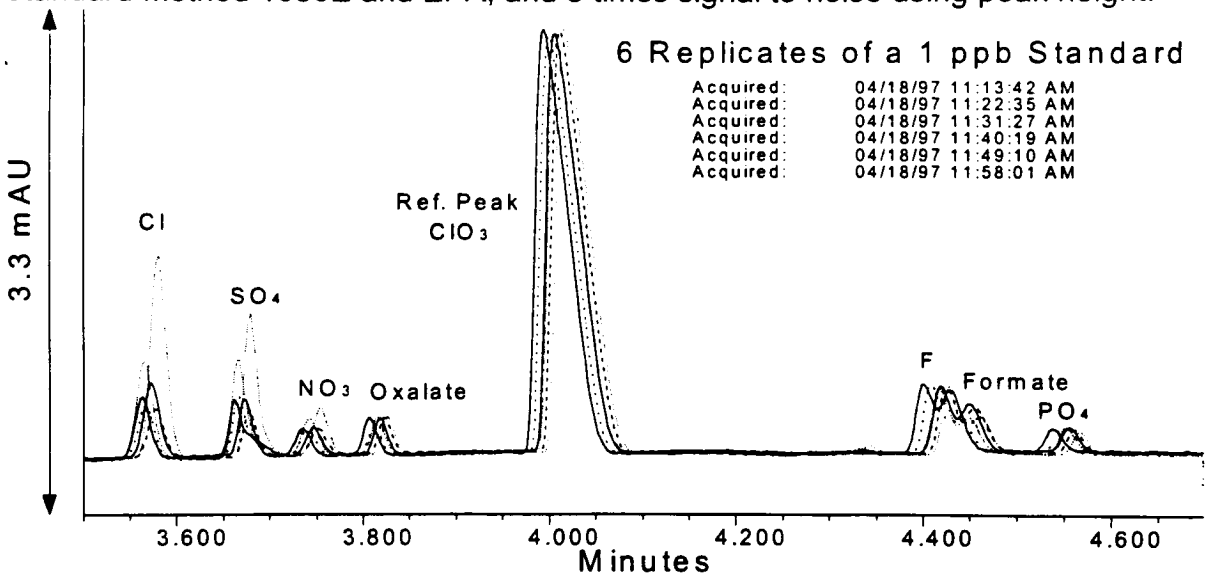
**Reference Peak Additive Solution (Reagent Blank):**

The Reference Peak Additive Solution is a 100 µL of a 70 mM NaOS / 0.6 mM $NaClO_3$ solution diluted to 100 mL with DI water (1:1000 dilution); or a 70 µM NaOS / 0.6 µM $NaClO_3$ (50ppb) Solution. A typical reagent blank is shown below. The Cl and $SO_4$ are attributed to impurities in the NaOS and $NaClO_3$ with formate attributed to the DI water.



**Method Detection Limits:**

Method detection limits were determined by analyzing a 1 ppb standard in 6 consecutive sample vials, and applying 2 different detection limit treatments, Standard Method 1030E and EPA, and 3 times signal to noise using peak height.




Based upon the above 1ppb pherograms, detection limits in ppb are calculated as;

| Anion | Cl | $SO_4$ | $NO_3$ | Oxalate | F | Formate | $PO_4$ |
|---|---|---|---|---|---|---|---|
| Std Mtd* | 0.43 | 0.25 | 0.07 | 0.03 | 0.13 | 0.09 | 0.17 |
| 3 x S/N | 0.14 | 0.13 | 0.23 | 0.16 | 0.11 | 0.16 | 0.32 |

* MDL = (Std Dev)(3.365); 3.365 = t-Test for 99% Confidence Interval at DF = 6

**Electromigration Sampling Precision**: Time Corrected Peak Area Precision, given as %RSD, of a minimum of 8 samplings per concentration from individual vials, one sampling per vial, used to generate the above response linearity.

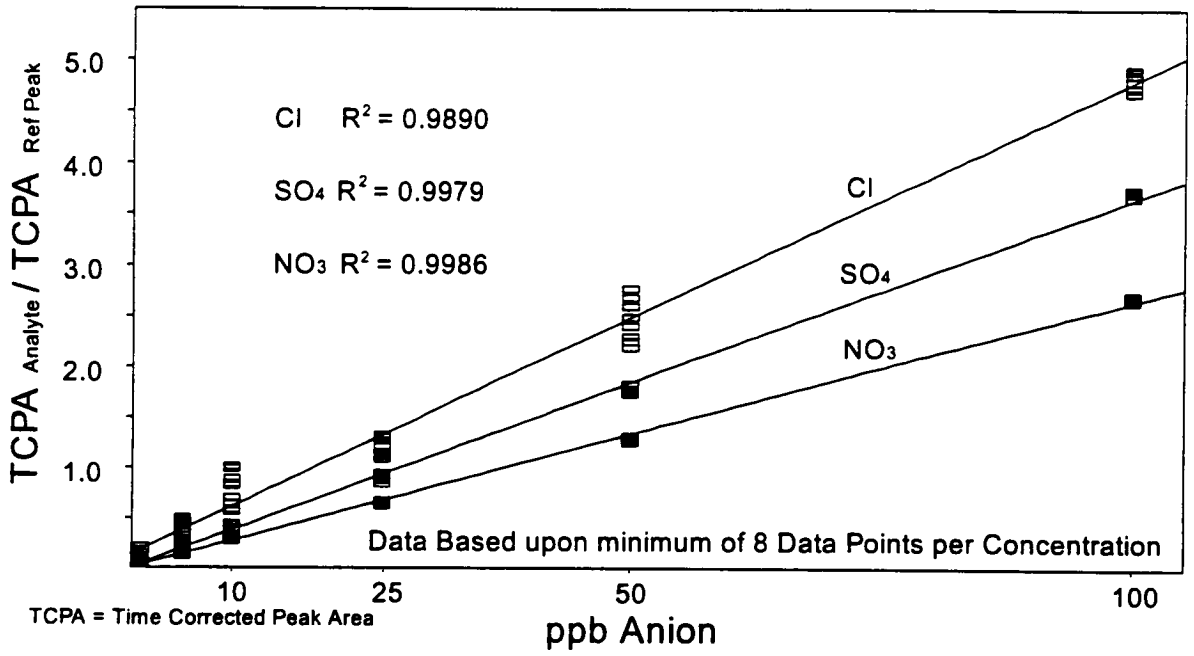
| Analyte | | Cl | $SO_4$ | $NO_3$ | Oxalate | Ref Peak | F | Formate | $PO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| ppb Concentration | 1 | 64.5 | 47.8 | 30.8 | 12.7 | 2.2 | 2.8 | 24.9 | 13.5 |
| | 5 | 27.2 | 14.3 | 12.3 | 15.0 | 8.00 | 14.5 | 39.0 | 12.9 |
| | 10 | 24.6 | 14.1 | 12.3 | 18.5 | 14,9 | 14.6 | 42.7 | 10.5 |
| | 25 | 11.0 | 6.9 | 6.6 | | 5.8 | 6.1 | | 6.7 |
| | 50 | 11.6 | 11.7 | 12.5 | | 12.4 | 11.8 | | 12.5 |
| | 100 | 9.6 | 8.5 | 8.0 | | 8.0 | 6.5 | | 5.9 |

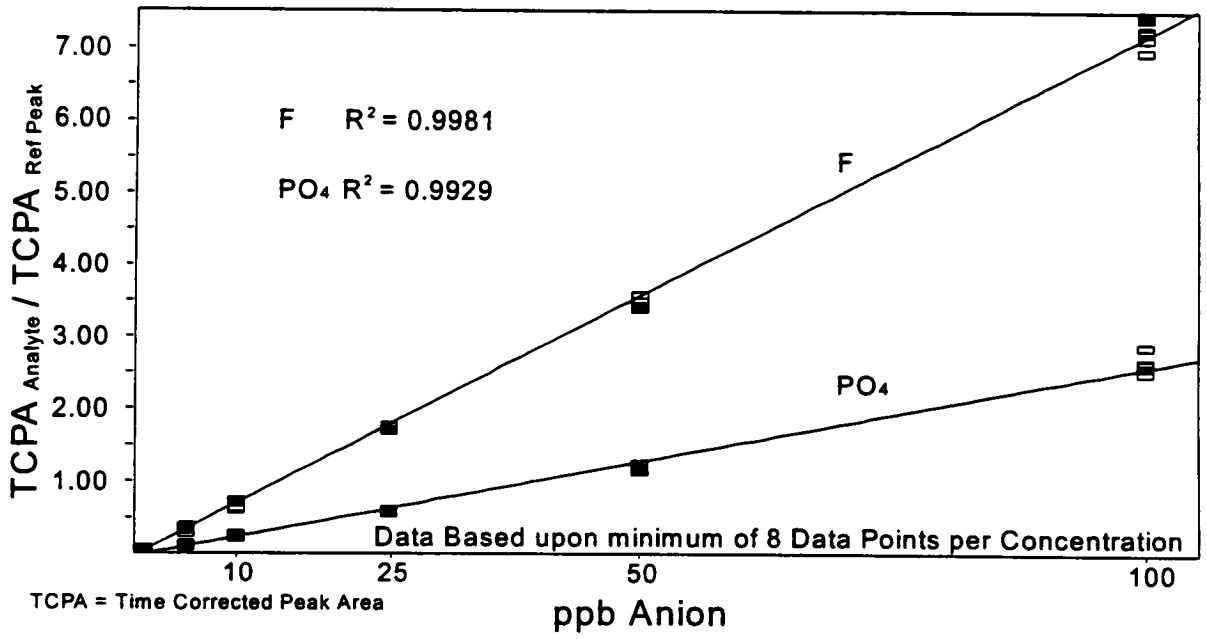
The overall sampling precision is less than 15% except for Cl and $SO_4$ at less than 10 ppb. Chloride, sulfate, and formate are the most common contaminants noted at low ppb concentrations, and is the main variable in precision..

The use of internal standard quantitation using the $ClO_3$ reference peak compensates for changes in electromigration efficiency due to the sample matrix. Chlorate is not a common contaminant.

**Method Linearity:**

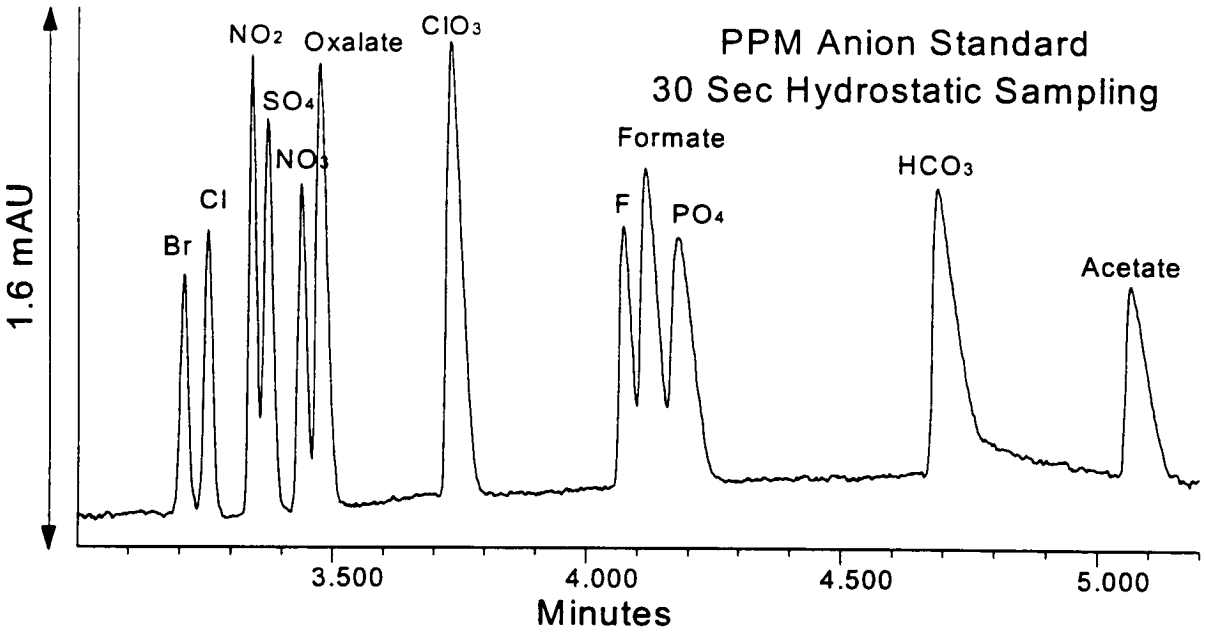
Linearity is based upon 8 replicates each standard, one sampling per vial. Standards contain an equal concentration of each anion with additive reference solution; ppb anion concentrations of 1, 5, 10, 25, 50, and 100. Analyte response determine using internal standard quantitation, with respect to chlorate.



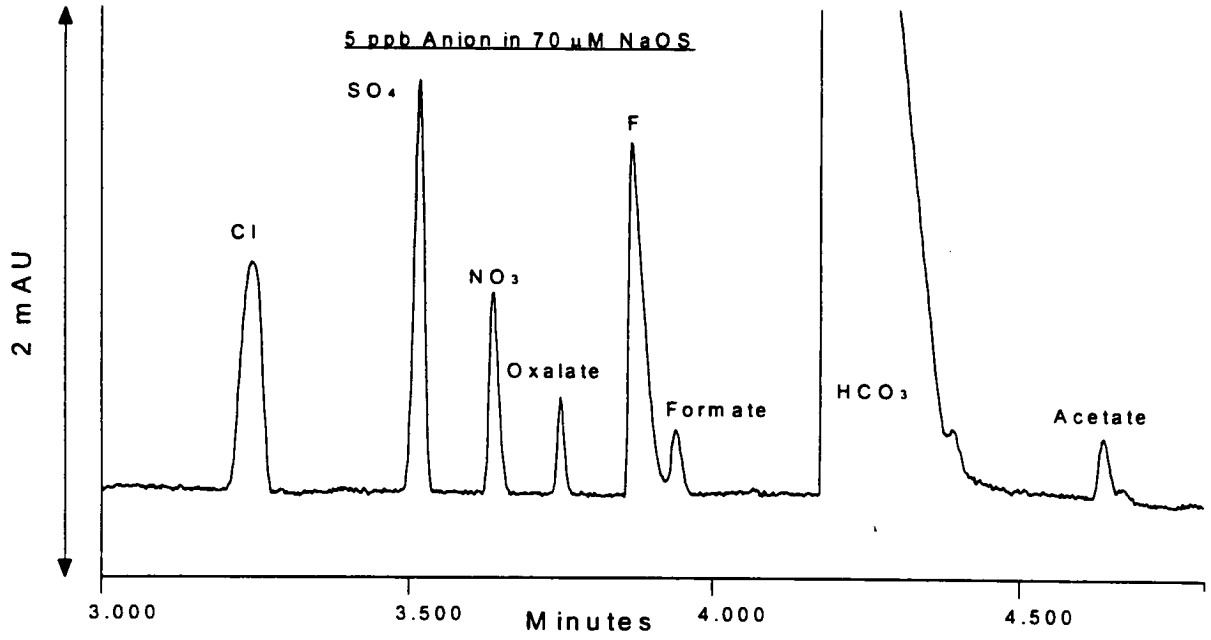



**Pertinent Information:**

Example pherogram of ppm anion standards using the electrolyte described in this method. Gives different selectivity compared to IonSelect High Mobility Anion Electrolyte due of a difference in OFM-OH concentration.




The Waters IonSelect High Mobility Anion Electrolyte has been used for ppb anion analysis as noted in the pherogram below. It is not used as the primary electrolyte for ppb analysis because of a potential risk of "peak doublets" or "peak splitting" for Cl and $SO_4$. If analyte peak doublets are observed the pherogram should be disregarded. Using the IonSelect High Mobility Anion Electrolyte, $ClO_3$ migrates just prior to the $HCO_3$ peak and may comigrate with $HCO_3$.



Observations and Comments:

-For best results always use at least 100 mL of sample for this method. Smaller samples volumes and smaller aliquots of Ref Peak Additive Solution may be used.

-Use 4 mL plastic sample vials for this analysis. Use of the 0.5 mL sample vials in the 20 position carousel will give 8 times less response and a higher risk of contamination.

-Only perform one sampling per sample vial. Run replicate samplings using consecutive sample vials containing the same sample.

-It is critical to minimize any source of contamination, including the DI water used to prepare the standards. Use dedicated plasticware, rinse all pipette tips and volumetrics with DI water before use, and wear non-talc gloves to minimize contamination from fingers.

-If the chloride and sulfate peaks shows a "peak doublet", or "peak splitting", or "flat top" peaks, disregard the analysis.

-Use of a 7 mM or 10 mM chromate based electrolyte will give increased analyte response. At 10 mM sulfate and nitrate are just baseline resolved.

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.

**600 mM Boric Acid Buffer Solution:** Dissolve 3.71 g of boric acid ($H_3BO_3$) in a 100 mL volumetric flask using 75 mL of DI water; use a heated magnetic stirrer to hasten dissolution. Fill to the mark with DI water. Store this solution in a capped plastic container for up to 1 year.

**100 mM Sodium Hydroxide Solution**:-- Dissolve 4 g of NaOH pellets in a 1 liter plastic 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.

**6 mM Sodium Chlorate Solution:** -- , Dissolve 0.637 g of high grade sodium chlorate ($NaClO_3$ in a 1 liter volumetric flask) with 500 mL of DI water, and fill to the mark with DI water. Store this solution in a glass or plastic container for up to 1 year.

**70 mM Sodium Octane Sulfonate / 0.6 mM Sodium Chlorate Solution:** -- In a 100 mL volumetric flask dissolve 1.51 g sodium octane sulfonate (NaOS) in 50 mL of DI water, add 10 mL of 6 mM sodium chlorate solution, and fill to the mark with DI water. Store is a pre-cleaned plastic container. Prepare fresh monthly to minimize contamination of reagent blank.

(High purity sodium octane sulfonate can be purchased from VHG Laboratories, Manchester, New Hampshire, 03109, 603/622-7660. Other suppliers can be used but it is the responsibility of the user to determine the anion impurities in the sodium octane sulfonate before use.)

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