Improved anions analysis: impact of newer technologies in older contaminants

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Outline

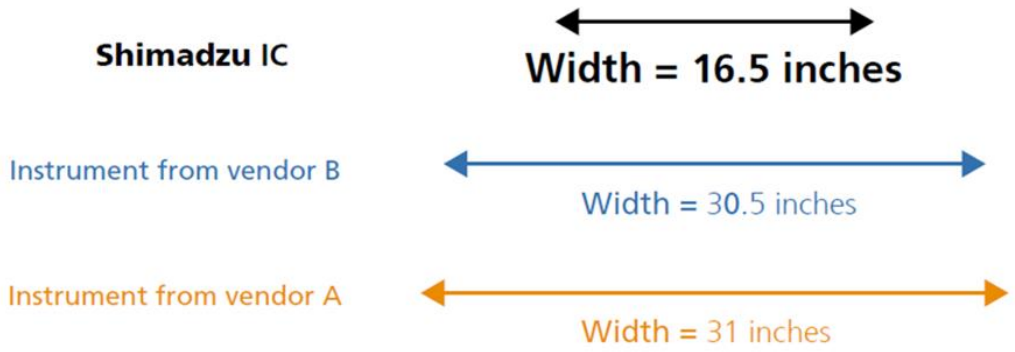
1. Objectives
2. Instrumentation
3. Results
    1. Method optimization (EPA 300.0)
    2. Method modifications
4. Conclusions
5. Q&A

Objectives

How can we use newer technology to improve turn-around-times and overall efficiency in the lab, without sacrificing quality of the data?

1. Method optimization EPA 300.0:
   a) Decrease sample-to-sample cycle time
   b) Minimize sample re-runs

2. Method modifications:
   a) Improve sensitivity, in the presence of interferences



Instrumentation – PROMINENCE IC

Conductivity Detector

Anion Suppressor

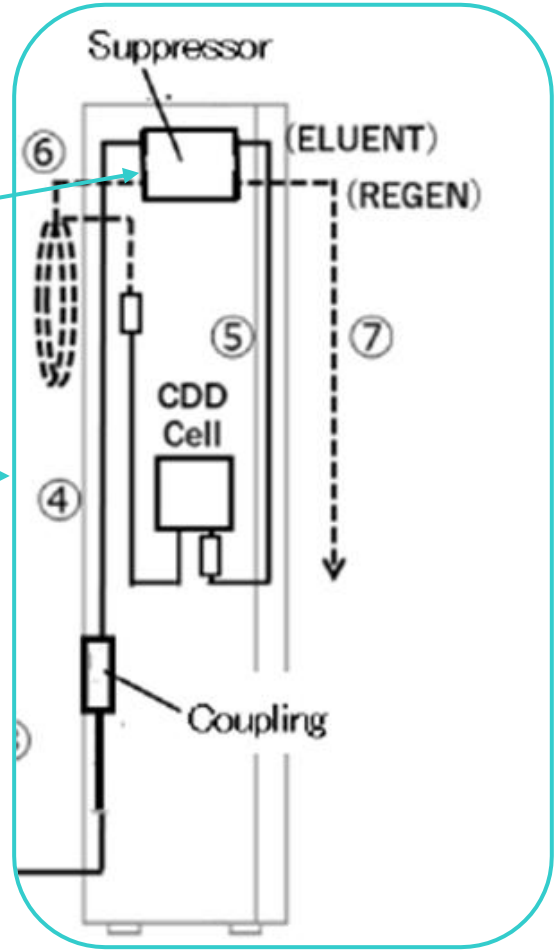
Eluent Delivery Pump

Column Oven

Autosampler

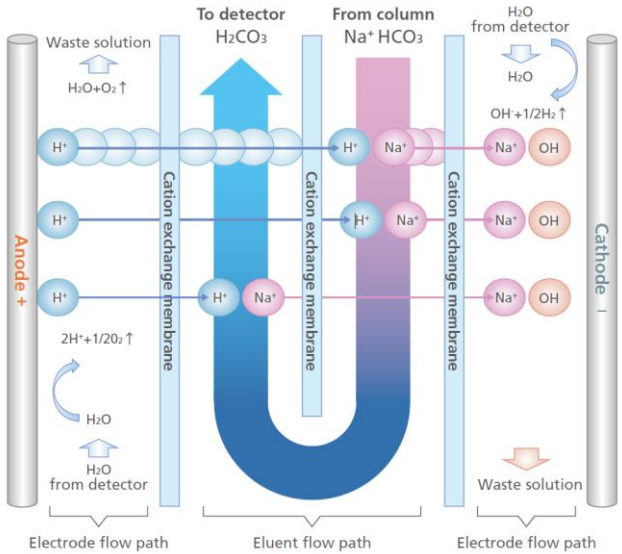
Instrumentation – PROMINENCE IC

Anion Suppressor



Anion Suppressor

- Alternative to Chemically or Electrolytically regenerated suppressors
- Based on commonly-used electrolytic suppression technique
- A unique folded flow path and patent-pending design
- Increased membrane surface area for higher efficiency of both background suppression and electrolysis regeneration
- Minimized internal volume reduces peak broadening and increases thermal stability
- No need to use acids or chemical regenerants



Structure and principles behind the ICDS-40A

Instrumentation – Modifications

PDA detector added in-line for method modifications after EPA 300.0 optimization

In current work, PDA detector was used as UV detector

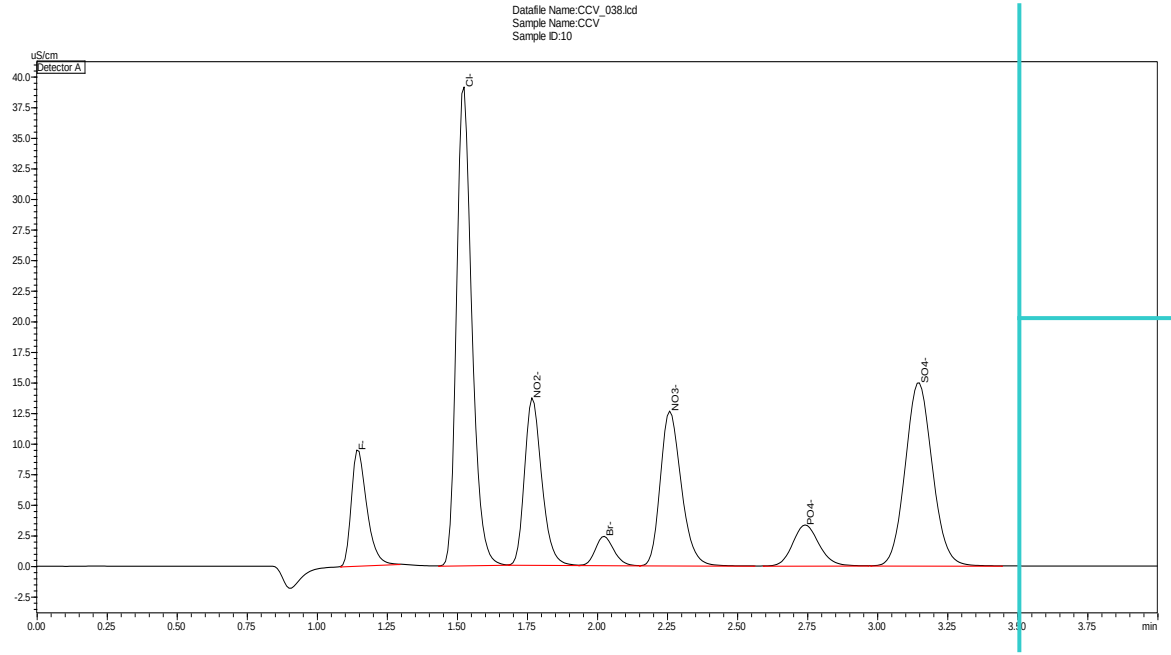
Results – Method Optimization EPA 300.0

Decrease sample-to-sample cycle time: METHOD CONDITIONS

Parameter Prominence IC	Conditions
Flow rate	2 ml/min
Column Temp	50 °C
Injection Volume	20 µl
Eluent	5.5 mM Na2CO2/1.5 mM NaHCO3
Column	AS22 Fast 4x150mm Column
Conductivity Detector	53 °C, Anion Suppressor

Results – Method Optimization EPA 300.0

Decrease sample-to-sample cycle time: CHROMATOGRAPHY



Run time can be reduced to ~3.5 min

- ✓ High throughput anion analysis with <4 min run time
- ✓ Total cycle time: 4 min, including washing and rinsing of needle for minimizing carry-over

20 second cycle time for injection and pre-rinse and post rinse while the sample is running

Results – Method Optimization EPA 300.0

Decrease sample-to-sample cycle time: PERFORMANCE DEMONSTRATION

Anions	Calibration range (ppm)	Linearity (R2)	MDL Standard (ppm)	Calculated MDL (ppm)
Fluoride (F-)	0.01-50	0.999	0.01	0.0035
Chloride (Cl-)	0.05-250	0.996	0.05	0.0086
Nitrite (NO2-)	0.01-50	0.999	0.01	0.0015
Bromide (Br-)	0.01-50	0.998	0.01	0.0035
Nitrate (NO3-)	0.01-50	0.998	0.01	0.0027
Phosphate (PO4-)	0.01-50	0.998	0.01	0.0058
Sulfate (SO4-)	0.05-250	0.999	0.05	0.0089

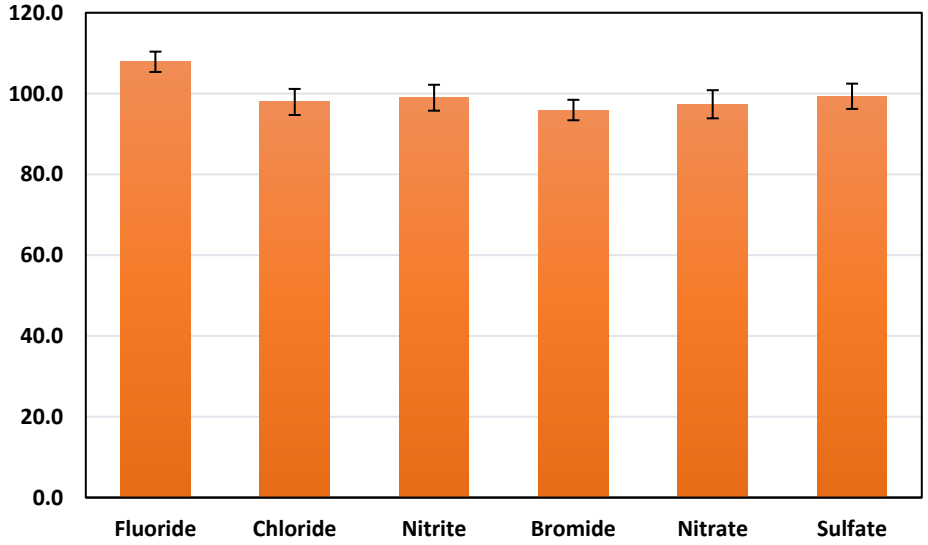
**MCL*
Nitrite: 1 ppm
Nitrate: 10 ppm**

- ✓ Dynamic range, for the 7 anions: 1 order of magnitude smaller than lowest calibration standard
- ✓ Excellent linearity observed
- ✓ Calculated MDLs ranged between 0.0015 (nitrite) and 0.0089 ppm (sulfate)

*** MCL: Maximum Contaminant Level in Drinking Water**

Results – Method Optimization EPA 300.0

Decrease sample-to-sample cycle time: PRECISION AND ACCURACY



✓ Excellent precision and accuracy observed for the 6 anions evaluated (phosphate not analyzed in this part of the study)

n=100	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Sulfate
%Recovery	107.9	97.9	99.0	95.9	97.4	99.3
SD	2.5	3.2	3.2	2.5	3.5	3.1
RSD	2.3	3.3	3.2	2.7	3.6	3.2
Limit of Reporting, ppm	0.100	0.100	0.050	0.050	0.050	0.200

Results – Method Optimization EPA 300.0

Minimize sample re-runs: VARIABLE INJECTION VOLUME

Advanced autosampler uses a needle-in-flow path design to:

- reduce *carryover* to undetectable levels maintain accuracy and
- precision necessary for robust quantitation while using different injection volumes

BENEFITS

Minimization of:

- ✓ labor for sample dilution
- ✓ potential analytical errors

Results – Method Optimization EPA 300.0

Minimize sample re-runs: VARIABLE INJECTION VOLUME

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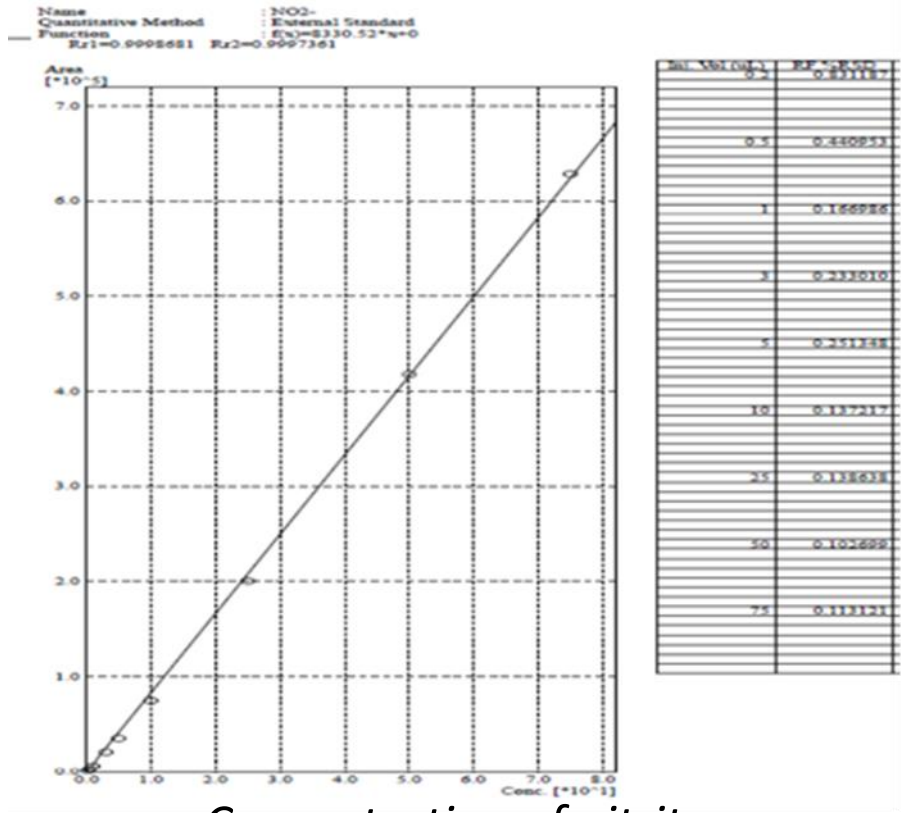
- reduce *carryover* to undetectable levels maintain accuracy and
- precision necessary for robust quantitation while using different injection volumes



Concentration of nitrite with increasing injection volume (0.2-75 µL)

Results – Method Optimization EPA 300.0

Minimize sample re-runs: VARIABLE INJECTION VOLUME

Anions	Injection Volume (µL)	Linearity (R2)	%RSD (V= 1 µl, n=5)
Fluoride (F-)	0.2-75	0.9999	0.2582
Chloride (Cl-)	0.2-75	0.999	0.3397
Nitrite (NO2-)	0.2-75	0.9998	0.1670
Bromide (Br-)	0.2-75	0.9991	0.8531
Nitrate (NO3-)	0.2-75	0.998	0.1187
Phosphate (PO4-)	0.2-75	0.998	1.3265
Sulfate (SO4-)	0.2-75	0.998	0.2742

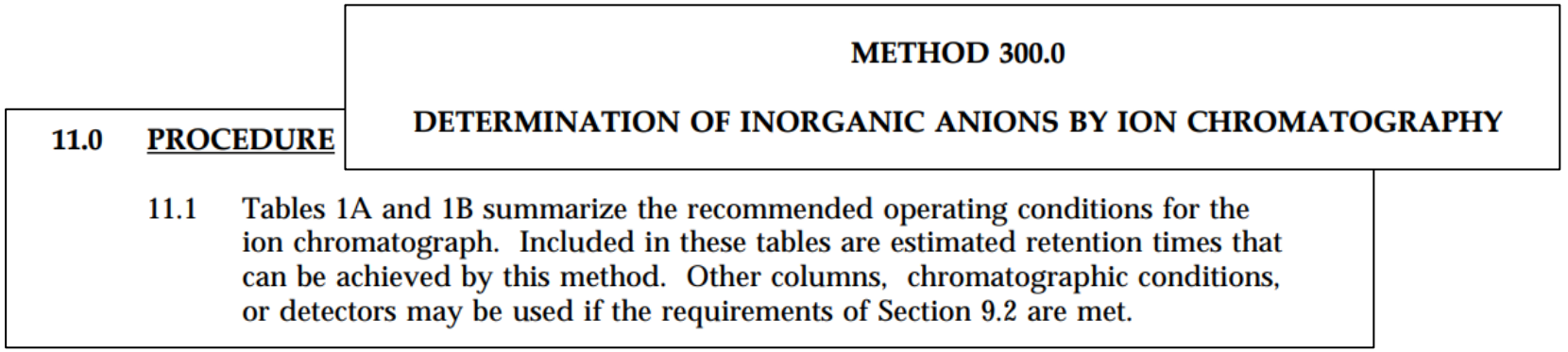
- ✓ Excellent linearity for the 7 anions with injection volume between 0.2 and 75 µL
- ✓ For injection volume of 1 µl, %RSD (n=5) ranged from 0.12 (nitrate) to 1.3 (phosphate)

Results – Method Modification

Improve sensitivity & minimize sample re-runs

- The presence of interferences (i.e., high concentrations of chloride) negatively impacts the sensitivity of nitrate and nitrite

- In-line UV detection allows for lower detection limits for nitrate, and nitrite, and their simultaneous analysis with other anions in EPA 300.0 and 300.1, in the presence of interferences



METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

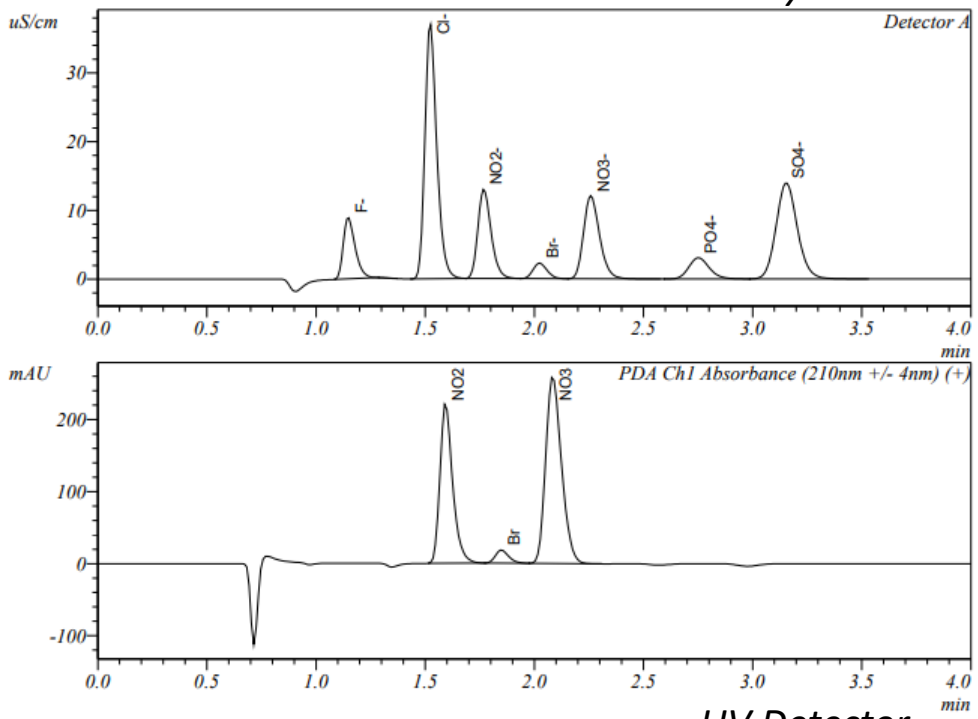
11.0 PROCEDURE

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.

Results – Method Modification

Improve sensitivity & minimize sample re-runs

Conductivity Detector



UV Detector

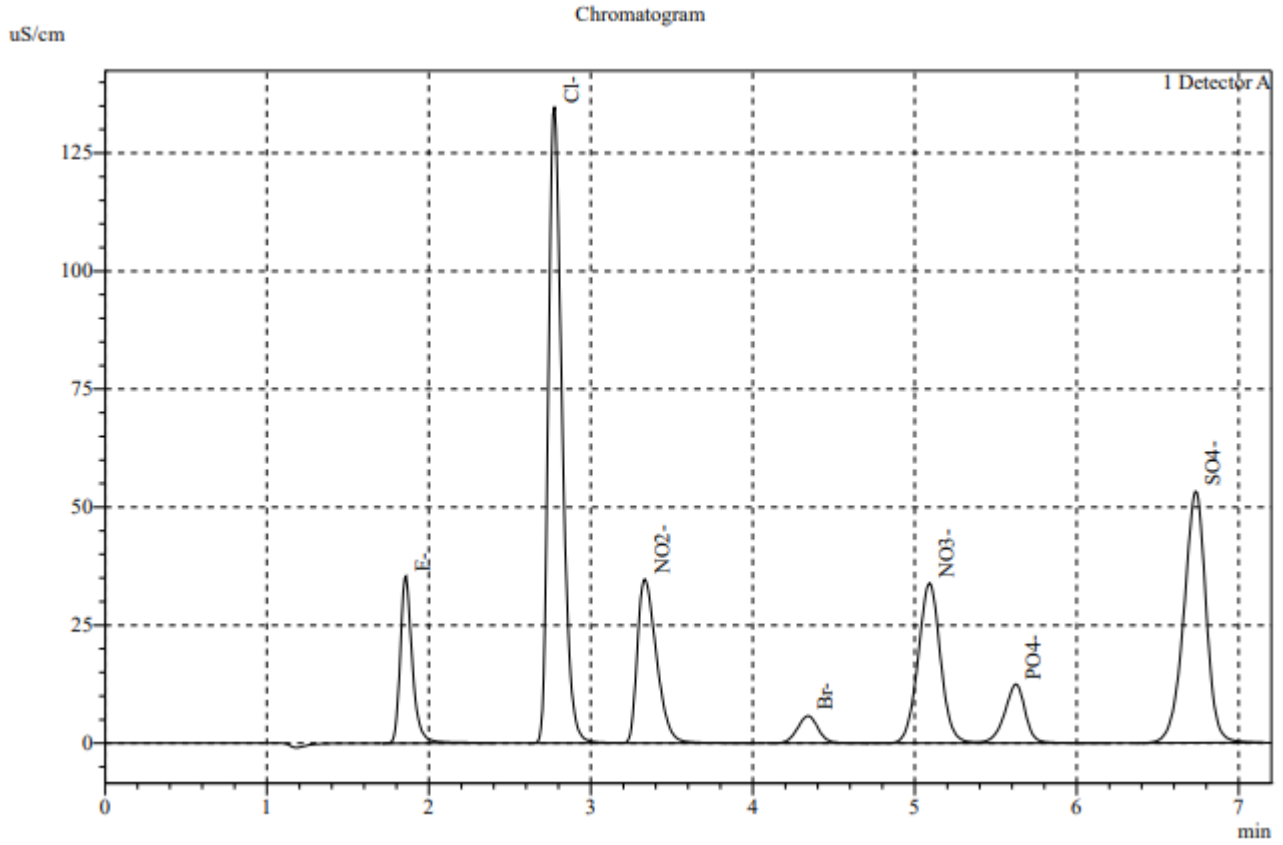
✓ Sensitivity for nitrate and nitrite decreased by 1 order of magnitude

Parameter	Conditions
Flow rate	2 ml/min
Column Temp	50 °C
Injection Volume	20 µl
Eluent	5.5 mM Na2CO2/1.5 mM NaHCO3
Column	AS22 Fast 4x150mm Column
UV Detector	50 °C, 210 nm
Conductivity Detector	53 °C, Anion Suppressor

Anions	CONDUCTIVITY Calibration range (ppm)	UV DETECTOR Calibration range (ppm)
Fluoride (F-)	0.01-50	
Chloride (Cl-)	0.05-250	
Nitrite (NO2-)	0.01-50	0.001-20
Bromide (Br-)	0.01-50	
Nitrate (NO3-)	0.01-50	0.001-20
Phosphate (PO4-)	0.01-50	
Sulfate (SO4-)	0.05-250	

Results – more conventional approach

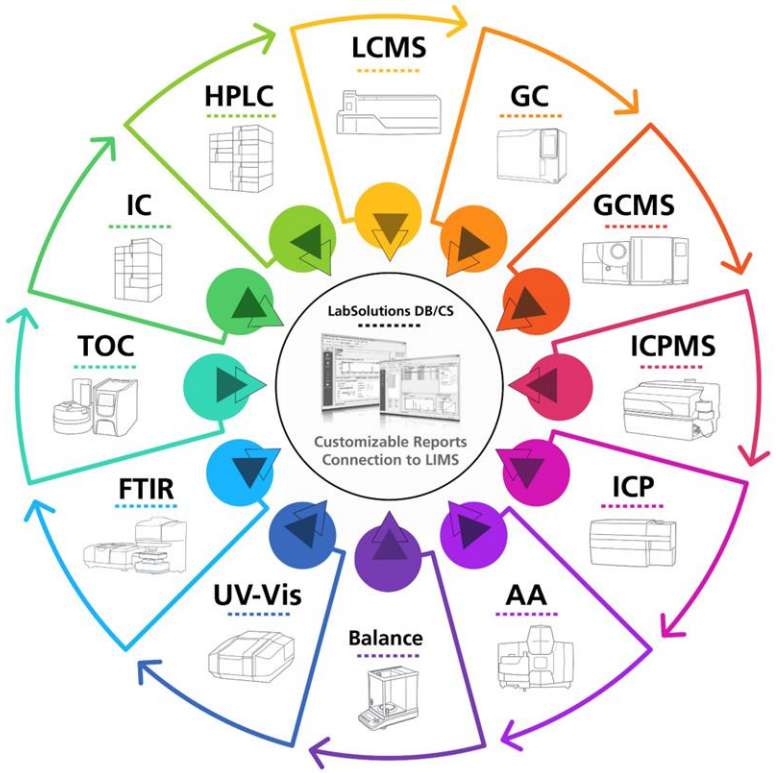
Parameter Prominence IC	Conditions
Flow rate	1.2 ml/min
Column Temp	50 °C
Injection Volume	20 µl
Eluent	2.1 mM Na2CO2/4.5 mM NaHCO3
Column	AS22 Fast 4x150mm Column
Conductivity Detector	53 °C, Anion Suppressor



Conclusions

- Method performance for EPA 300.0 with minimized sample-to-sample cycle time was demonstrated:
  - Cycle time: 4 min
  - MDLs between 0.0015 (nitrite) and 0.0089 ppm (sulfate)
- Advanced autosampler enables alternatives to minimize:
  - Labor for sample re-run, and use of space in autosampler's tray
  - Potential analytical error
- Conductivity and UV-detectors in-line improve productivity:
  - Ability to analyze nitrate and nitrite in the presence of high concentrations of chloride in a single injection
  - Sensitivity for nitrate and nitrite: 1 order the magnitude lower by UV than conductivity detector

Q&A



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