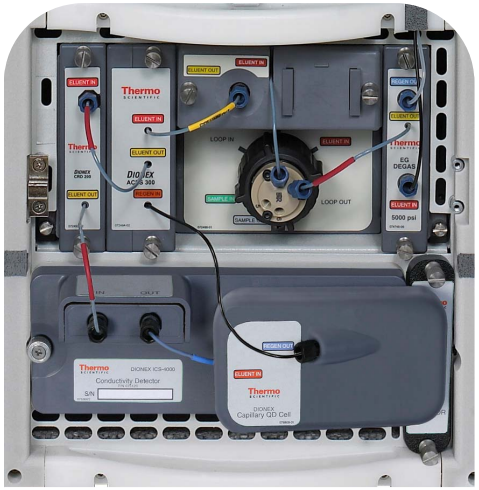
Identification of Unknowns using Charge Detection (QD) in Ion Chromatography

Talk Outline

- What is a Charge Detector?
- Instrument Set up
- Charge Detector Operation Parameters
- Confirmation with Two Detectors in Series
- Example Applications
- Conclusions

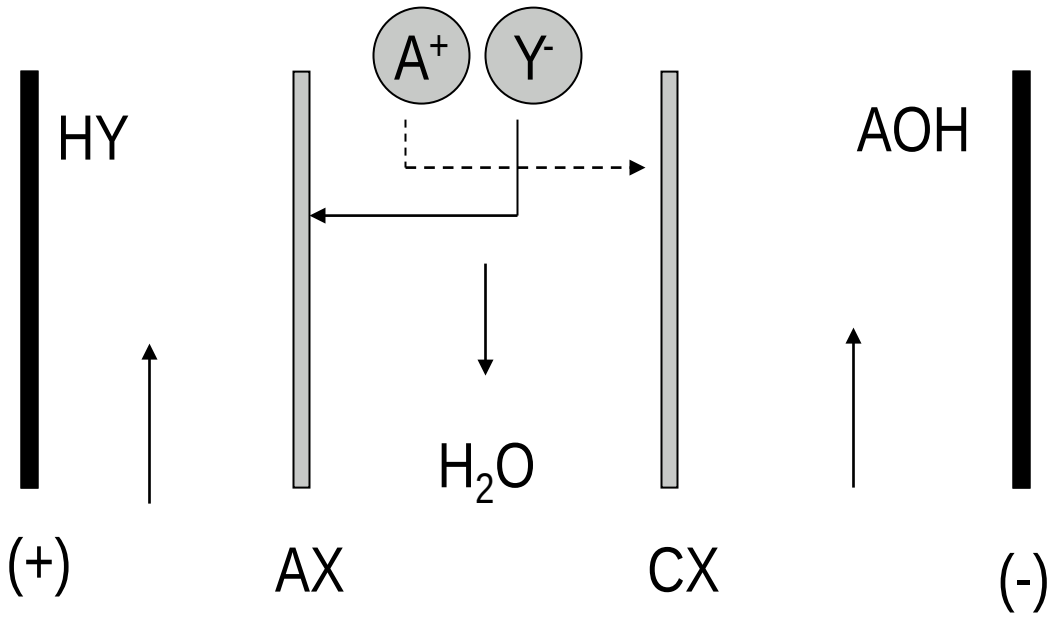
What is a Charge Detector?

- Responds to ionic species by drawing a current at a fixed potential
- Uses a membrane device similar
- Response is proportional to charge, universal calibration
- Weakly dissociated (suppressed) analytes will show higher response
  - Response vs. Concentration will be linear for weakly dissociated species
    - Organic acids, amines, silicate, borate
- Complements suppressed conductivity detection

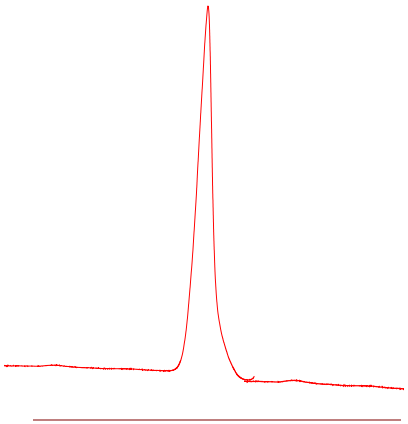


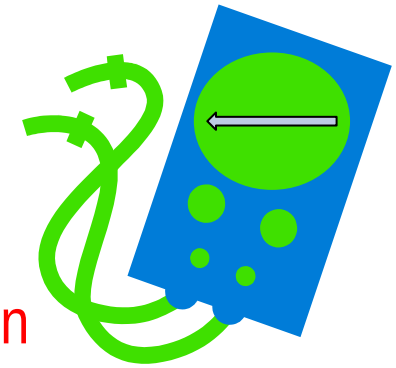
Quantification of unknowns at low cost with universal, linear calibration

Charge Detector Operation Principle



Signal ∝ total charges





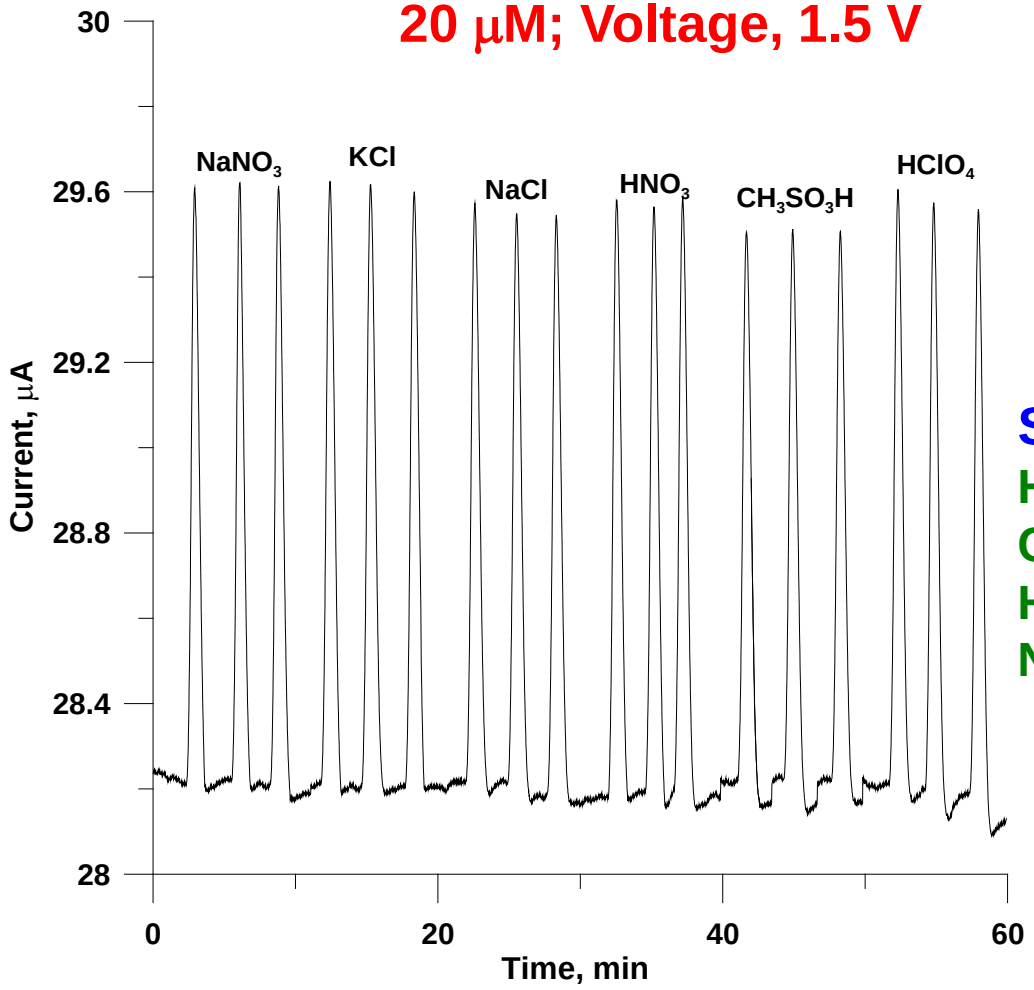
Signal is depending on charge state of the ion

Charge Detector Characteristics

- Background is due to dissociation of water
- Baseline noise stems from dissociation of water
- The applied voltage impacts the signal as well as the noise
- Removal efficiency depends on the applied voltage as well as residence time
- Response high for all ions
  - Super faradaic behavior
  - Hypothesis: Dissociation of water is enhanced due to the relatively lower resistance during the transition of an analyte peak
- Weak acids and bases show a relatively higher response
- S/N is slightly worse than conductivity

Reference: Dasgupta et. al., *Anal. Chem.,* **2010**, *82*(3), 951–958

Charge Detector Response (Flow Injection)



Specific Conductance

HNO_3 = 421 μS/cm/mM

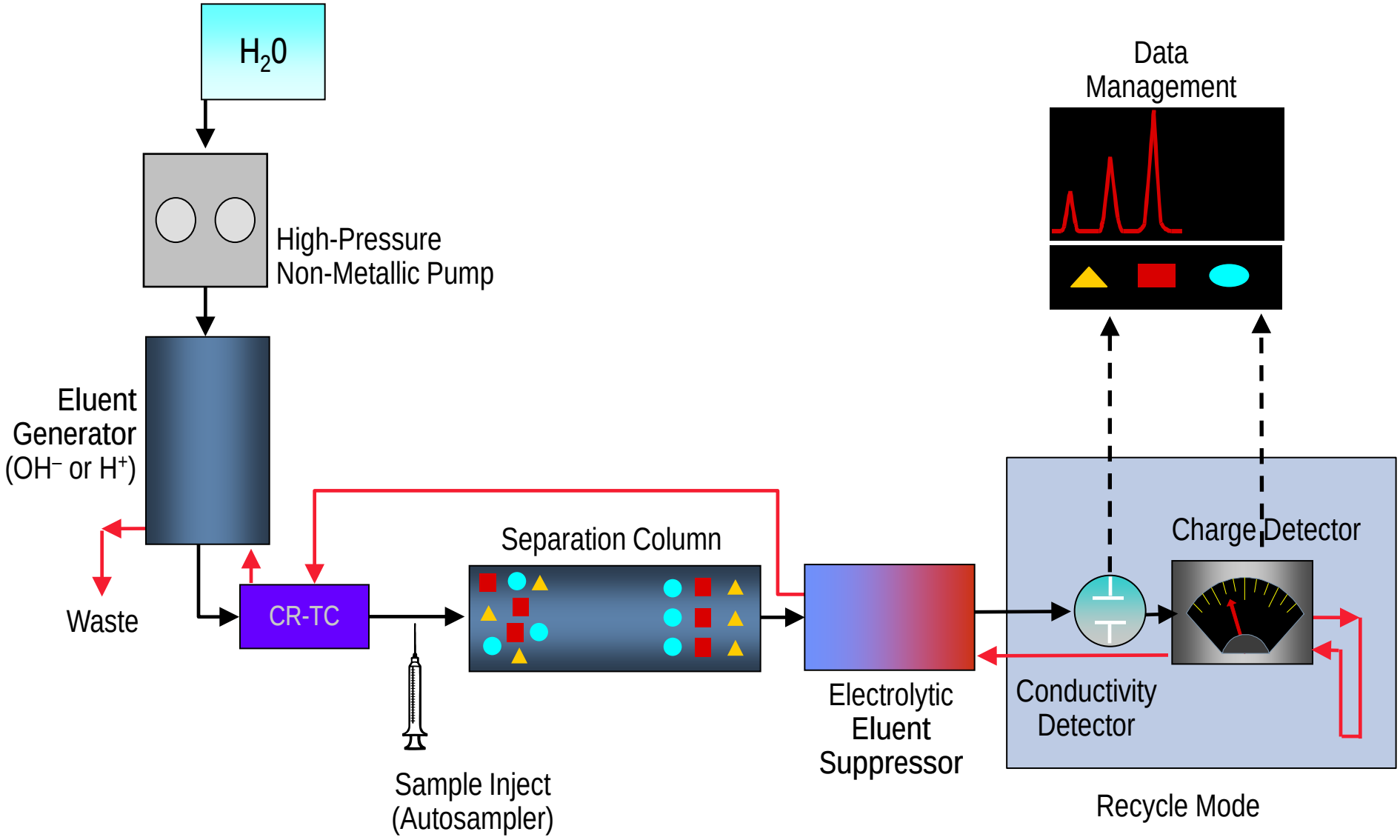
CH_3SO_3H = 380 μS/cm/mM;

$HClO_4$ = 418 μS/cm/mM

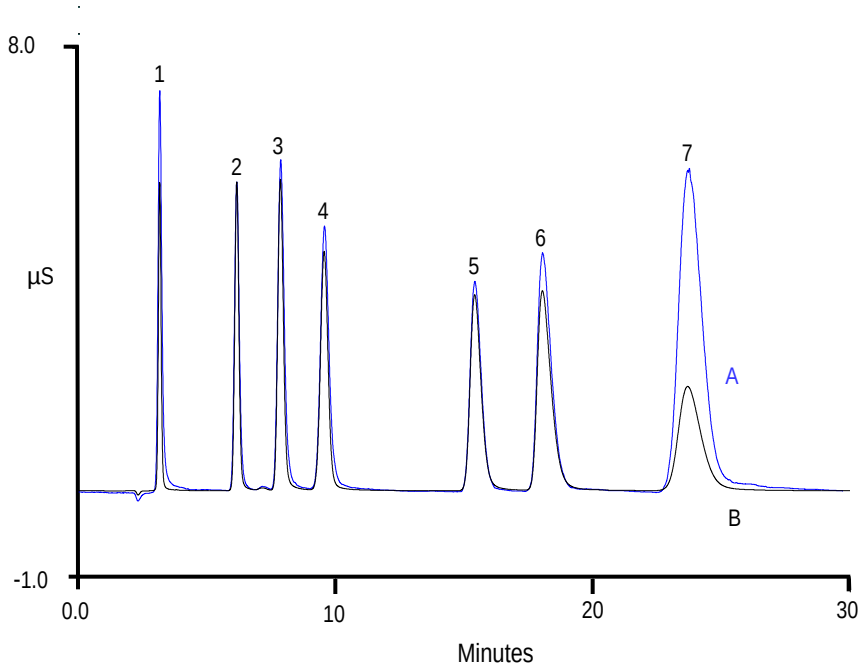
$NaNO_3$ = 121 μS/cm/mM

Similar Response for different ions with the same charge

Ion Chromatography System Setup



IonPac AS15- 9 µm Capillary (0.4 x250mm) Column Combined with CD and QD

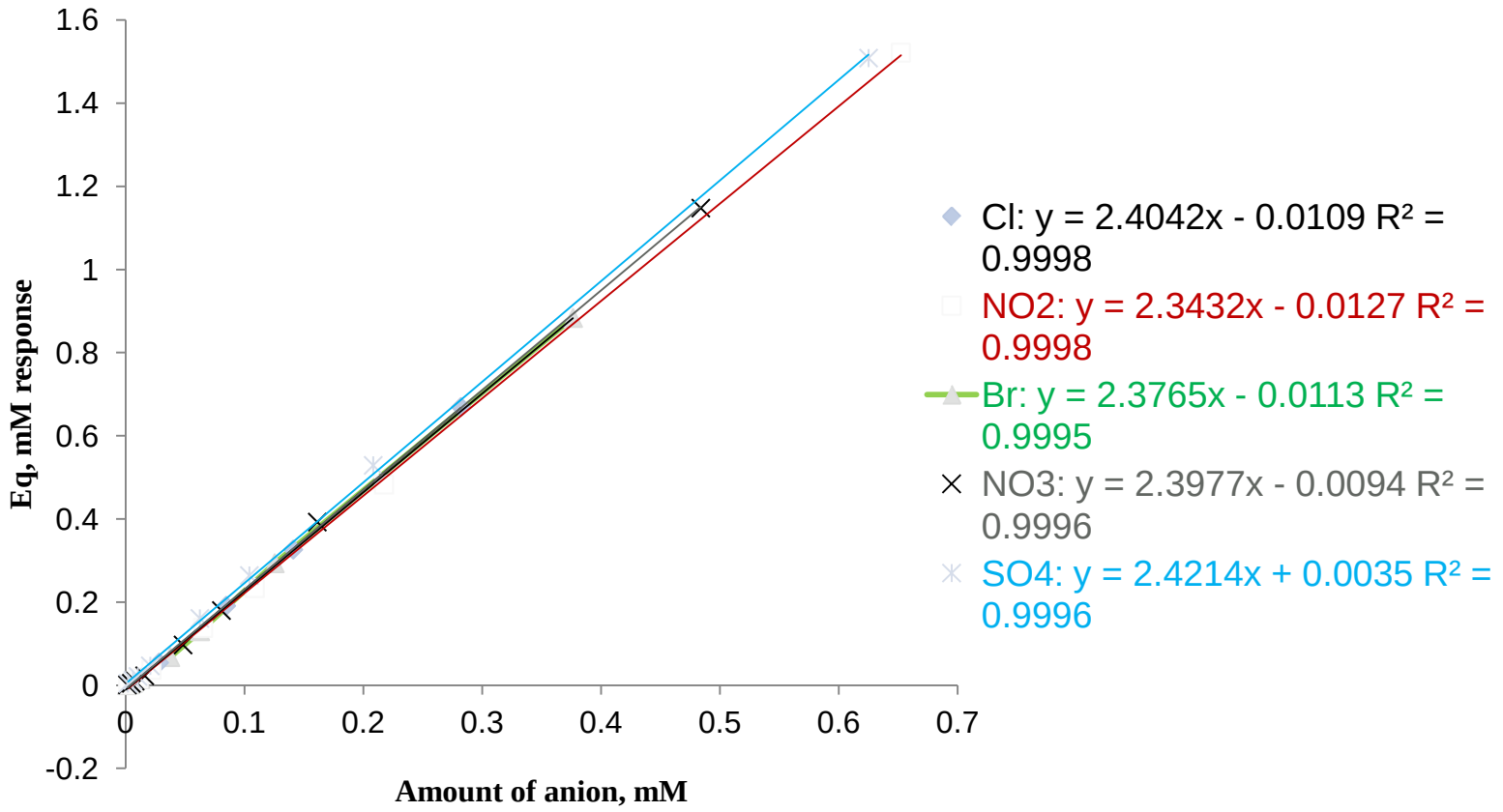


Column:	Thermo Scientific™ Dionex™ IonPac™ AS15-9µm Capillary (0.4 x 250 mm)
Instrument:	Thermo Scientific™ Dionex™ ICS 5000 HPIC™ system
Eluent Source:	Thermo Scientific Dionex EGC-EG Eluent Generator Cartridges
Eluent:	38mM Potassium Hydroxide,
Flow Rate:	0.012 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity
Suppressor:	Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor , AutoSuppression™ Recycle Mode
A:	Charge Detection
B:	Conductivity Detection

Peaks:			
	1.Fluoride	1.0	mg/L
	2.Chloride	2.5	
	3.Nitrite	5.0	
	4.Sulfate	5.0	
	5.Bromide	10.0	
	6.Nitrate	10.0	
	7.Phosphate	15.0	

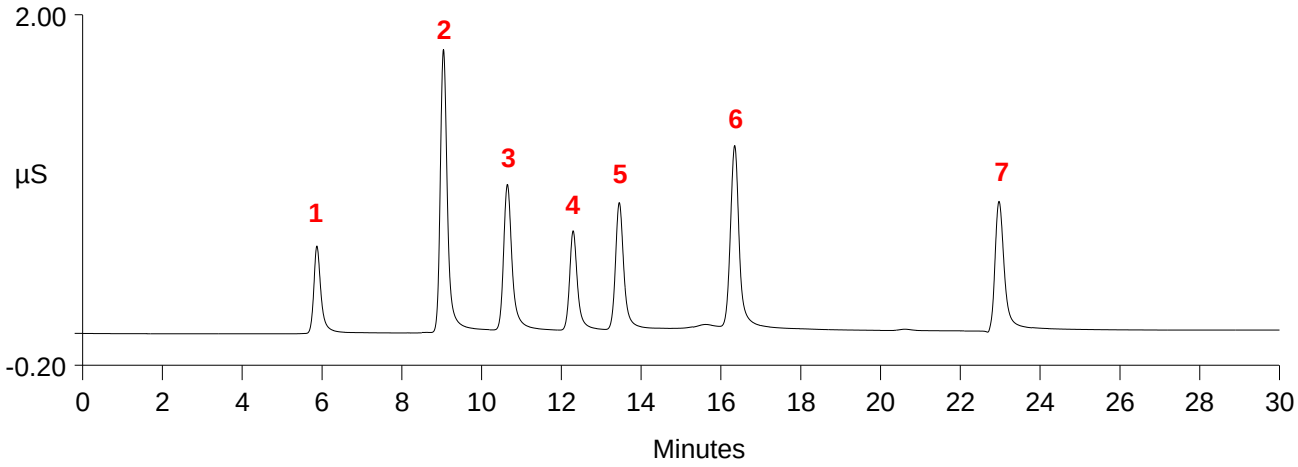
Phosphate 3x more sensitive with QD – Important for water analysis

Response versus Concentration (Charge Detector)

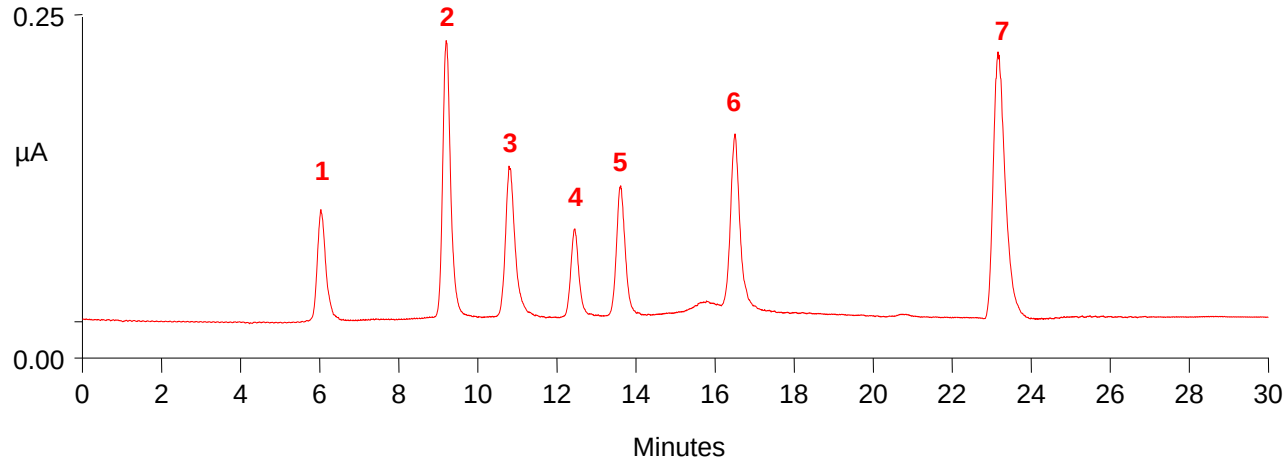


Conductivity versus Charge Detector, Capillary Setup (Dionex IonPac AS19 0.4 x 250 mm, 10 µL/min)

A) Conductivity Detection



B) Charge Detection



Column:	Thermo Scientific Dionex IonPac AS19-HC Capillary (0.4 x 250 mm)
Instrument:	Dionex ICS-3000
Eluent Source:	Dionex EGC-KOH (Capillary)
Eluent:	Potassium Hydroxide, 5 mM from 0 to 5min, 5–40 mM from 5 to 30 min
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	20 °C
Detection:	A) Dionex ACES 300, AutoSuppression, Recycle Mode
	B) Thermo Scientific Dionex QD Charge Detector

Peaks:		Conc.(ppm)
1.	Fluoride	0.2
2.	Chloride	1.0
3.	Nitrite	1.0
4.	Bromide	1.0
5.	Nitrate	1.0
6.	Sulfate	1.0
7.	Phosphate	2.0

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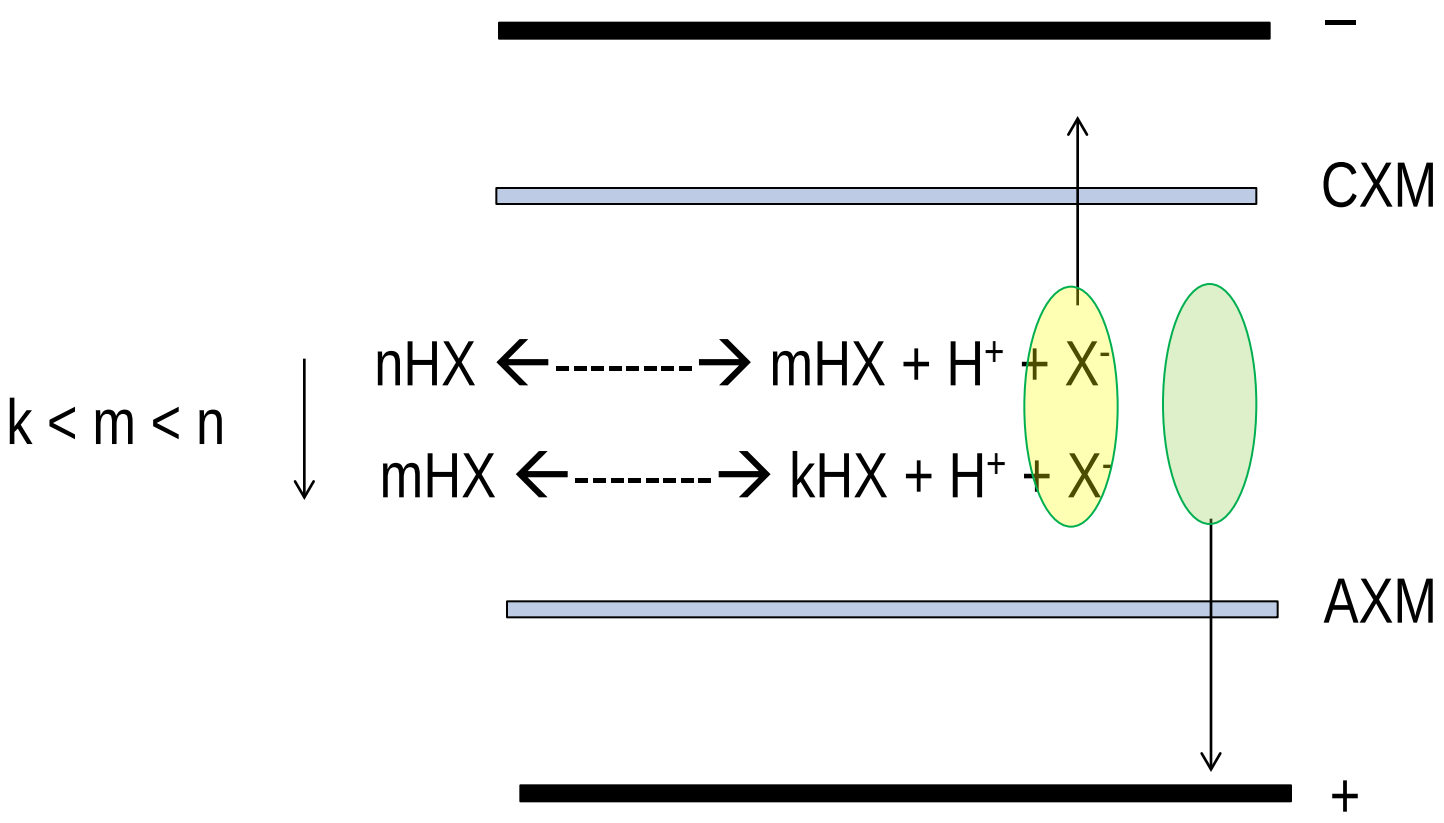
QD Detector S/N Ratio (2V)

CD				
Injection#	CD Signal (1:750 , n=7)	CD Nosie (form Report n=7)	Noise= / 1000 (µ)	S/N
1	0.0054	0.52	0.00052	
2	0.0055	0.44	0.00044	
3	0.0055	0.55	0.00055	
4	0.0056	0.52	0.00052	
5	0.0054	0.45	0.00045	
6	0.0054	0.51	0.00051	
7	0.0057	0.51	0.00051	
Mean	**0.0055**	**0.50**	**0.00050**	**11.00**
QD				
Injection#	QD Signal (1:750 , n=7)	QD Nosie (form Report n=7)	Noise= / 1000 (µ)	S/N
1	0.0007	0.08	0.00008	
2	0.0006	0.07	0.00007	
3	0.0007	0.08	0.00008	
4	0.0007	0.07	0.00007	
5	0.0007	0.07	0.00007	
6	0.0006	0.08	0.00008	
7	0.0006	0.08	0.00008	
Mean	**0.0007**	**0.08**	**0.00008**	**8.68**

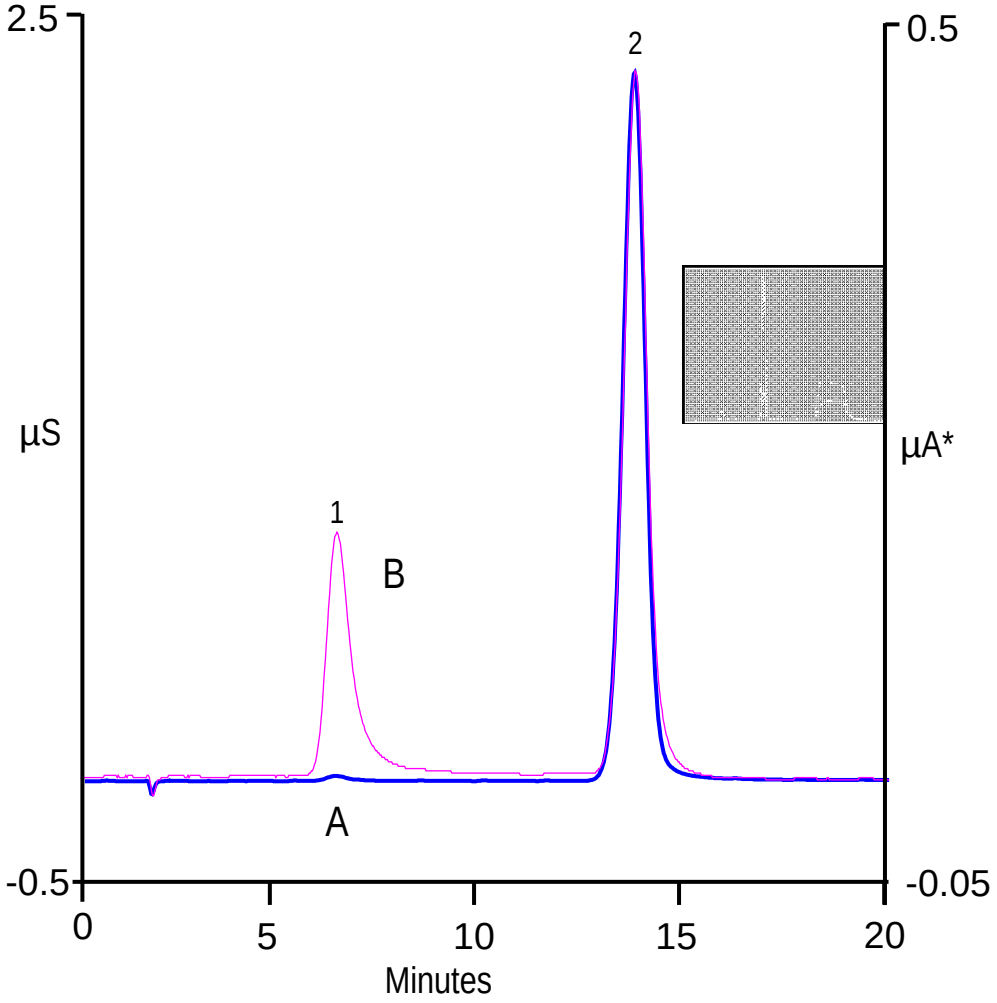
Factor (CD/QD) **1.27**

Weak Acid Detection Using the Charge Detector



AXM – Anion-exchange membrane
CXM – Cation-exchange membrane

QD Detection of Borate



Columns:	Dionex IonPac AG15, Dionex IonPac AS15, 0.4 × 250 mm
Eluent Source:	Dionex EGC-KOH (Capillary)
Gradient:	10 mM KOH
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	A: Suppressed conductivity, Dionex ACES 300, recycle B: QD Charge Detection, *normalized peak response and retention time to chloride peak

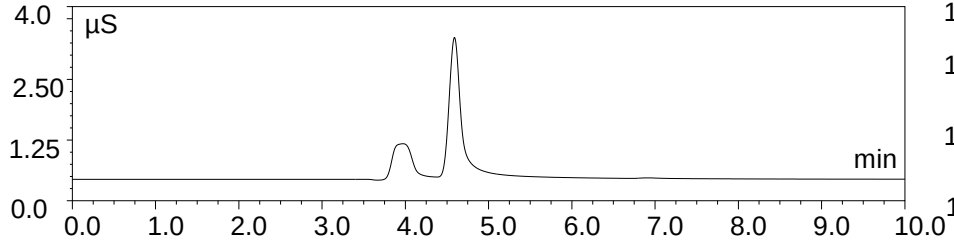
Peaks:	1. Borate	1.0 mM
	2. Chloride	0.1

Borate can be detected with QD – important for HPW analysis

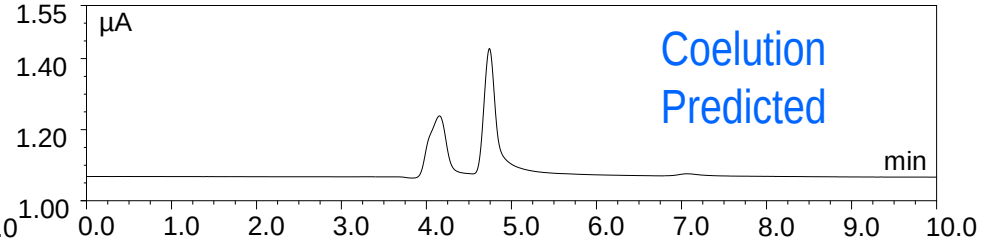
Confirmation with Two Detectors in Series

- Compare the predicted concentrations for unknowns from the calibration of standards from each of the two detectors
- If predicted amounts are in agreement in the two detectors then identity is confirmed
- Acceptance criteria can be set to allow for some variance
- The approach works well for pure, well-resolved components
- For coeluting species, when one of the component is a significantly smaller contributor to the response, then prediction may favor the larger response contributor
- In conjunction with retention time based identification, the method can be valuable

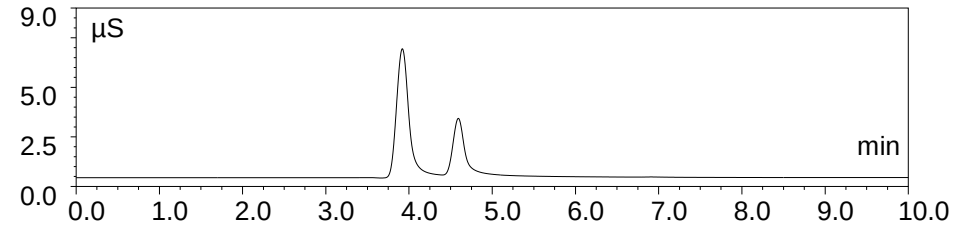
Confirmation with Two Detectors in Series



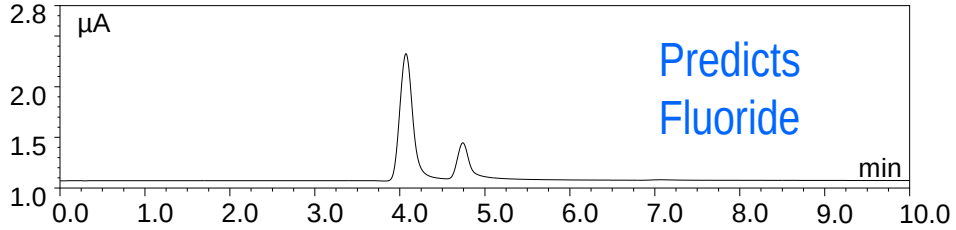
CD Traces, F (0.1 ppm)+Ac (1 ppm)+Cl (1 ppm)



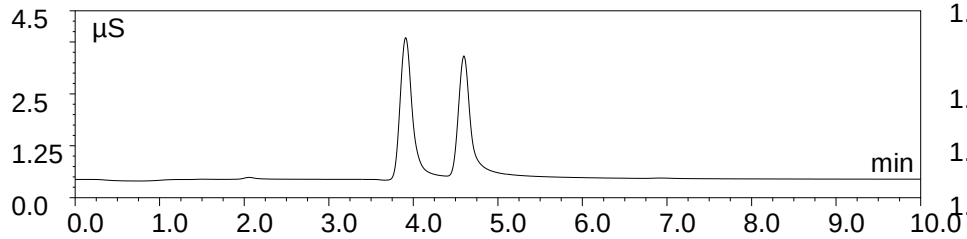
QD Traces, F (0.1 ppm)+Ac (1 ppm)+Cl (1 ppm)



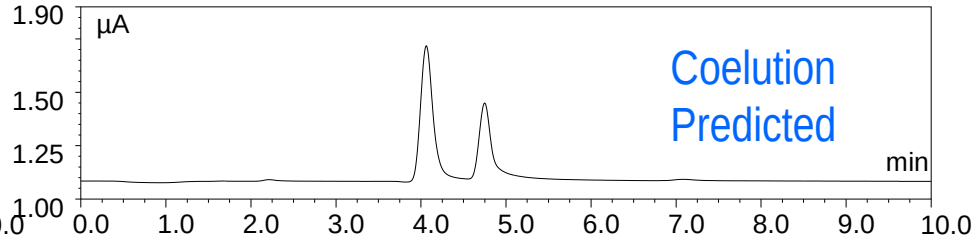
CD Traces, F (1 ppm)+Ac (0.1 ppm)+Cl (1 ppm)



QD Traces, F (1 ppm)+Ac (0.1 ppm)+Cl (1 ppm)



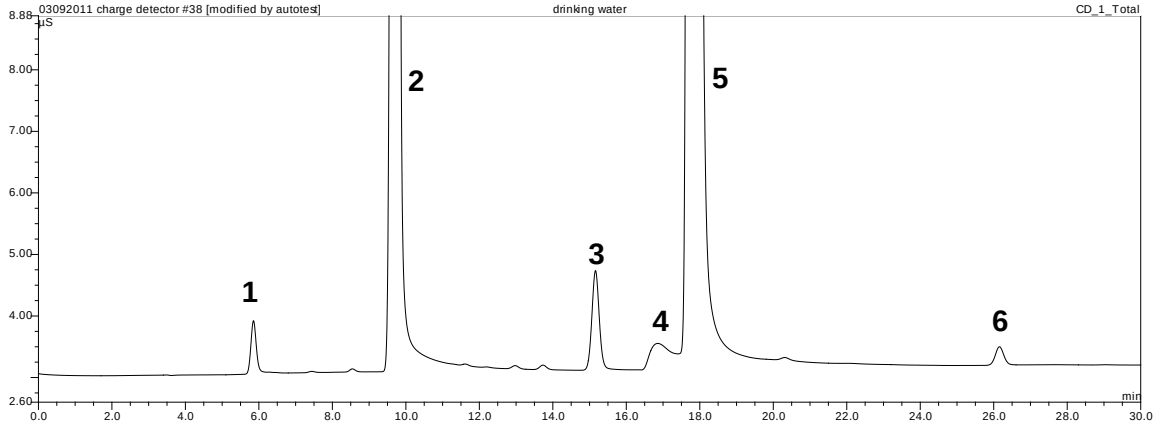
CD Traces, F (0.5 ppm)+Ac (0.5 ppm)+Cl (1 ppm)

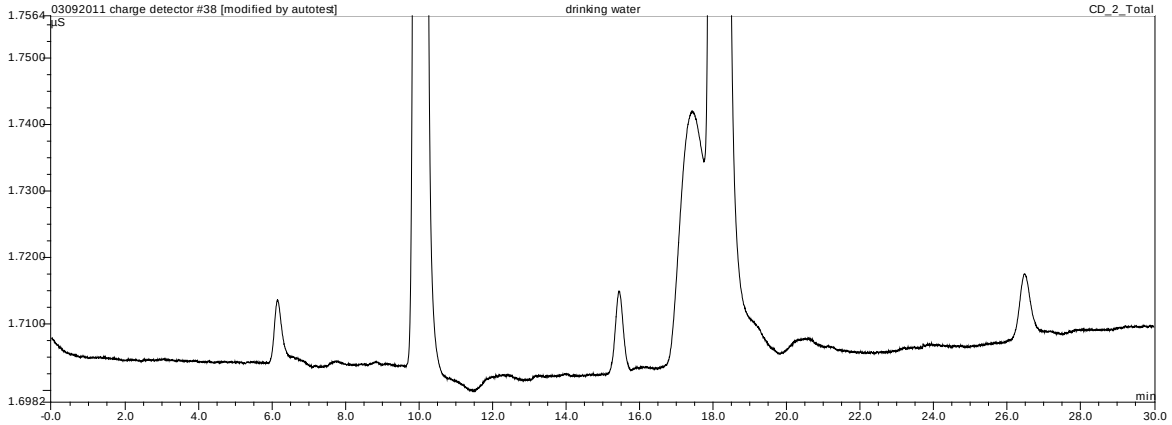


QD Traces, F (0.5 ppm)+Ac (0.5 ppm)+Cl (1 ppm)

QD APPLICATIONS

Drinking water analysis (Conductivity vs. Charge Detector)

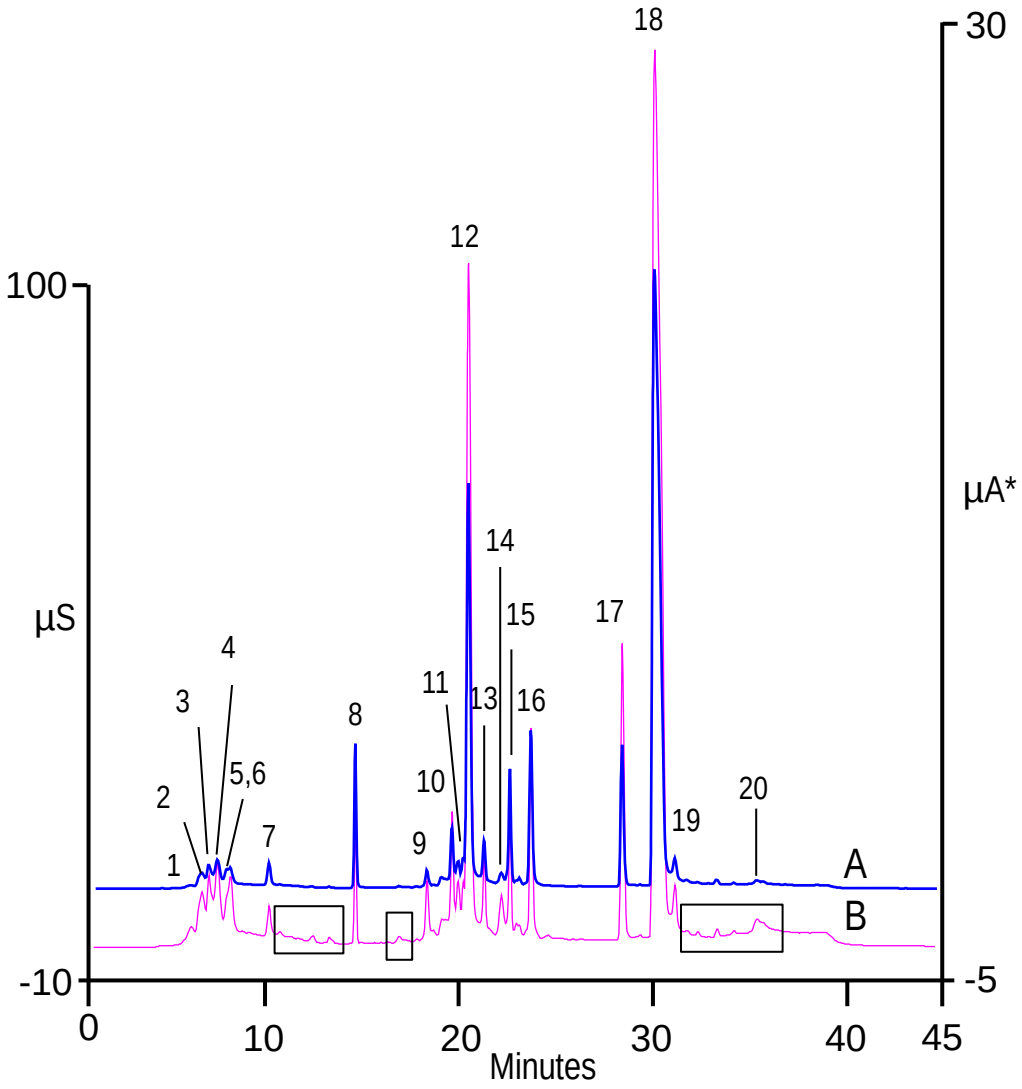




1. Fluoride
2. Chloride
3. Nitrate
4. Carbonate
5. Sulfate
6. Phosphate

Carbonate more sensitive with QD – CRD to remove carbonate peak

Orange Juice – CD/QD Detection



Column:	Dionex IonPac AS11-HC-4µm set, 0.4 mm
Eluent Source:	Dionex EGC-KOH (Capillary)
Gradient:	1 mM KOH (5 min), 1–15 mM KOH (5–15 min), 15–30 mM KOH (14–23 min), 30–60 mM KOH (23–31 min), 60 mM KOH (31–45 min)
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	A: Suppressed conductivity, Dionex ACES 300, recycle B: QD Charge Detection, *normalized to chloride peak
Sample Prep.:	Diluted 10-fold, filtered, 0.2 µm

Peaks:

1. Quinate	8. Chloride	15. Sulfate
2. Glycolate	9. Nitrate	16. Oxalate
3. Lactate	10. Glutarate	17. Phosphate
4. Acetate	11. Unknown	18. Citrate
5. Formate	12. Malate	19. Isocitrate
6. Pyruvate	13. Maleate	20. Unknown
7. Galacturonate	14. Unknown	

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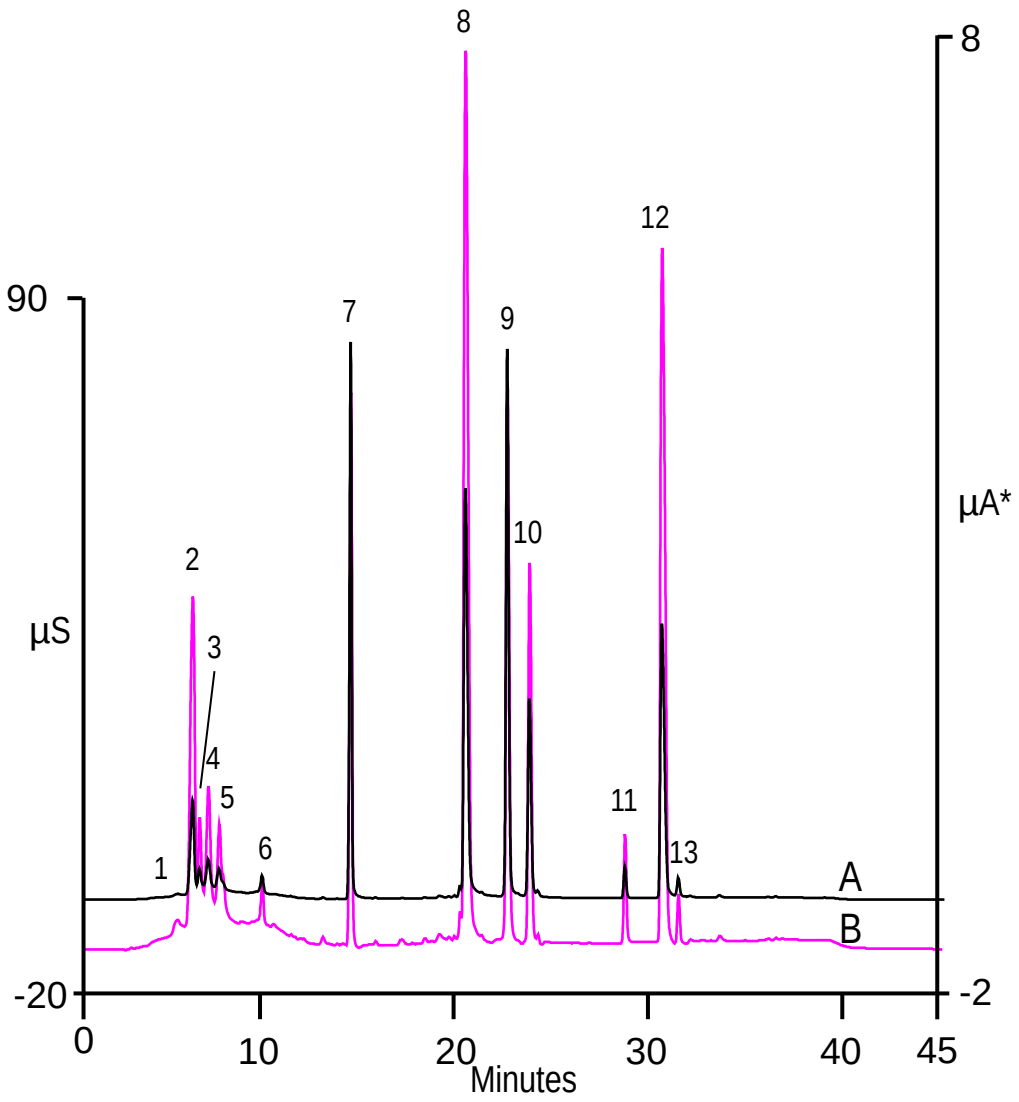
Guava Juice – CD/QD Detection

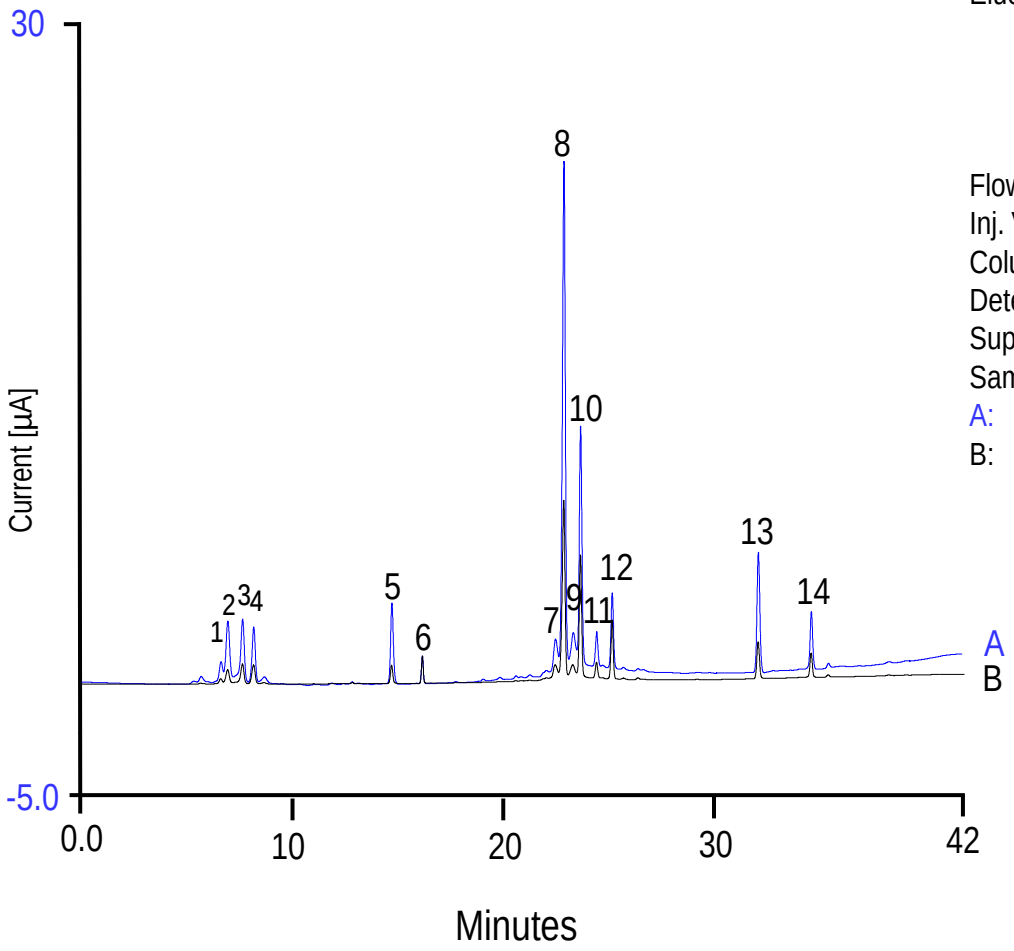


Columns:	Dionex IonPac AS11-HC-4µm set, 0.4 mm
Eluent Source:	Dionex EGC-KOH (Capillary)
Gradient:	1 mM KOH (5 min), 1–15 mM KOH (5–15 min), 15–30 mM KOH (14–23 min), 30–60 mM KOH (23–31 min), 60 mM KOH (31–45 min)
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	A: Suppressed conductivity, Dionex ACES 300, recycle B: QD Charge Detection, *normalized to chloride peak
Sample Prep.:	Diluted 5-fold, filtered, 0.2 µm

Peaks:

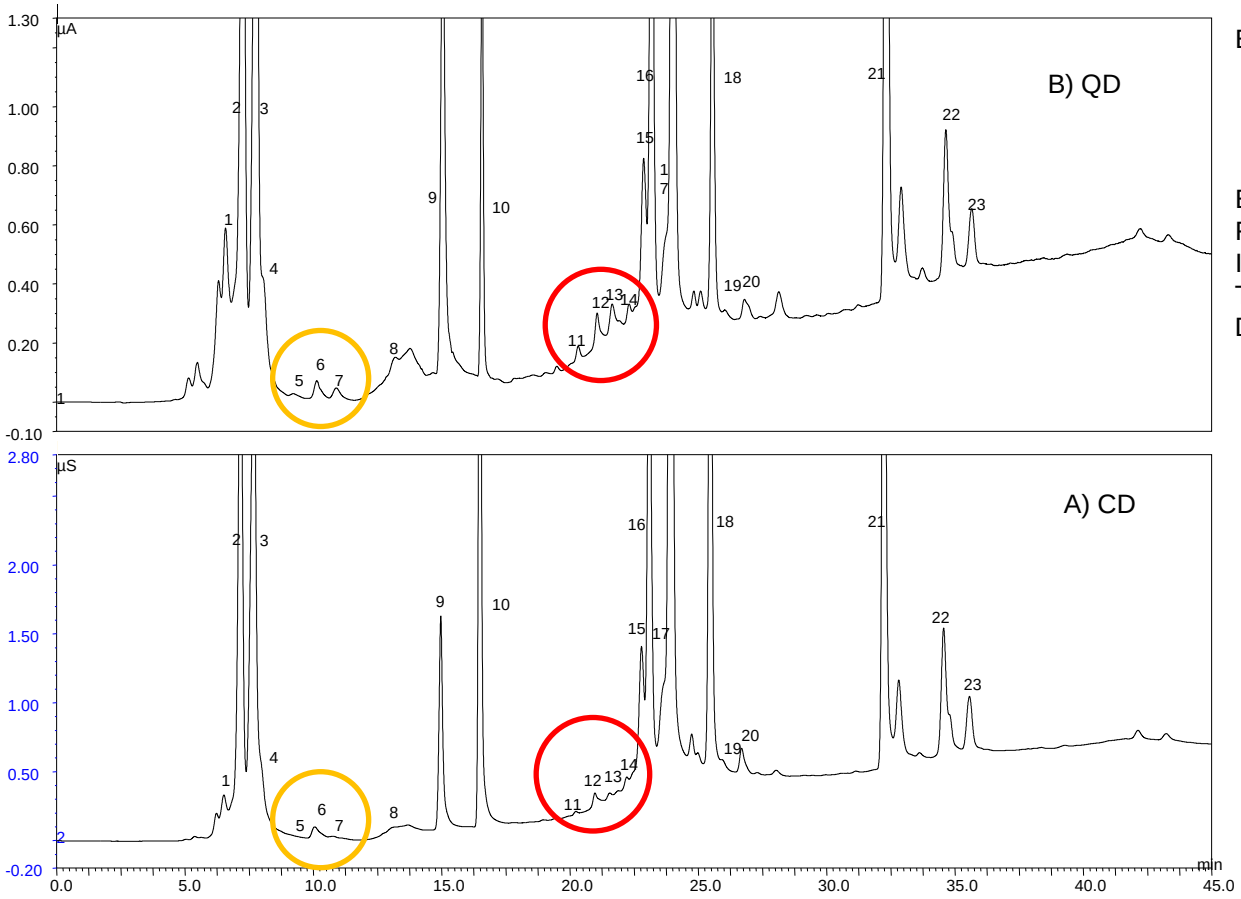
1. Quinate
2. Lactate
3. Acetate
4. Glycolate
5. Propionate
6. Formate
7. Chloride
8. Malate-Succinate
9. Sulfate
10. Oxalate
11. Phosphate
12. Citrate
13. Isocitrate

White Wine - Charge and Conductivity Detection



Column:	Dionex IonPac AS11-HC-4µm Capillary (0.4x250 mm)
Instrument:	Dionex ICS 5000 HPIC system
Eluent Source:	Dionex EGC-EG
Eluent:	30mM Potassium Hydroxide, 1 mM from 0 to 8min, 1mM to 30mM from 8 to 28 min, 30mM to 60 mM from 28 to 38 min, 60 mM from 38 to 42 min
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity
Suppressor:	Dionex ACES 300, AutoSuppression Recycle Mode
Samples:	1:200 Dilution with DI Water
A:	Charge Detection
B:	Conductivity Detection

Comparison of QD vs. CD for Analysis of Red Wine Sample

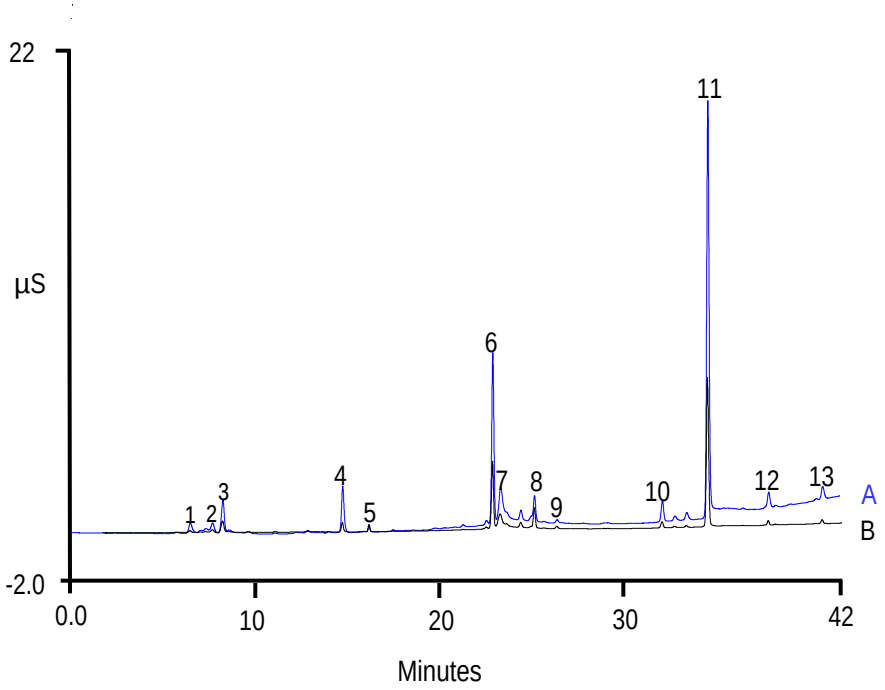


Column:	Dionex IonPac AG11-HC-4µm, AS11-HC-4µm , 0.4 mm
Eluent:	1 mM KOH for 8min, 1–15 mM KOH from 8 to 18 min; 15–30 mM KOH from 18-28 min; 30 to 60 mM KOH from 28 to 38 min
Eluent Source:	Dionex EGC-KOH
Flow Rate:	0.015mL/min
Inj. Volume:	0.4µL
Temperature:	30˚C
Detection:	A) Suppressed conductivity, Dionex ACES 300, AutoSuppression , recycle mode B) Charge Detection

Peaks:

1. Quinate
2. Fluoride
3. Lactate
4. Acetate
5. Propionate
6. Formate
7. Butyrate
8. Pyruvate
9. Galacturonate
10. Chloride
11. Tartrate
12. Bromide
13. Nitrate
14. Glutarate
15. Succinate
16. Malate
17. Carbonate
18. Sulfate
19. Fumrate
20. Oxalate
21. Phosphate
22. Citrate
23. Isocitrate

Pomegranate Berry Juice - Charge and Conductivity Detection



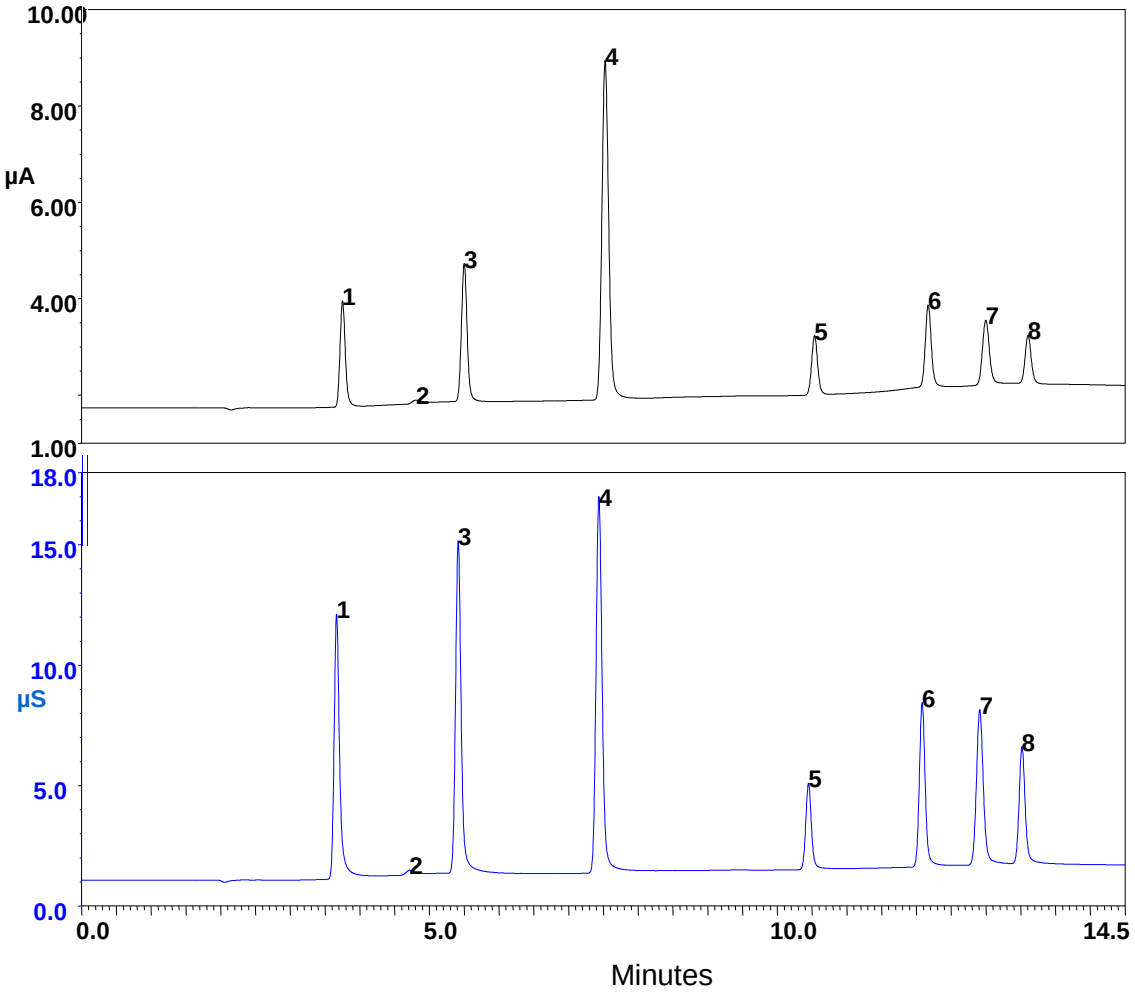
Column:	Dionex IonPac AS11-HC-4µm Capillary (0.4x250 mm)
Instrument:	Dionex ICS 5000 HPIC system
Eluent Source:	Dionex EGC-EG
Eluent:	30mM Potassium Hydroxide, 1 mM from 0 to 8min, 1mM to 30mM from 8 to 28 min, 30mM to 60 mM from 28 to 38 min, 60 mM from 38 to 42 min
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity
Suppressor:	Dionex ACES 300, AutoSuppression Recycle Mode
Samples:	1:40 Dilution with DI Water
A:	Charge Detection
B:	Conductivity Detection

Peaks:

1. Quinate
2. Lactate
3. Acetate
4. Valerate
5. Chloride
6. Nitrate
7. Carbonate
8. Maleate
9. Oxalate
10. Phosphate
11. Citrate
12. trans-Aconitate
13. Unknown

Adulteration of this expensive juice is of high interest – QD detects organic acids with high sensitivity

Polyphosphates - Charge and Conductivity Detection

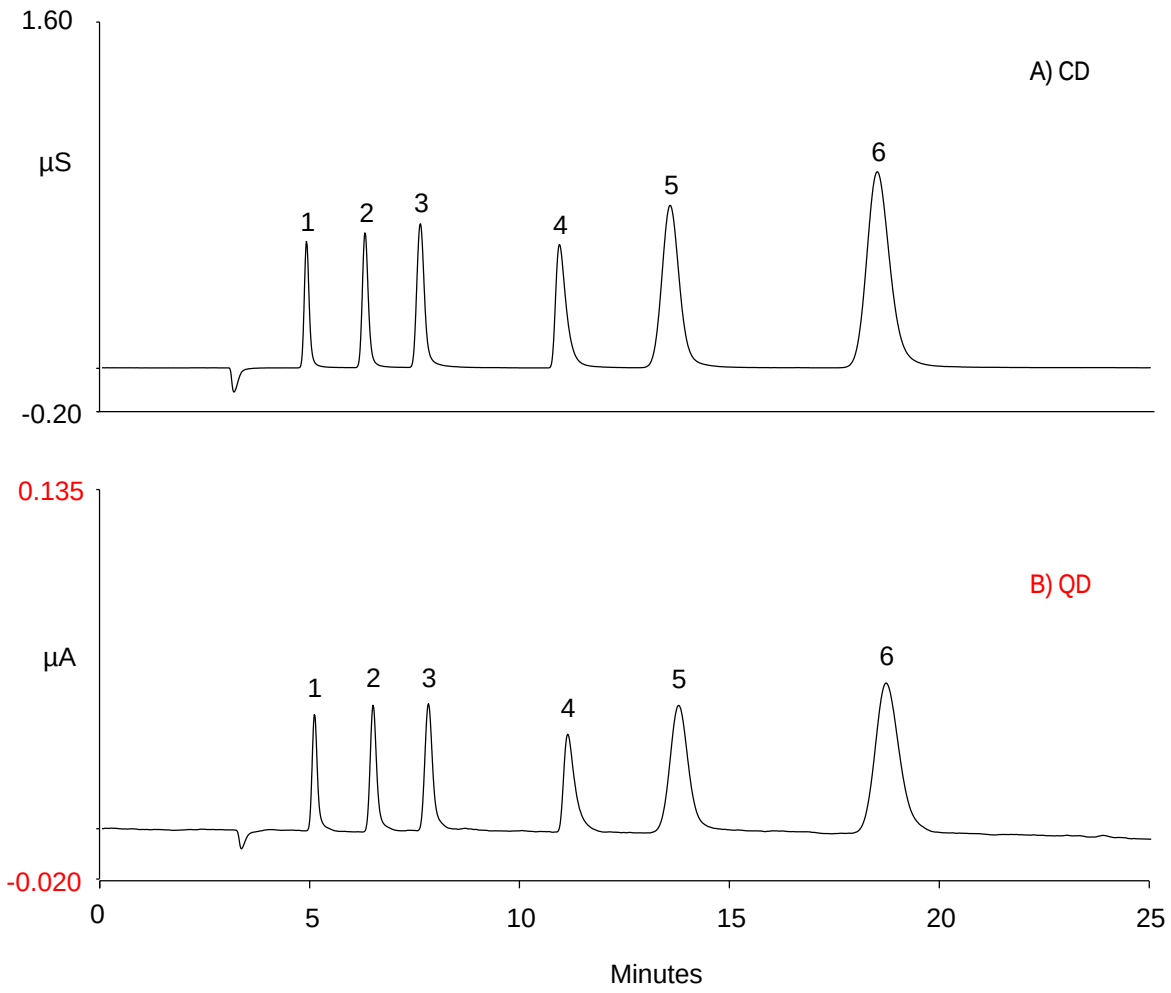


Column:	Dionex IonPac AS11-HC-4µm (250 mm x 0.4 mm)
Temperature:	30 °C
Eluent Source:	Dionex EGC-KOH (Capillary)
Eluent:	20 – 80 mmol/L in 10 min
Flow:	0.015 mL/min
Inj.-Volume:	0.4 µL
Detection:	Suppressed Conductivity Dionex ACES 300
A:	Charge Detection
B:	Conductivity Detection

Peaks:

1. Chloride
2. Carbonate
3. Sulfate
4. Orthophosphate
5. Pyrophosphate
6. Trimetaphosphate
7. Tripolyphosphate
8. Tetrapolyphosphate

Comparison of QD vs. CD for Cation Chemistry on Dionex ICS-4000 System Using Dionex IonPac CS16 0.4 mm Column



Column:	Dionex IonPac CS16, 0.4 mm
Eluent:	30 mM MSA
Eluent Source:	Dionex EGC-MSA(Capillary)
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Temperature:	30 ˚C
Detection:	A) Suppressed conductivity, Thermo Scientific™ Dionex™ CCES™ 300 Cation Capillary Electrolytic Suppressor, AutoSuppression, recycle mode
	B) Charge Detection

Peaks:

1. Lithium
2. Sodium
3. Ammonium
4. Potassium
5. Magnesium
6. Calcium

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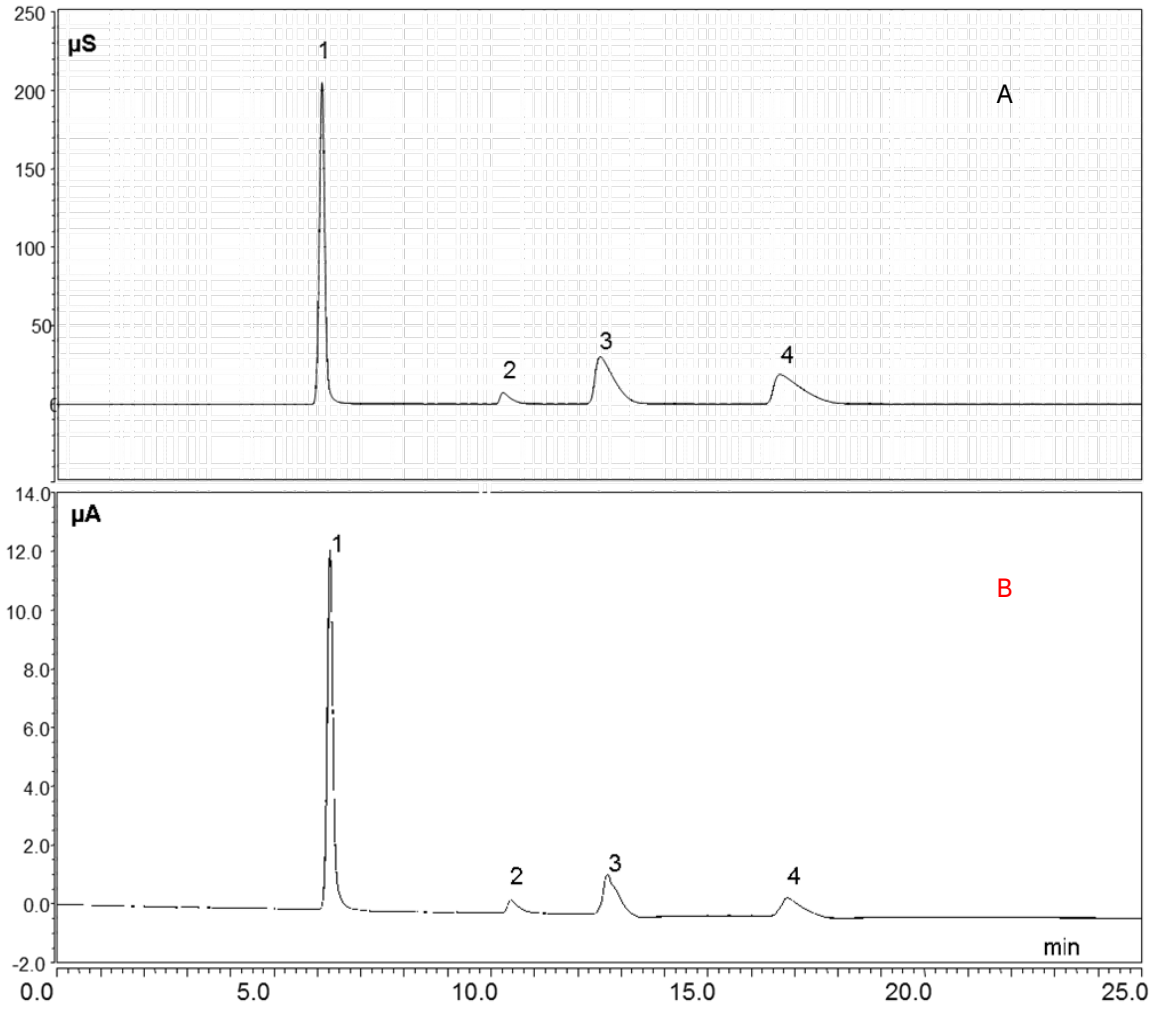
Comparison of CD vs. QD for Wastewater sample



Column:	Dionex IonPac CS16, 0.4 mm
Eluent:	30 mM MSA
Eluent Source:	Dionex EGC-MSA(Capillary)
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Temperature:	40 ˚C
Detection:	A) Suppressed conductivity, Dionex CCES 300, AutoSuppression , recycle mode
	B) Charge Detection

Peaks:

1. Sodium
2. Potassium
3. Magnesium
4. Calcium

Market Application Values

- Environmental
  - Ease of use for operators with linear calibration plots for weakly dissociated analytes
  - Peak purity information, resulting in high confidence in results
  - Quantification of unknowns in waste water and soil extracts
  - Low cost compared to MS
  - Orthogonal detection which can avoid secondary confirmatory analysis

- Chemicals
  - Linear calibration plots for amines
  - Quantification of unknown peaks in chemical products
  - Identification of impurities in competitors products
  - Detection of all ionic analytes

Market Application Values

- Food and Beverage
  - Determination of organic acids and biogenic amines with linear calibration plots
  - Low investment cost
  - Easy to learn and operate

- Pharma/Bio Research
  - Detection of all ionic compounds
  - Peak purity analysis
  - Easy to learn and use
  - Orthogonal detection in addition to suppressed CD

Feature, Benefit, Values of QD

Feature	Benefit	Customer Value
Linear Response for weakly dissociated ions	Faster, easier calibration, reduced error	Greater precision, confidence and time saving
Stronger relative response for very weakly dissociated and multi-valent ions	Higher sensitivity, better reproducibility	Greater precision, confidence and time saving
Detects all ionizable species	More universal detection	Economically providing more information
Peak purity information	Identify co-elution issues	Greater confidence
Small, does not affect footprint	Easy to get into the lab	Conserves bench space, saves money
Low investment cost	Easier to get purchase approved	Affordable, ROI
Long consumables lifetime, low maintenance cost	High up time	Low Cost of Ownership
Easy to use	Easy to learn	Less training, saving time, lower labor cost
Orthogonal Detector CD/QD filling a gap between CD and MS	No confirmatory analysis required	Additional information at low cost

Charge Detector – Summary

- Benefits and Values:
  - New methodology based on charge/current detection
  - Unified response for strongly and weakly dissociated ions
  - Quantification of unknown ions
  - Peak purity
  - Identification of unknowns
- Charge Detector integrated in Thermo Scientific Dionex ICS-4000 System

Thank you!

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