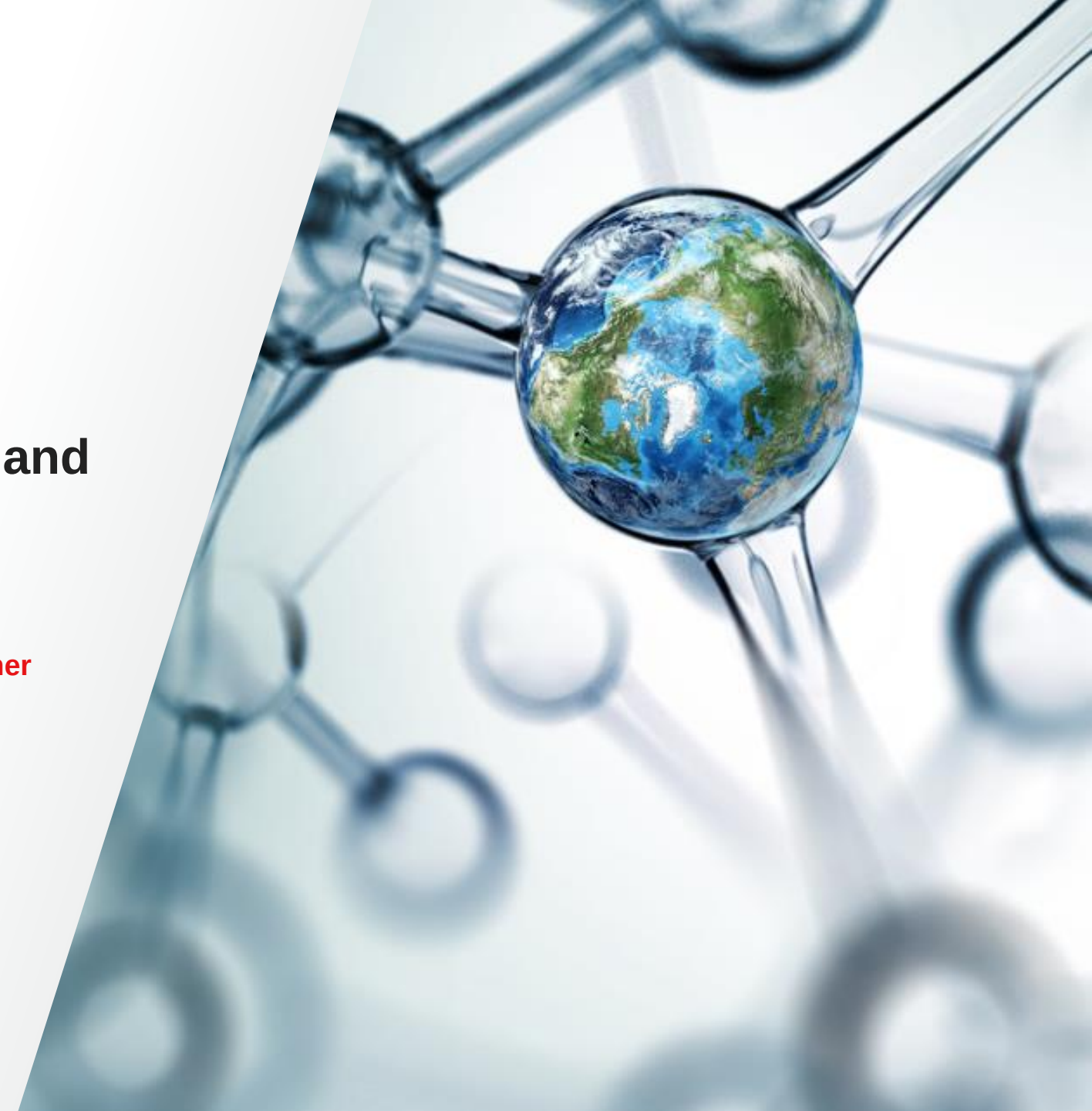
Applying new ion chromatography technology to enable faster determinations of inorganic anions and disinfection byproducts in drinking water

Jingli Hu, Hua Yang, Jeff Rohrer, Chris Shevlin, and **Carl Fisher**

August 4, 2023



The world leader in serving science

Agenda

1. Drinking water analysis
2. Inorganic anion determinations
3. Shortening runtime
4. IC innovations
5. Resources

Drinking water analysis

- National Primary Drinking Water Regulations (NPDWR)
  - Microorganisms
  - Disinfectants
  - Disinfection byproducts
  - Inorganic chemicals
    - US EPA 300
  - Organic chemicals
  - Radionuclides

Drinking water analysis

- National Primary Drinking Water Regulations (NPDWR)
  - Microorganisms
  - Disinfectants
  - Disinfection byproducts
  - Inorganic chemicals
    - US EPA 300
  - Organic chemicals
  - Radionuclides

EPA Method 300.0 and 300.1

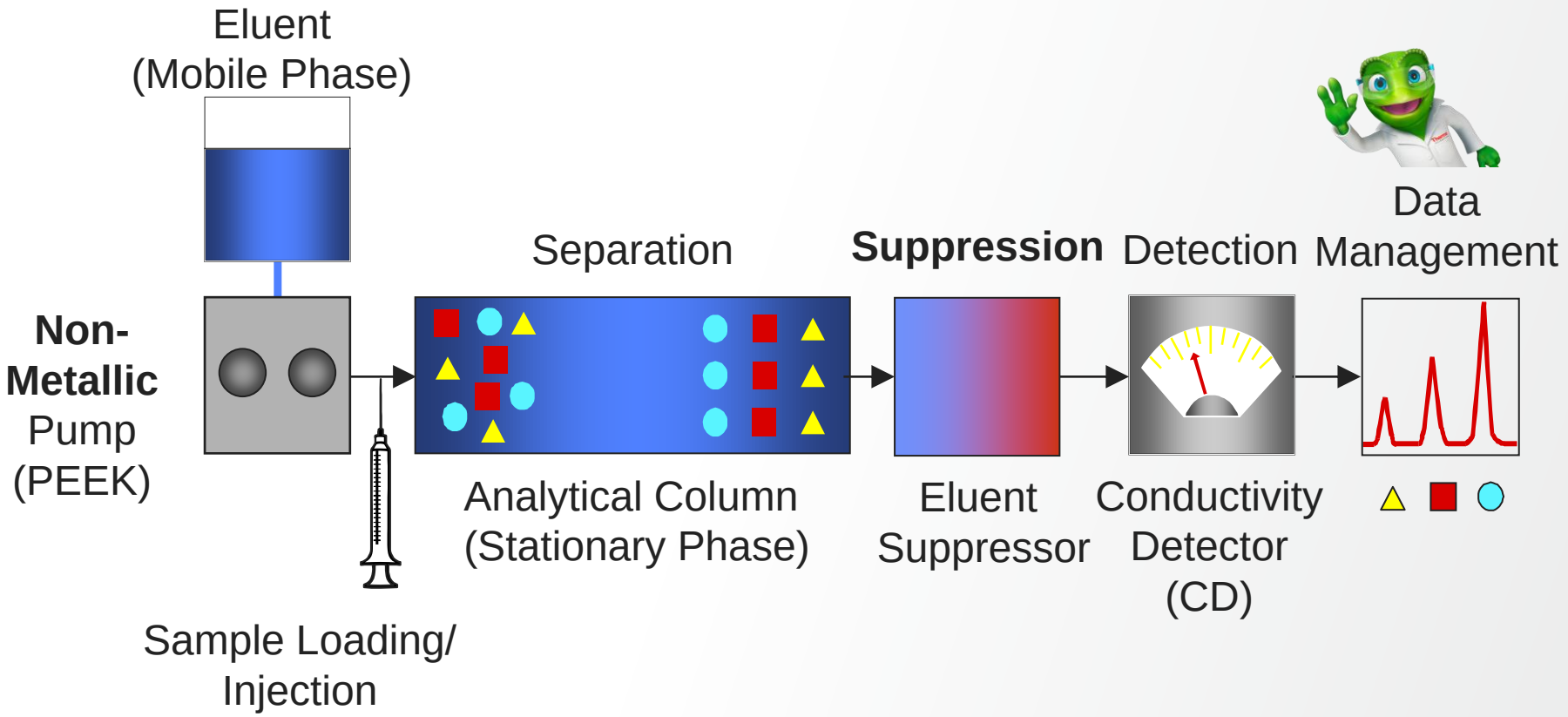
Outlines the method for determination of inorganic anions by ion chromatography (IC).

- Specifies use of suppressed conductivity for determination of:

Part A- Common Anions	Part B- Inorganic Disinfection Byproducts
Bromide	Bromide
Chloride	Bromate
Fluoride	Chlorite
Nitrate	Chlorate
Nitrite	
ortho-Phosphate-P	
Sulfate	

- Applies to:
  - Drinking water
  - Ground and Surface water
  - Wastewater (domestic and industrial)
  - Raw water (unfinished drinking water)

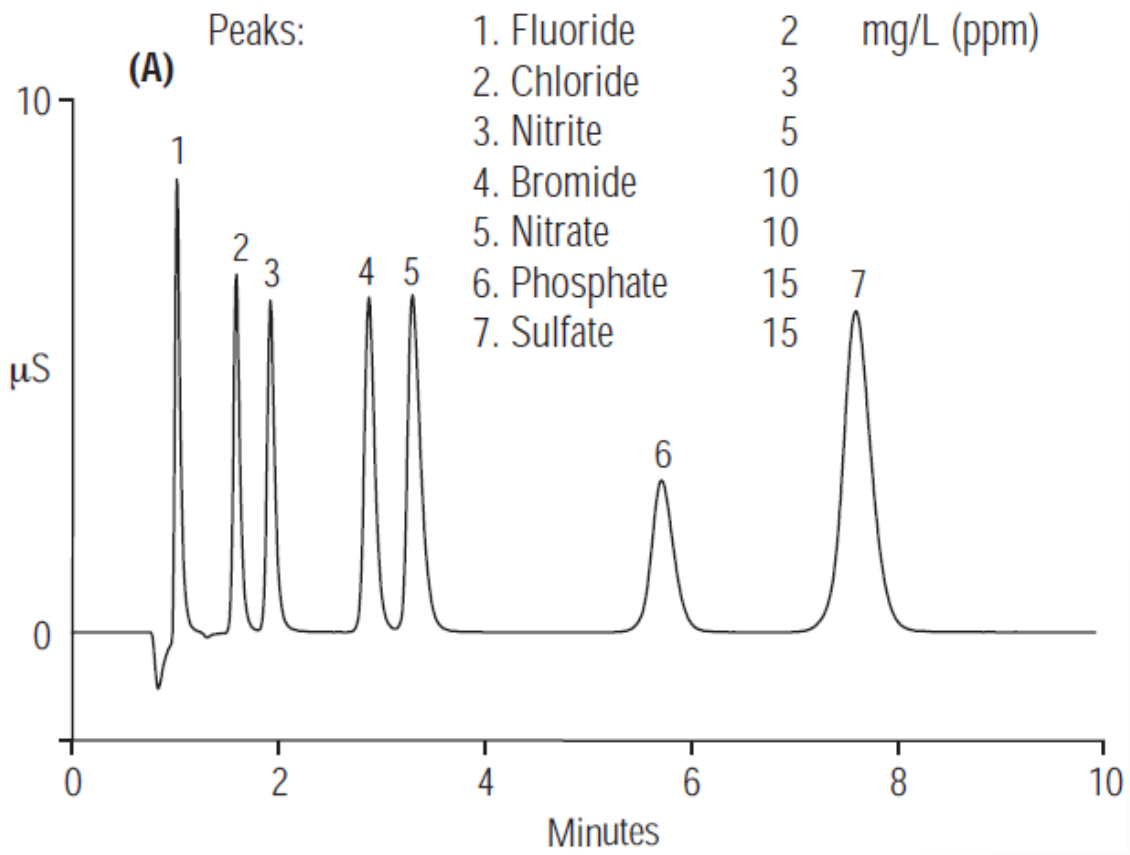
IC system


Eluent
(Mobile Phase)
Non-
Metallic
Pump
(PEEK)
Separation
Analytical Column
(Stationary Phase)
Suppression
Eluent
Suppressor
Detection
Conductivity
Detector
(CD)
Data
Management
Sample Loading/
Injection

Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS4A column

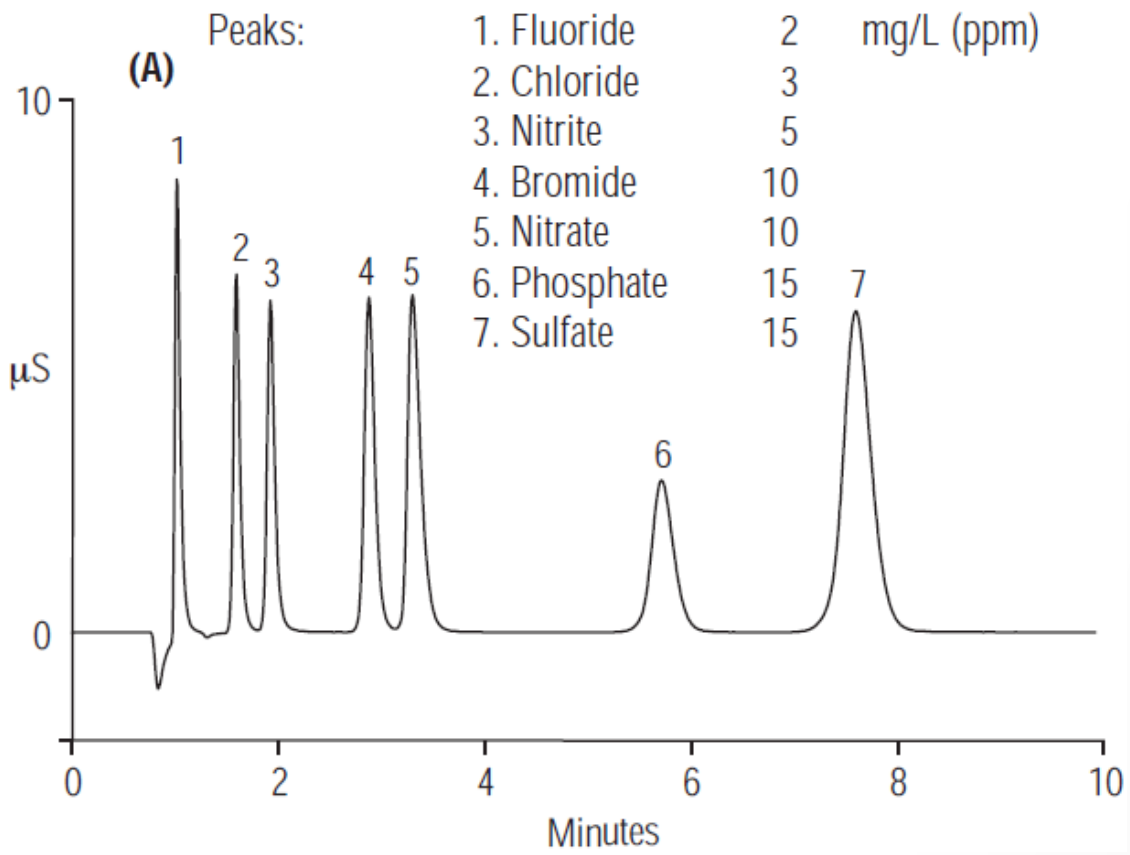
1.7 mM Na_2CO_3 / 1.8 mM $NaHCO_3$



Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS4A column

1.7 mM Na_2CO_3 / 1.8 mM $NaHCO_3$



Carbonate-based eluents

Benefits

- Strong elution potential
- Inexpensive

Limitations

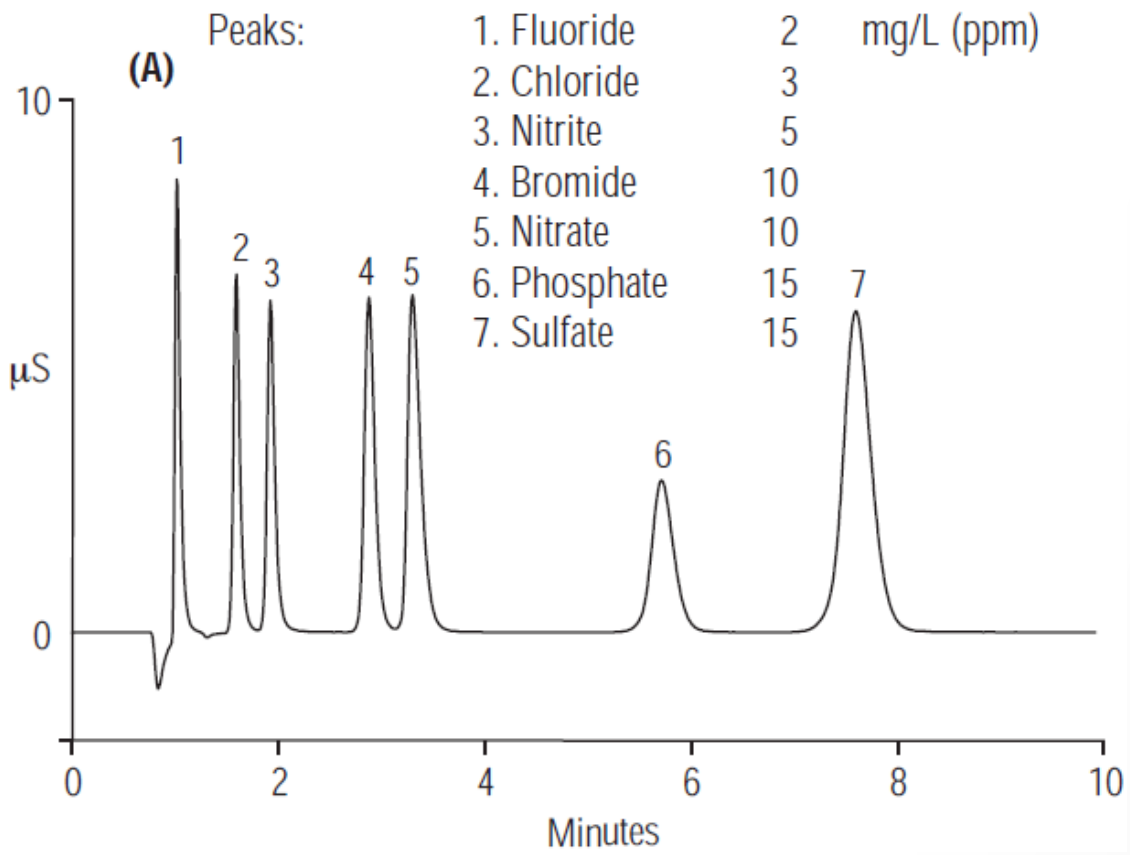
- Conductivity is 10–20x higher than pure water which impacts sensitivity
- Response is nonlinear at lower analyte concentrations
- Gradient separations are difficult
  - Ramping, baseline disturbances, slow buffering

Solution: Hydroxide-based eluent

Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS4A column

1.7 mM Na_2CO_3 / 1.8 mM $NaHCO_3$



Carbonate-based eluents

Benefits

- Strong elution potential
- Inexpensive

Limitations

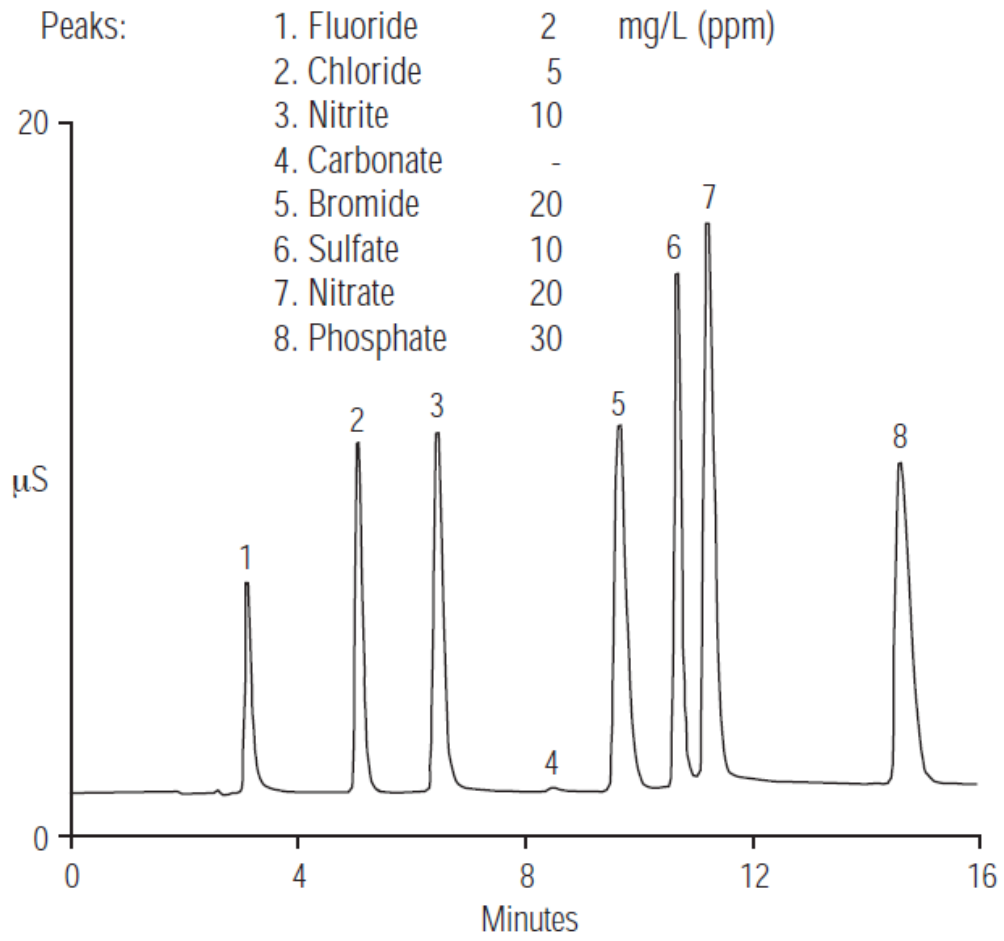
- Conductivity is 10–20x higher than pure water which impacts sensitivity
- Response is nonlinear at lower analyte concentrations
- Gradient separations are difficult
  - Ramping, baseline disturbances, slow buffering

Solution: Hydroxide-based eluent

Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS18 column

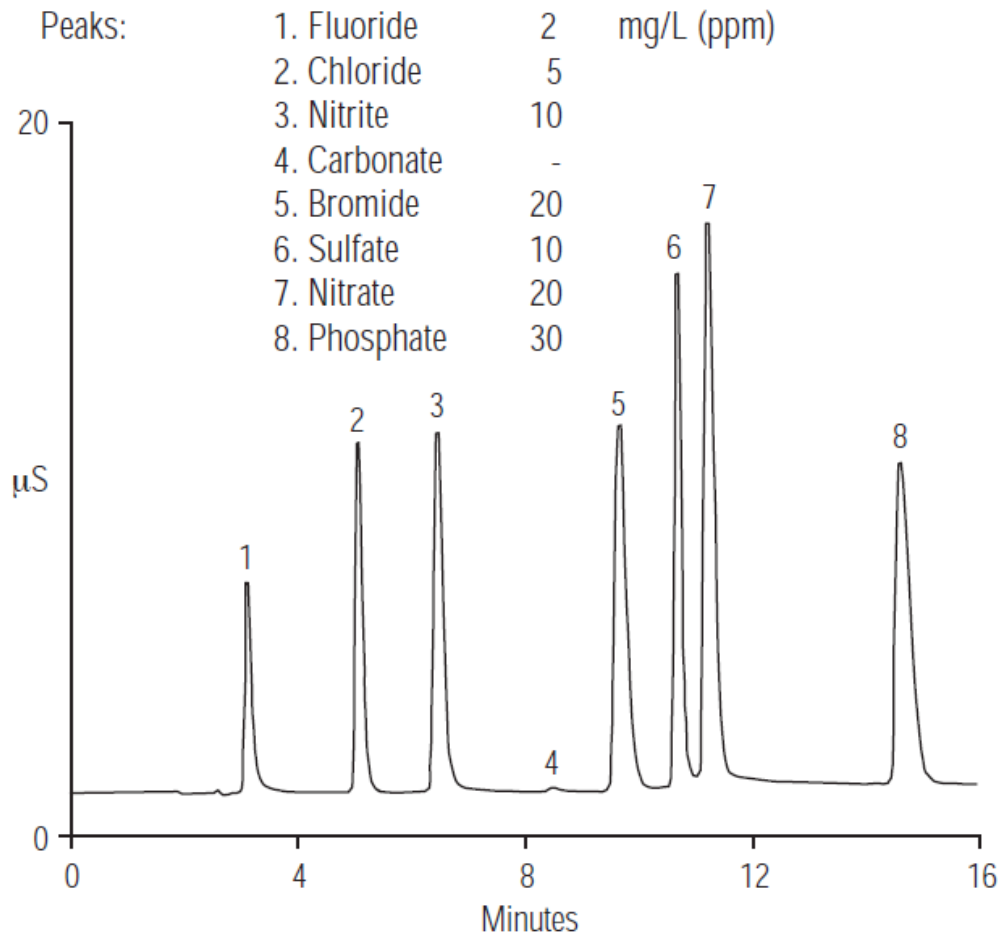
22–40 mM KOH



Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS18 column

22–40 mM KOH



Hydroxide-based eluents

Benefits

- Suppressed to water, yielding low background, greater sensitivity
- Produces linear gradients

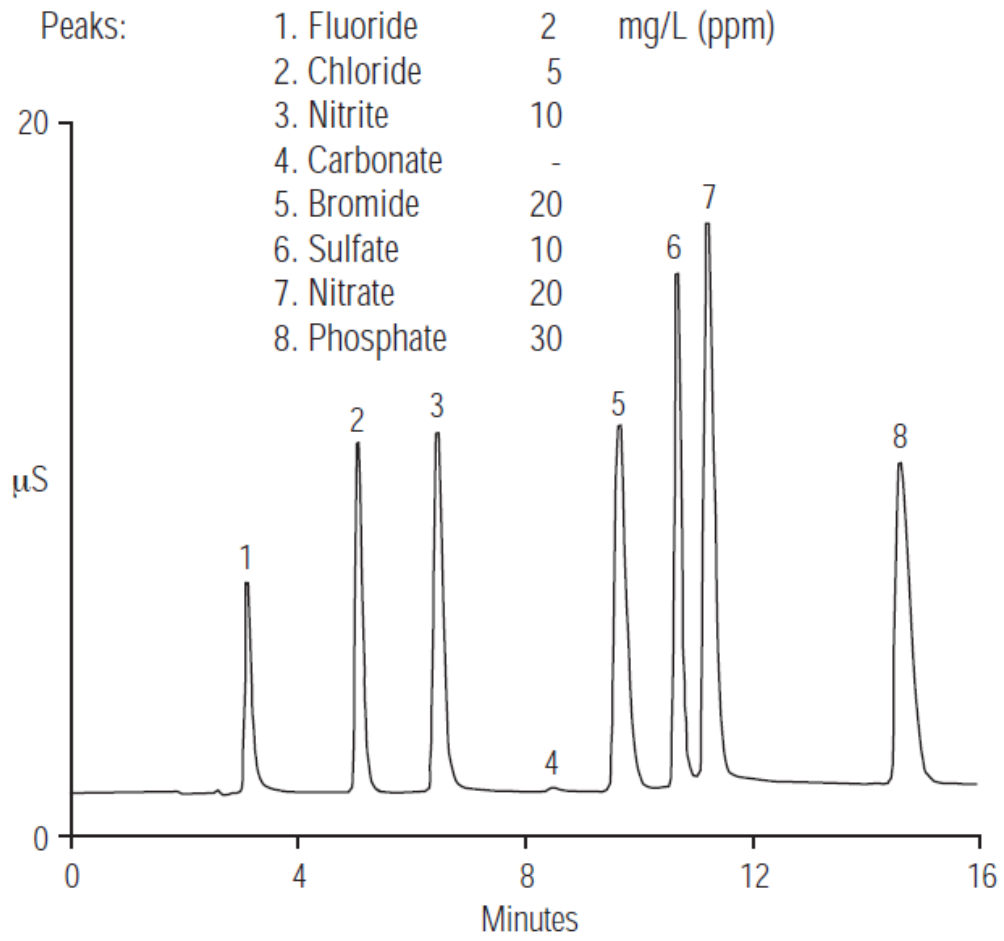
Limitations of manual eluent preparation

- Absorbance of CO_2 from the air causes instability of
  - Retention time, peak area, baseline
- For gradients, a proportioning pump is required

Inorganic ion determination

Thermo Scientific™ Dionex™ IonPac™ AS18 column

22–40 mM KOH



Hydroxide-based eluents

Benefits

- Suppressed to water, yielding low background, greater sensitivity
- Produces linear gradients

Limitations of manual eluent preparation

- Absorbance of CO_2 from the air causes instability of
  - Retention time, peak area, baseline
- For gradients, a proportioning pump is required

Solution: Electrolytic eluent generation (Reagent-free IC (**RFIC**))

- Precise and accurate eluent concentrations
- An isocratic pump can be used for gradients

Automated eluent generation (EG)

ONE current for
ONE concentration
(of eluent)

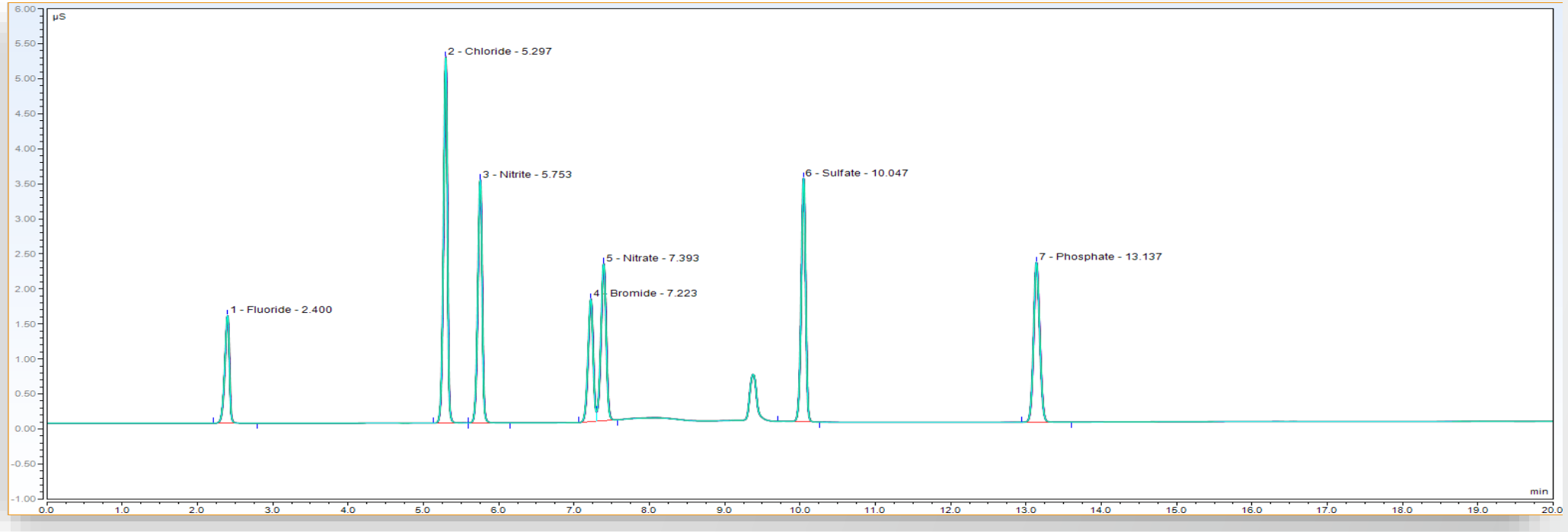
Deionized water used as the carrier
- Eliminates need to handle acids or bases
- Decreases pump maintenance

Electrolysis automatically generates high purity acid, base, or carbonate eluents in-line

Delivers concentrations specified in Chromeleon CDS through control of electrical **current**

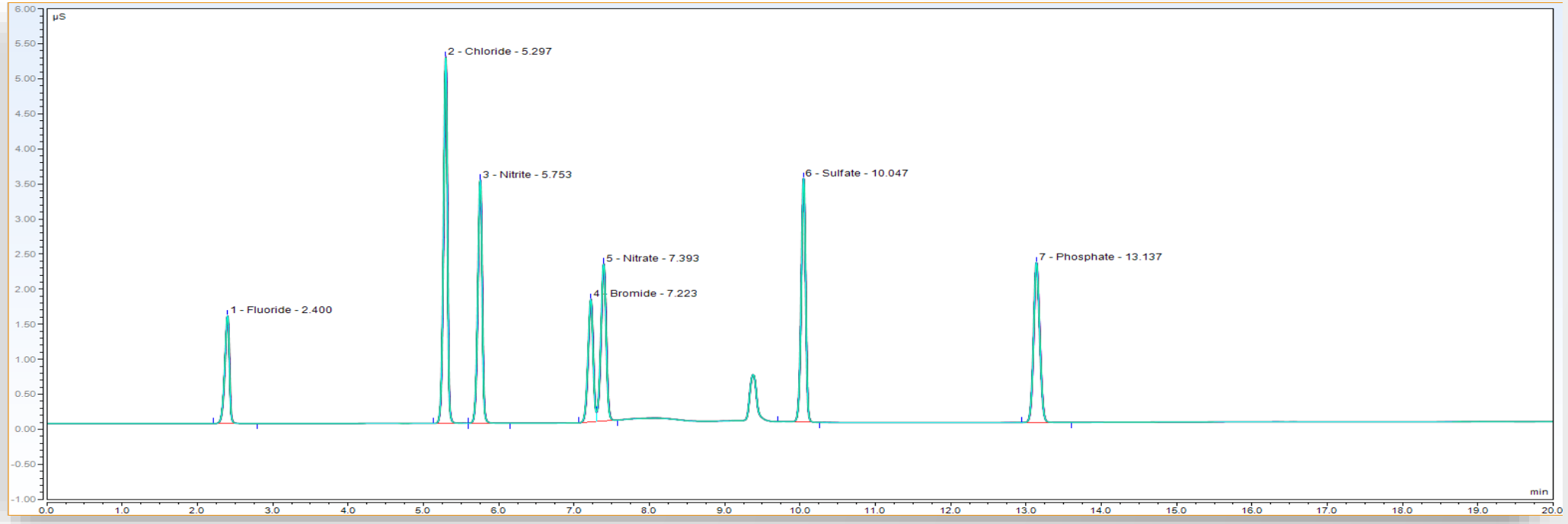
Gradients created without need for a more costly, proportioning pump

Gradient reproducibility: Thermo Scientific Dionex IonPac AS11 4 mm (n=30)



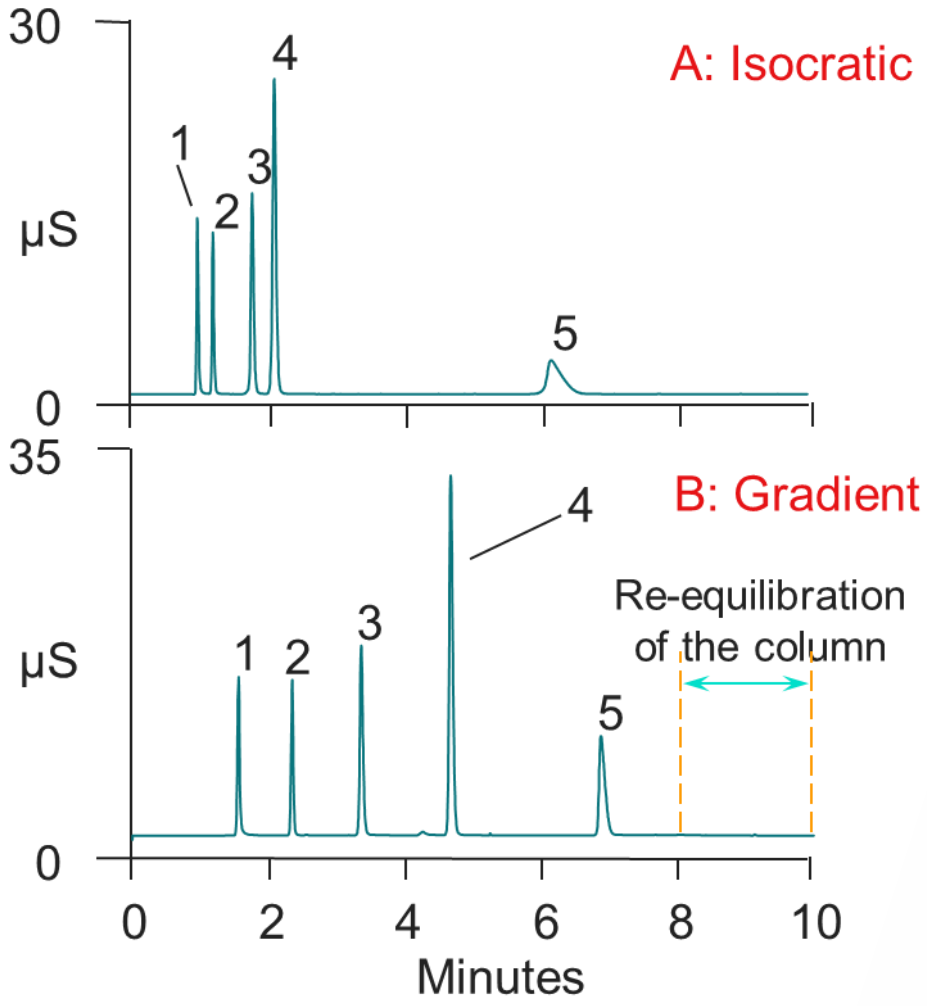
	Fluoride	Chloride	Nitrite	Sulfate	Bromide	Nitrate	Phosphate
Area (µS·min)	0.110	0.324	0.236	0.137	0.242	0.182	0.217
% RSD Area	0.059	0.075	0.075	0.130	0.061	0.101	0.049
Ret. Time (min)	2.400	5.297	5.755	7.223	10.047	7.394	13.139
%RSD Ret.	0.060	0.020	0.029	0.021	0.014	0.023	0.022

Gradient reproducibility: Thermo Scientific Dionex IonPac AS11 4 mm (n=30)



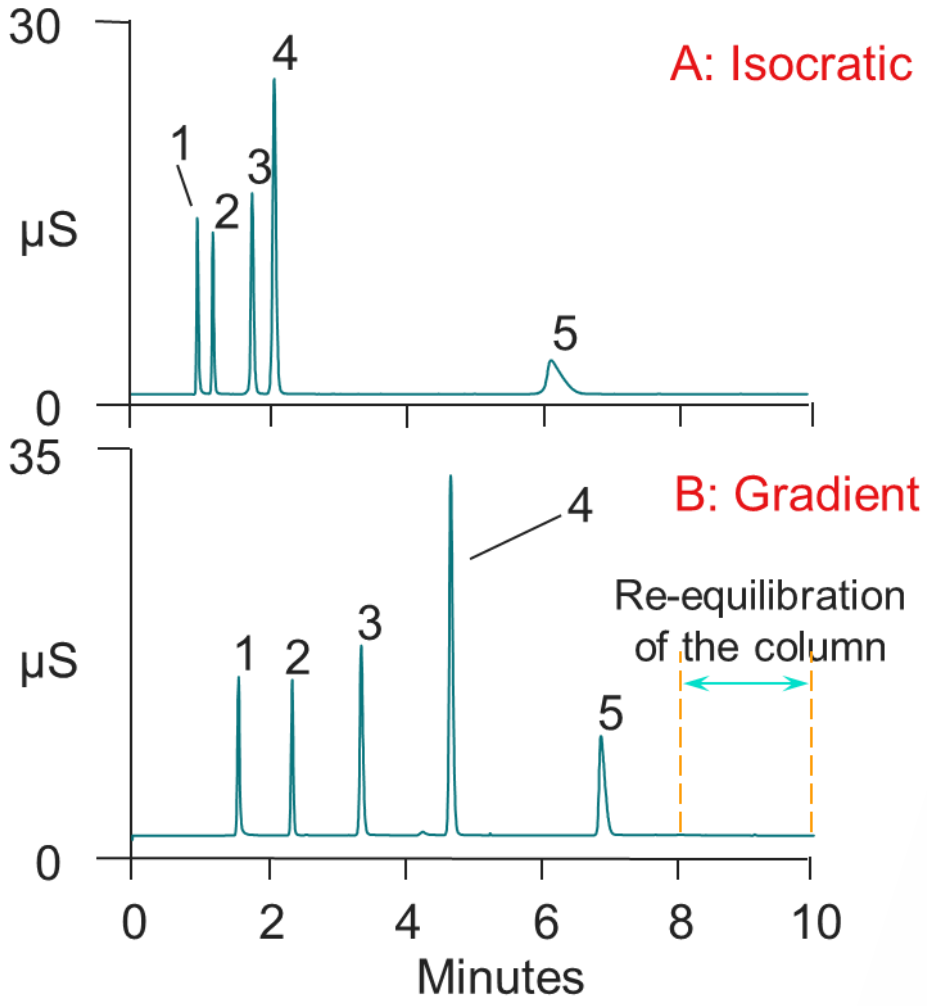
	Fluoride	Chloride	Nitrite	Sulfate	Bromide	Nitrate	Phosphate
Area (µS·min)	0.110	0.324	0.236	0.137	0.242	0.182	0.217
% RSD Area	0.059	0.075	0.075	0.130	0.061	0.101	0.049
Ret. Time (min)	2.400	5.297	5.755	7.223	10.047	7.394	13.139
%RSD Ret.	0.060	0.020	0.029	0.021	0.014	0.023	0.022

Peak focusing using a KOH eluent generator



Separator:	Thermo Scientific™ Dionex™ IonPac™ AG11, AS11, 4-mm		
Eluent:	A: 15.5 mmol/L KOH		
	B: 0.5 to 25 mmol/L KOH in 8 min		
Flow rate:	2 mL/min		
Inj. volume:	25 µL		
Detection:	Suppressed conductivity		
Suppressor:	ASRS, AutoSuppression Recycle Mode		
Peaks:	1. Fluoride	2	[mg/L]
	2. Chloride	3	
	3. Nitrate	10	
	4. Sulfate	15	
	5. Orthophosphate	15	

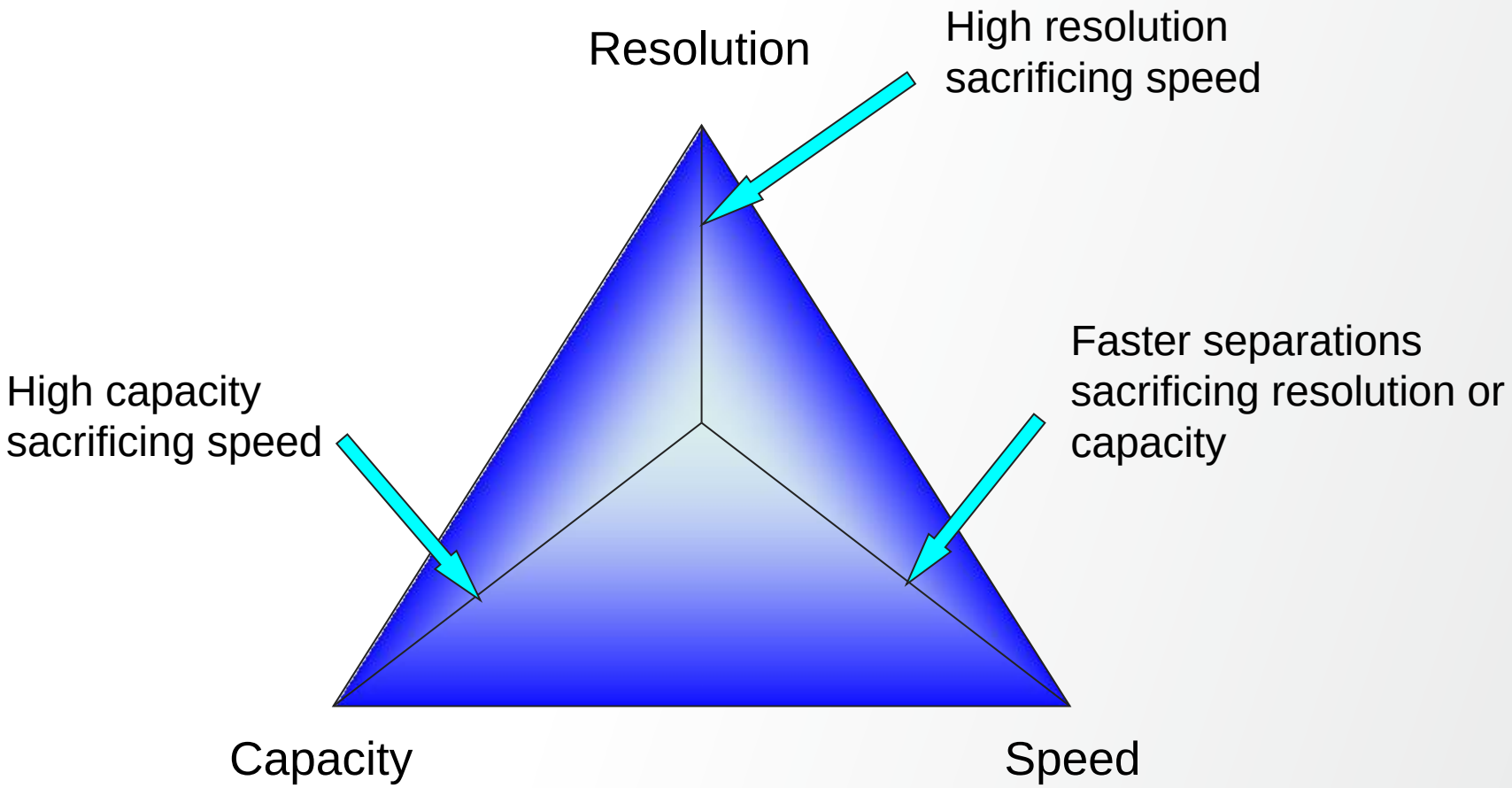
Peak focusing using a KOH eluent generator



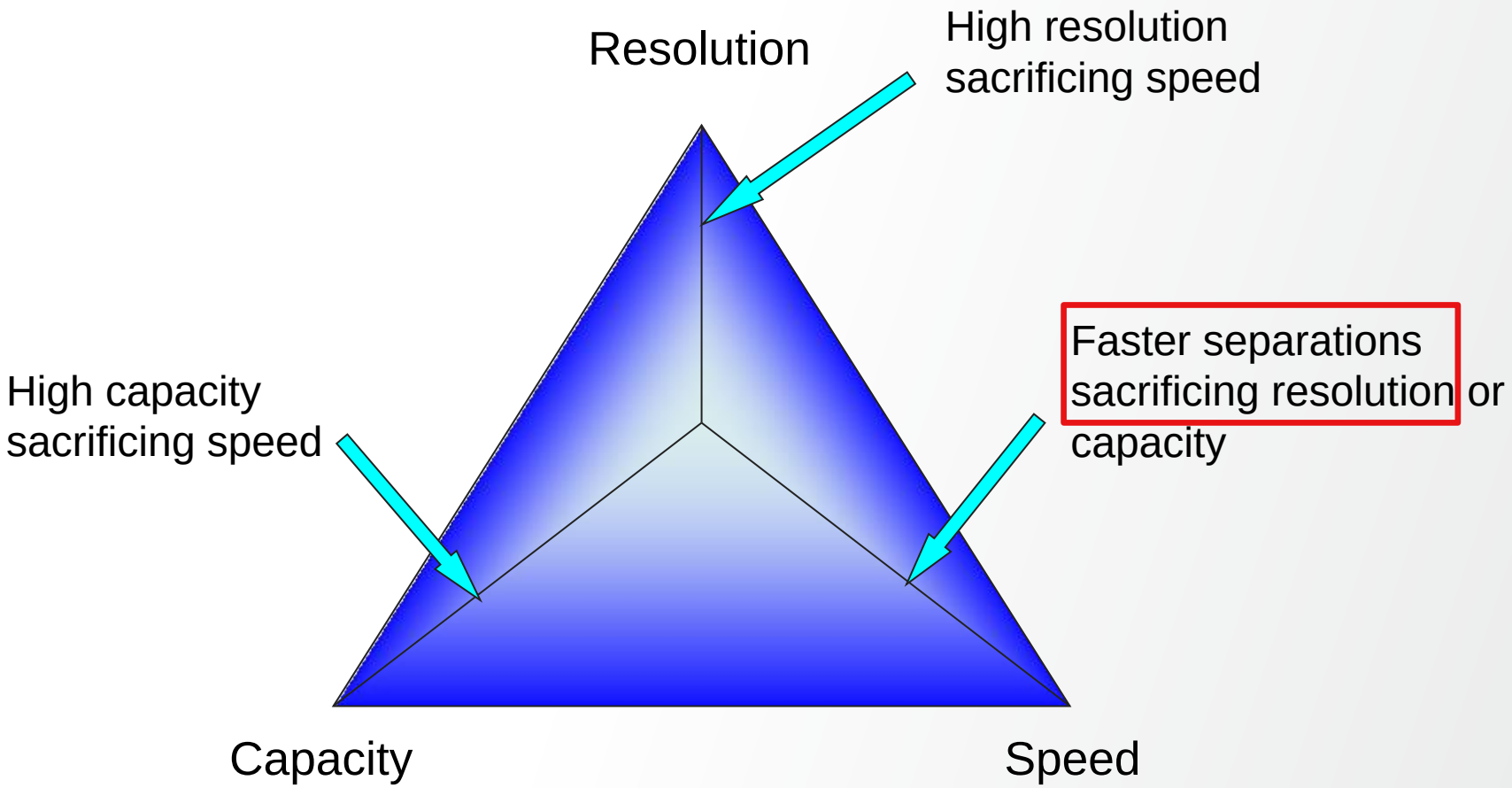
Separator:	Thermo Scientific™ Dionex™ IonPac™ AG11, AS11, 4-mm		
Eluent:	A: 15.5 mmol/L KOH		
	B: 0.5 to 25 mmol/L KOH in 8 min		
Flow rate:	2 mL/min		
Inj. volume:	25 µL		
Detection:	Suppressed conductivity		
Suppressor:	ASRS, AutoSuppression Recycle Mode		
Peaks:	1. Fluoride	2	[mg/L]
	2. Chloride	3	
	3. Nitrate	10	
	4. Sulfate	15	
	5. Orthophosphate	15	

Ease of use and consistency of RFIC, but how do we shorten run time?

IC column parameters: Speed, capacity, and resolution

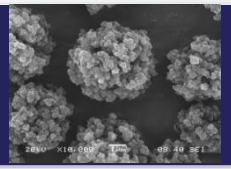


IC column parameters: Speed, capacity, and resolution



Column efficiency: Increase with smaller particles (4 µm)

Smaller Particle Columns:



- Produce more efficient peaks
- Impact chromatographic speed and resolution
- Improve peak integration – more accurate and reliable results
- Increase sample throughput without compromising data quality
- Improve quality of analytical results

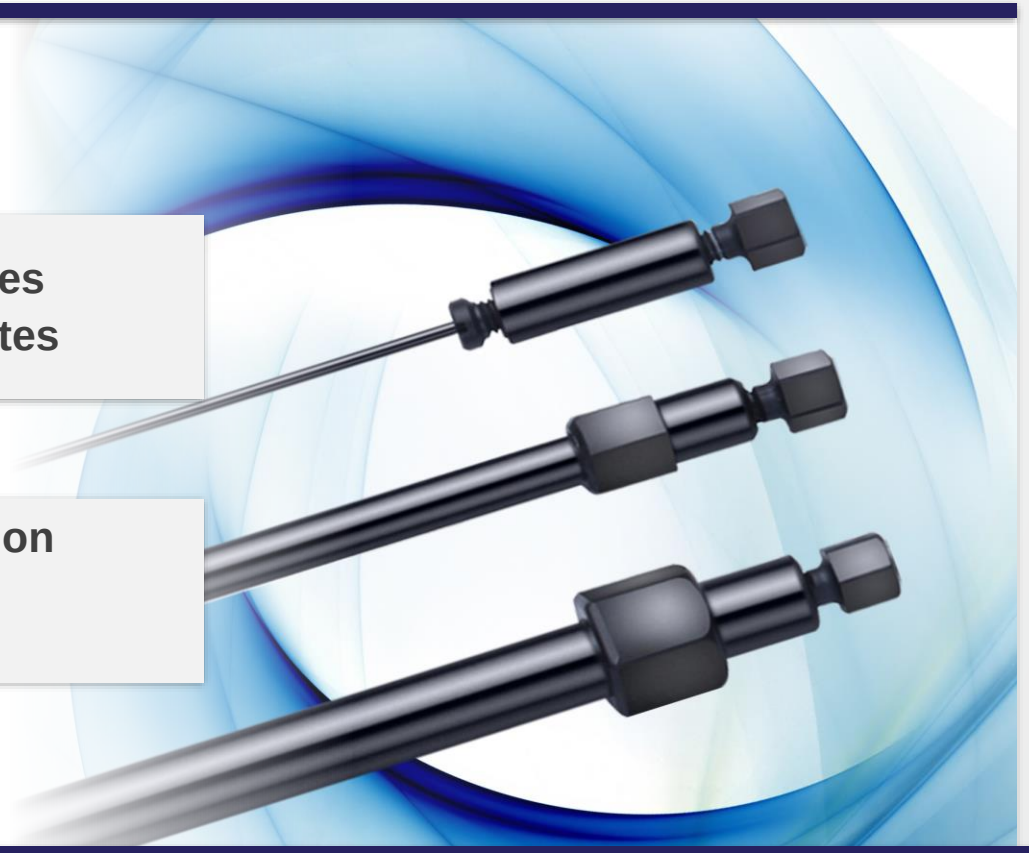
4 µm columns: Combining speed and resolution

150mm

- Faster run times
- Higher flow rates

250mm

- Better resolution
- Standard flow rates



Achieving the optimal combination of speed and resolution

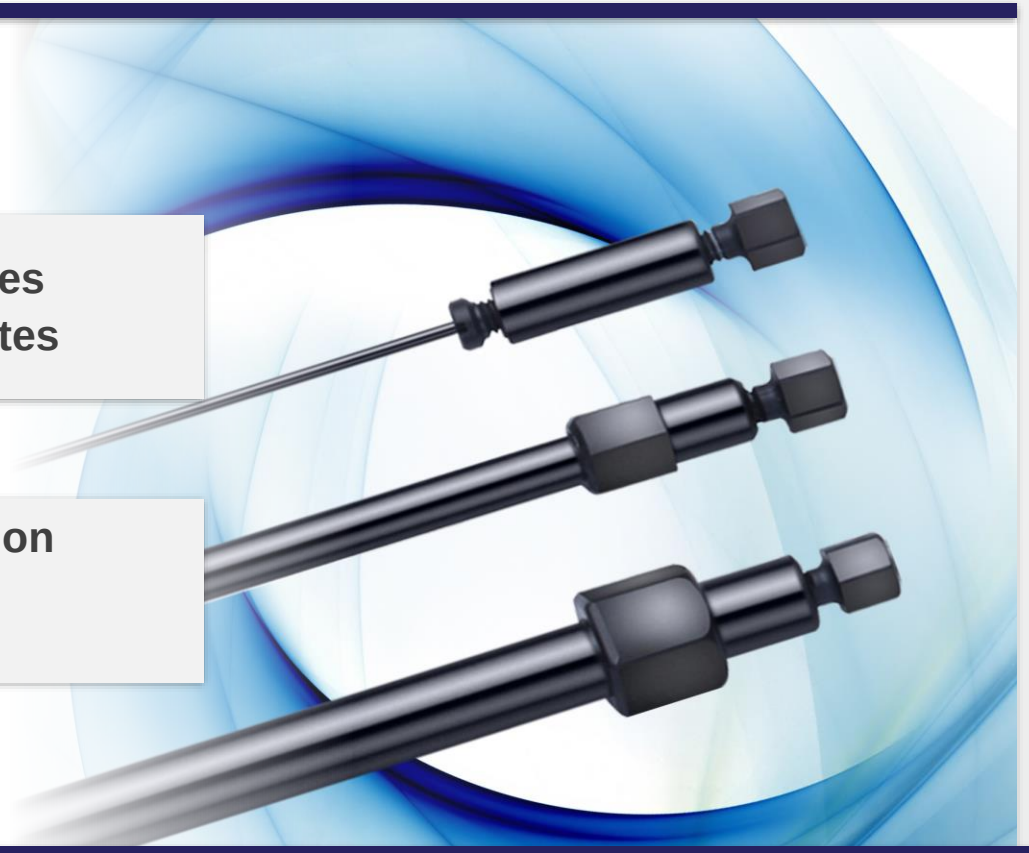
4 µm columns: Combining speed and resolution

150mm

- Faster run times
- Higher flow rates

250mm

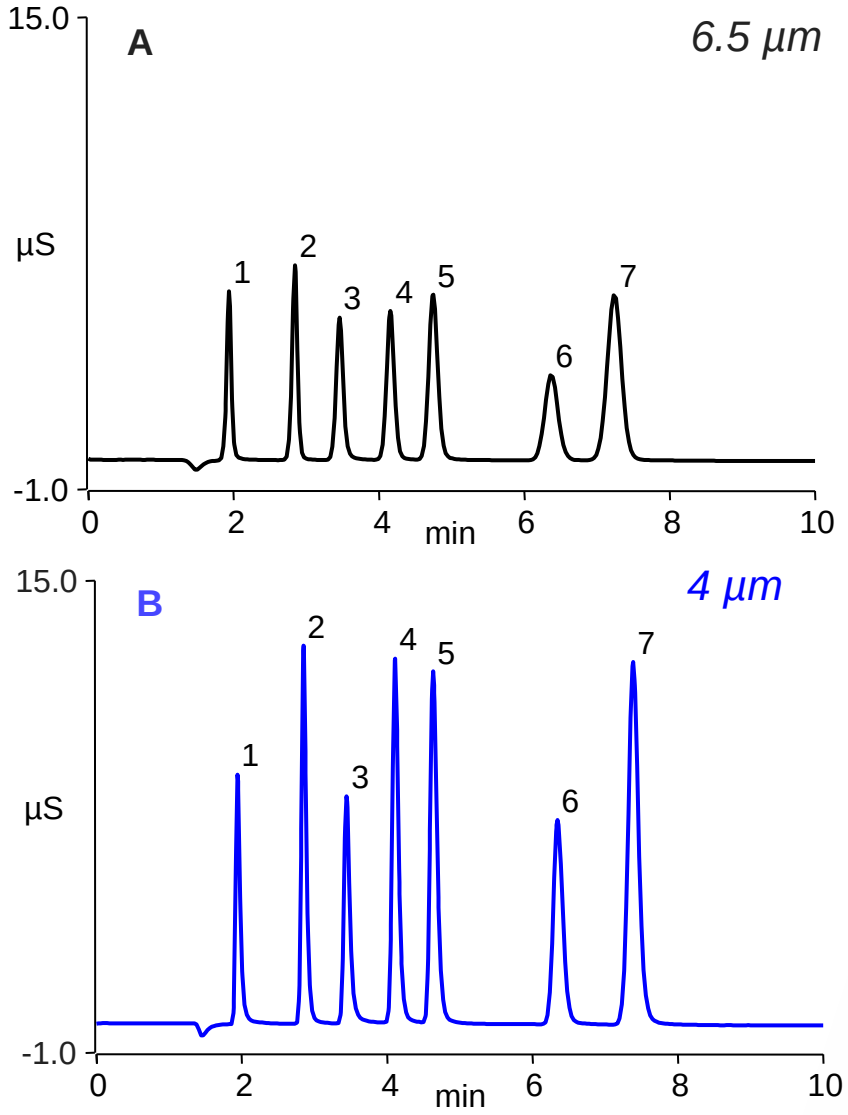
- Better resolution
- Standard flow rates



Achieving the optimal combination of speed and resolution

Need High Pressure IC (HPIC) system to take full advantage of benefits

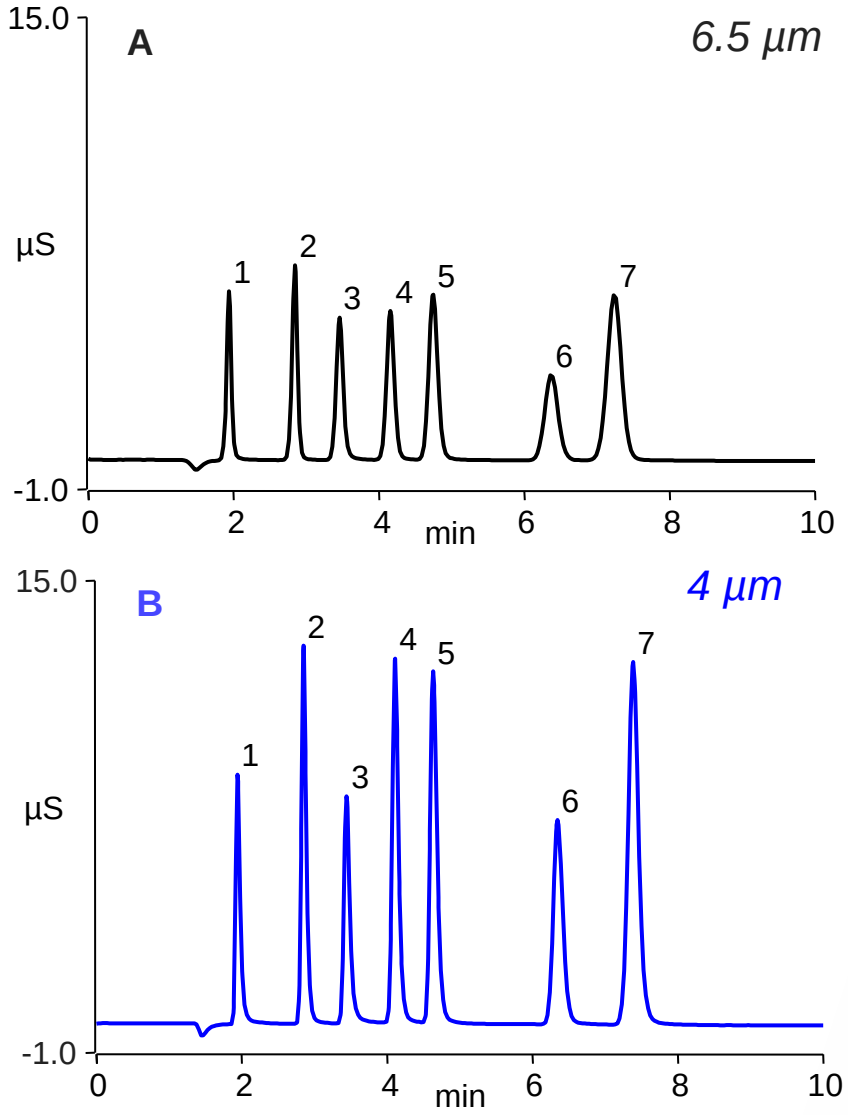
Column efficiency: 4 µm vs. 6.5 µm particles



Column A:	Thermo Scientific™ Dionex™ IonPac™ AS22-Fast (2 x 150 mm)
Column B:	Thermo Scientific™ Dionex™ IonPac™ AS22-Fast-4µm (2 x 150 mm)
Eluent:	4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Flow Rate:	0.3 mL/min
Inj. Volume:	2.5 µL
Temperature:	30˚C
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS 500 (2 mm) Suppressor, AutoSuppression, Recycle mode

Peaks:	mg/L (ppm)
1. Fluoride	5.0
2. Chloride	10.0
3. Nitrite	15.0
4. Bromide	25.0
5. Nitrate	25.0
6. Phosphate	40.0
7. Sulfate	30.0

Column efficiency: 4 µm vs. 6.5 µm particles

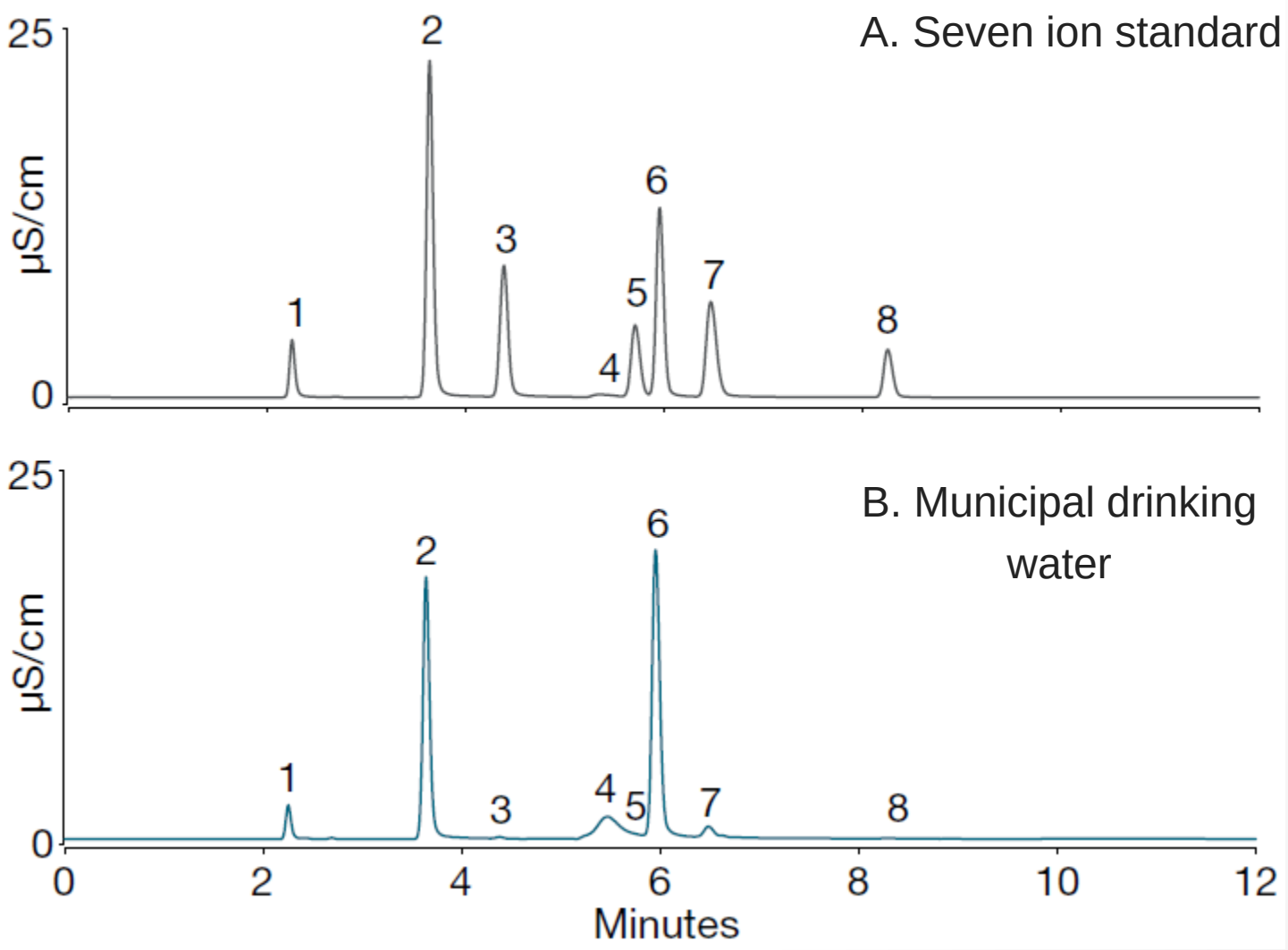


Column A:	Thermo Scientific™ Dionex™ IonPac™ AS22-Fast (2 x 150 mm)
Column B:	Thermo Scientific™ Dionex™ IonPac™ AS22-Fast-4µm (2 x 150 mm)
Eluent:	4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Flow Rate:	0.3 mL/min
Inj. Volume:	2.5 µL
Temperature:	30˚C
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS 500 (2 mm) Suppressor, AutoSuppression, Recycle mode

Peaks:	mg/L (ppm)
1. Fluoride	5.0
2. Chloride	10.0
3. Nitrite	15.0
4. Bromide	25.0
5. Nitrate	25.0
6. Phosphate	40.0
7. Sulfate	30.0

Smaller particles deliver more efficient peaks and higher resolution.

Faster runs using smaller particle columns

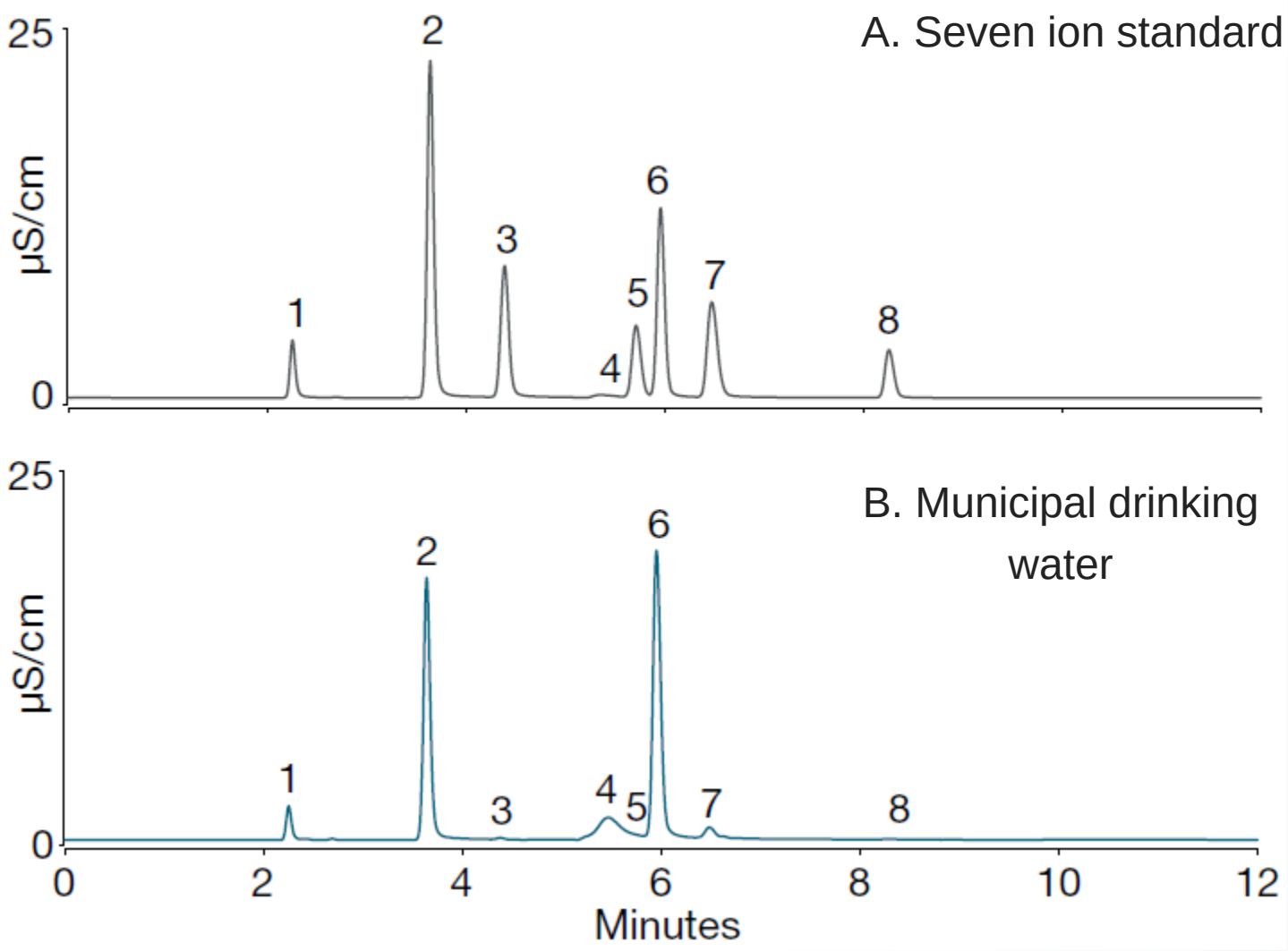


Thermo Scientific™ Dionex™ IonPac™ AS18-Fast-4µm column (4 x 150 mm)

15–44 mM KOH

Peaks:	A	B	
1. Fluoride	1	0.63	mg/L
2. Chloride	12	9.7	
3. Nitrite	8	0.023	
4. Carbonate	NA	NA	
5. Bromide	9	NA	
6. Sulfate	10	16.3	
7. Nitrate	9	1.3	
8. Phosphate	6.5	0.085	

Faster runs using smaller particle columns



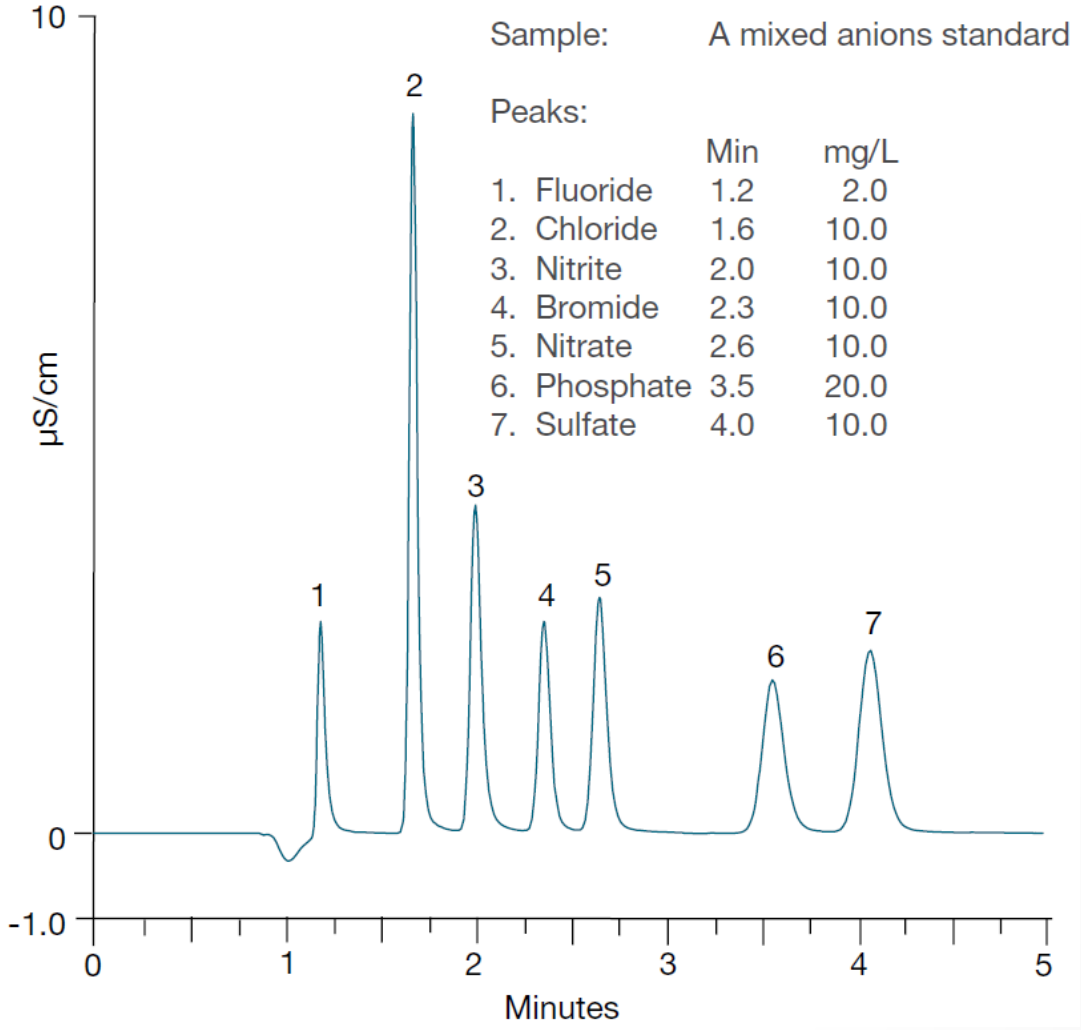
Thermo Scientific™ Dionex™ IonPac™ AS18-Fast-4µm column (4 x 150 mm)

15–44 mM KOH

Peaks:	A	B	
1. Fluoride	1	0.63	mg/L
2. Chloride	12	9.7	
3. Nitrite	8	0.023	
4. Carbonate	NA	NA	
5. Bromide	9	NA	
6. Sulfate	10	16.3	
7. Nitrate	9	1.3	
8. Phosphate	6.5	0.085	

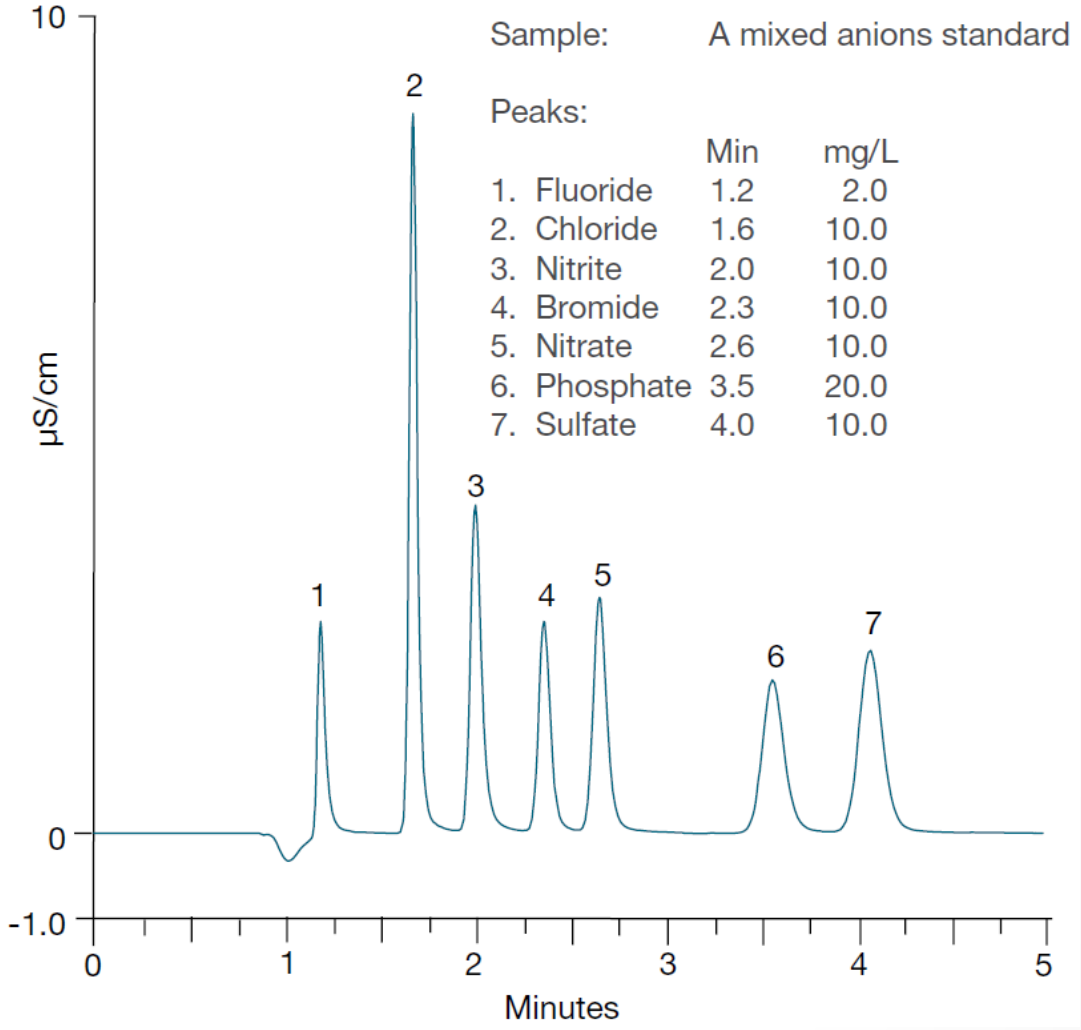
Run time reduced by 25%

Fast determinations using carbonate eluent



Column:
Thermo Scientific™ Dionex™ IonPac™ AS22-Fast-4µm, 4 mm
Eluent:
4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Flow rate:
2 mL/min

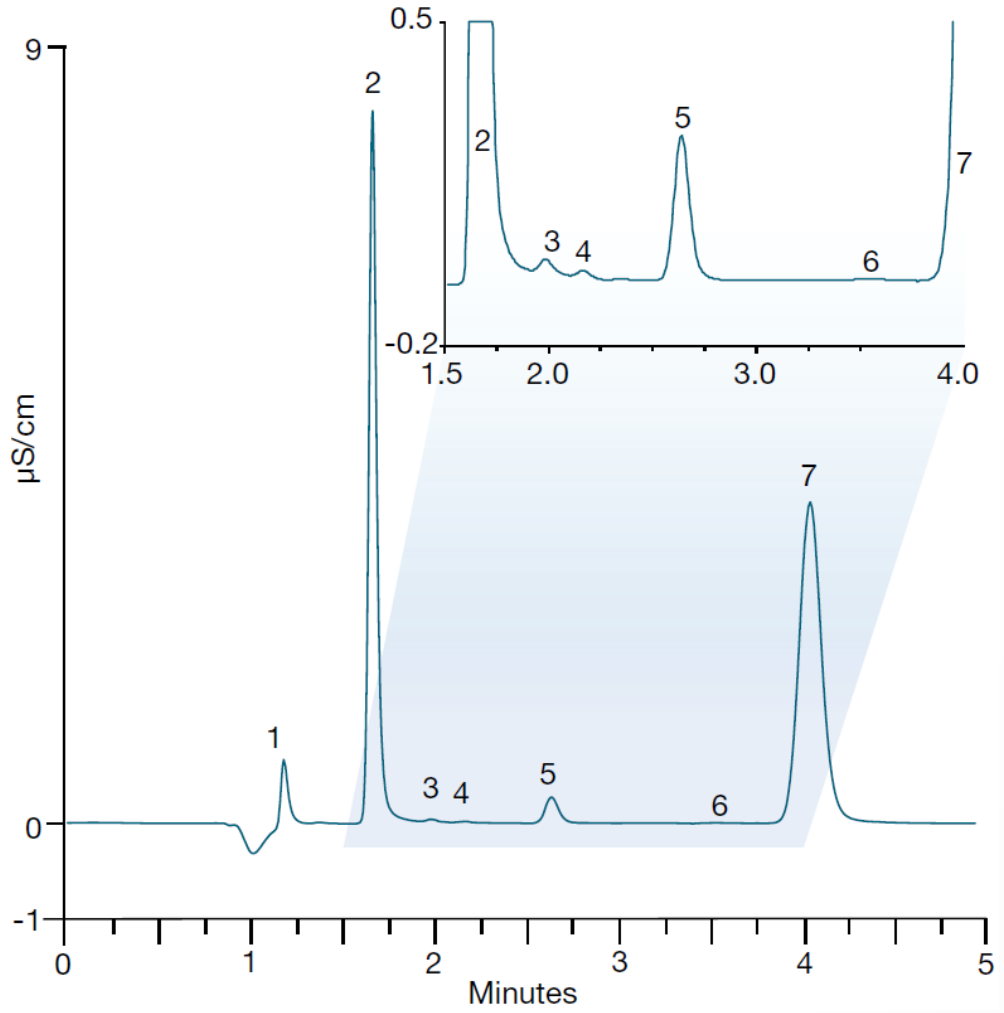
Fast determinations using carbonate eluent



Column:
Thermo Scientific™ Dionex™ IonPac™ AS22-Fast-4µm, 4 mm
Eluent:
4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Flow rate:
2 mL/min

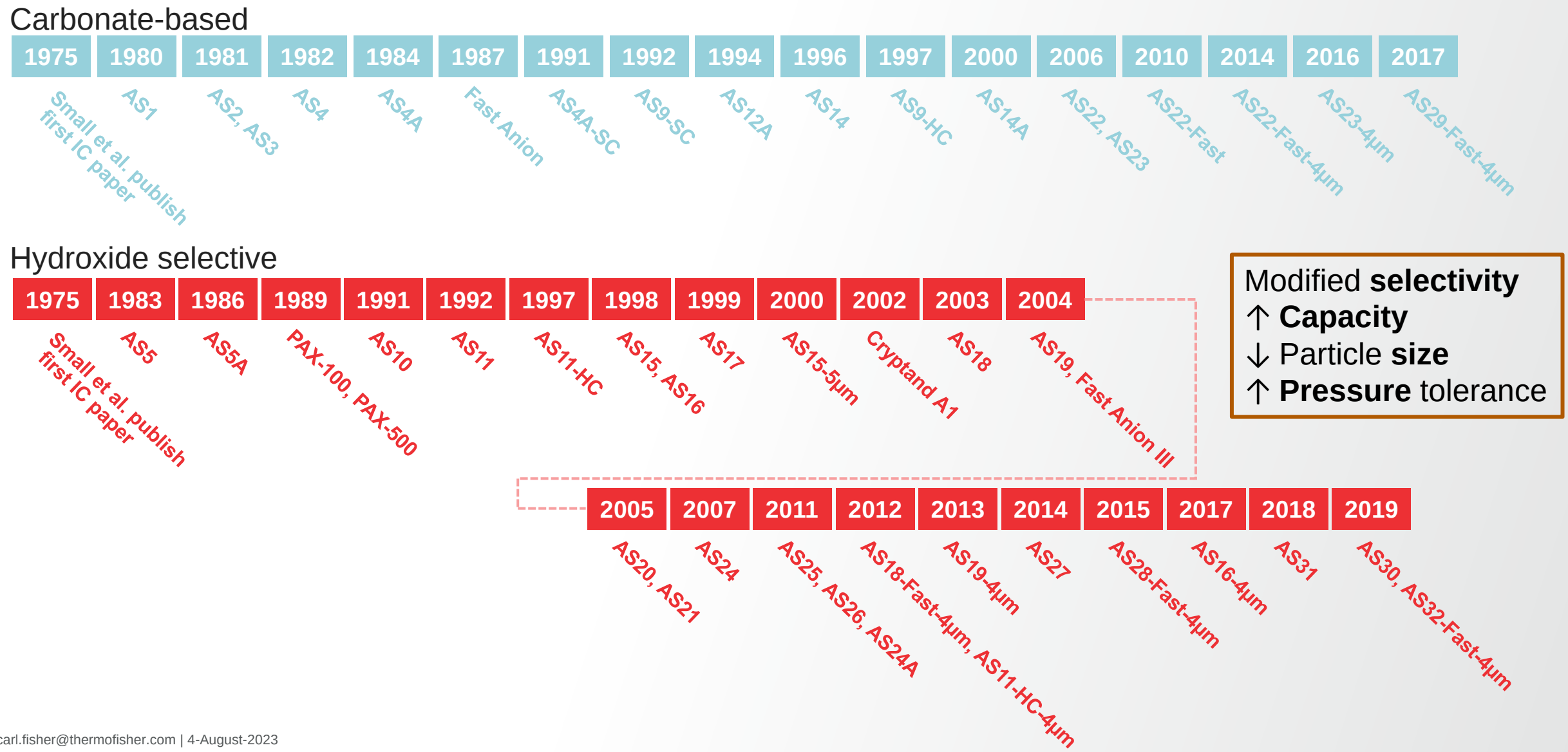
Baseline resolution in under five minutes.

Fast anion determinations: drinking water

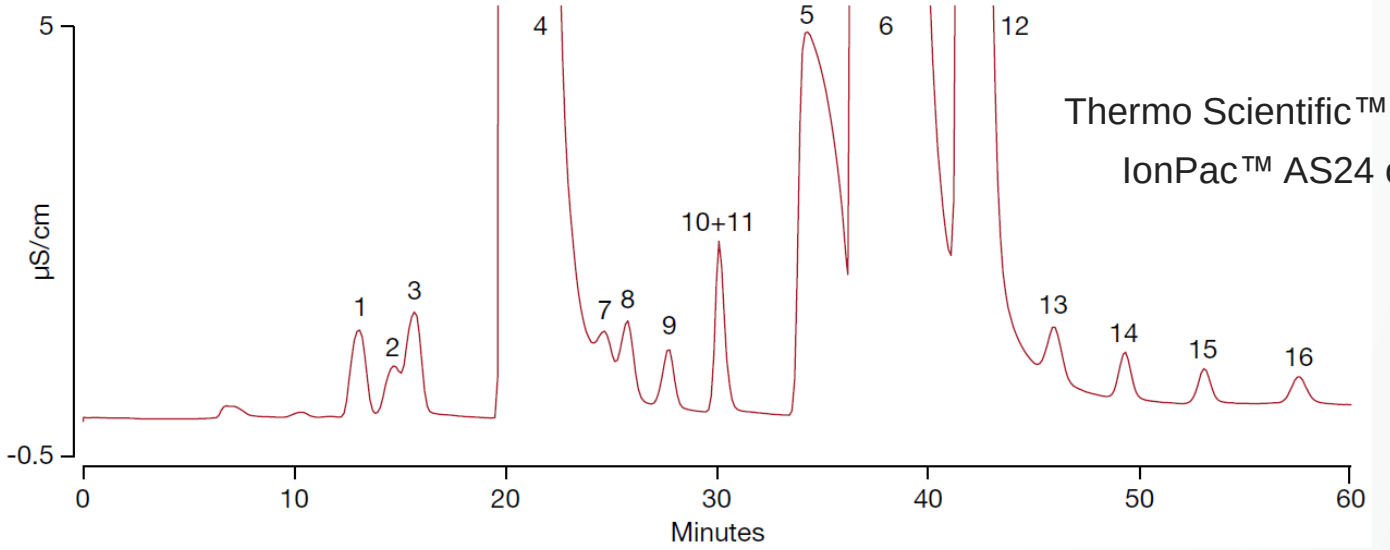


Sample:	Municipal drinking water	
Peaks:		
	Min	mg/L
1. Fluoride	1.2	0.6
2. Chloride	1.6	9.5
3. Nitrite	2.0	0.2
4. Unknown	—	—
5. Nitrate	2.6	1.2
6. Phosphate	3.5	0.2
7. Sulfate	4.0	16.5

Thermo Scientific Dionex IonPac anion exchange column development



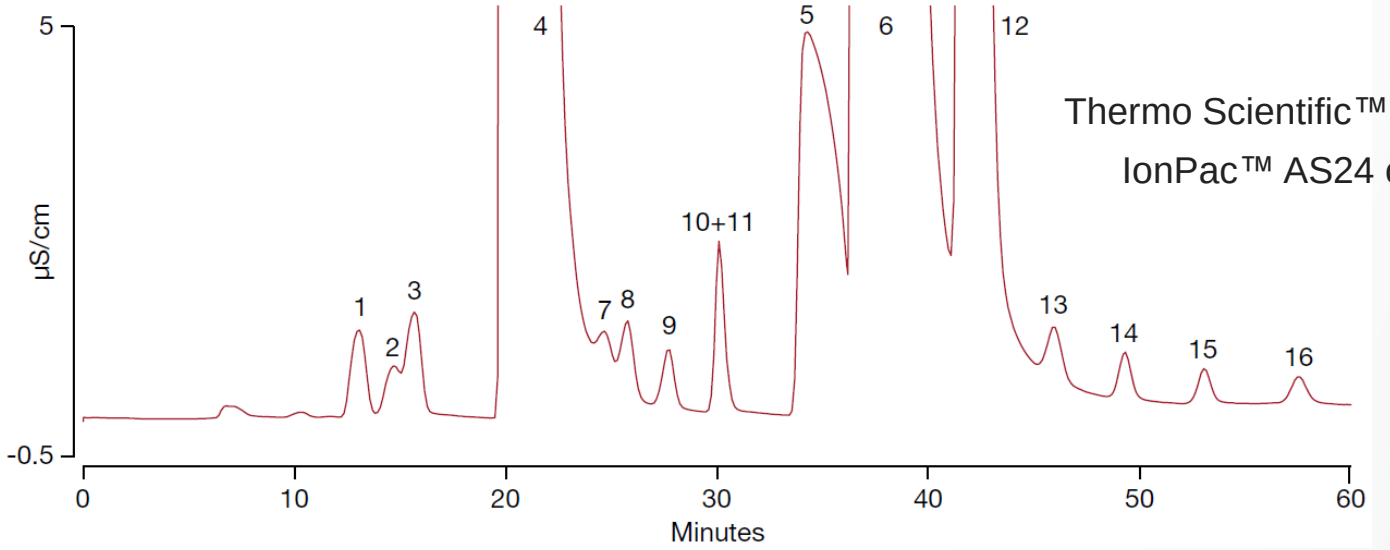
Faster haloacetic acid determinations



Thermo Scientific™ Dionex™ IonPac™ AS24 column

Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

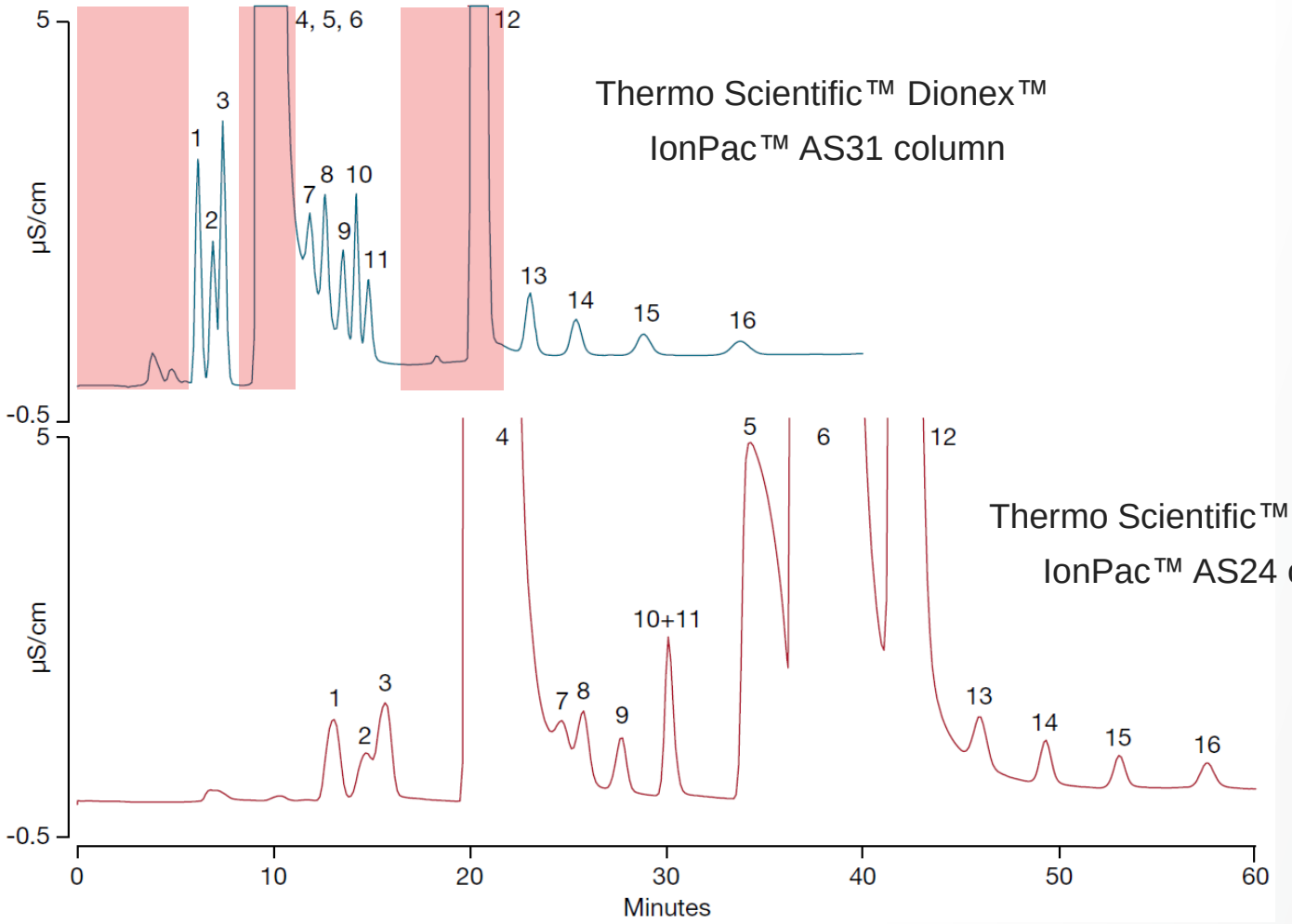
Faster haloacetic acid determinations



Thermo Scientific™ Dionex™
IonPac™ AS24 column

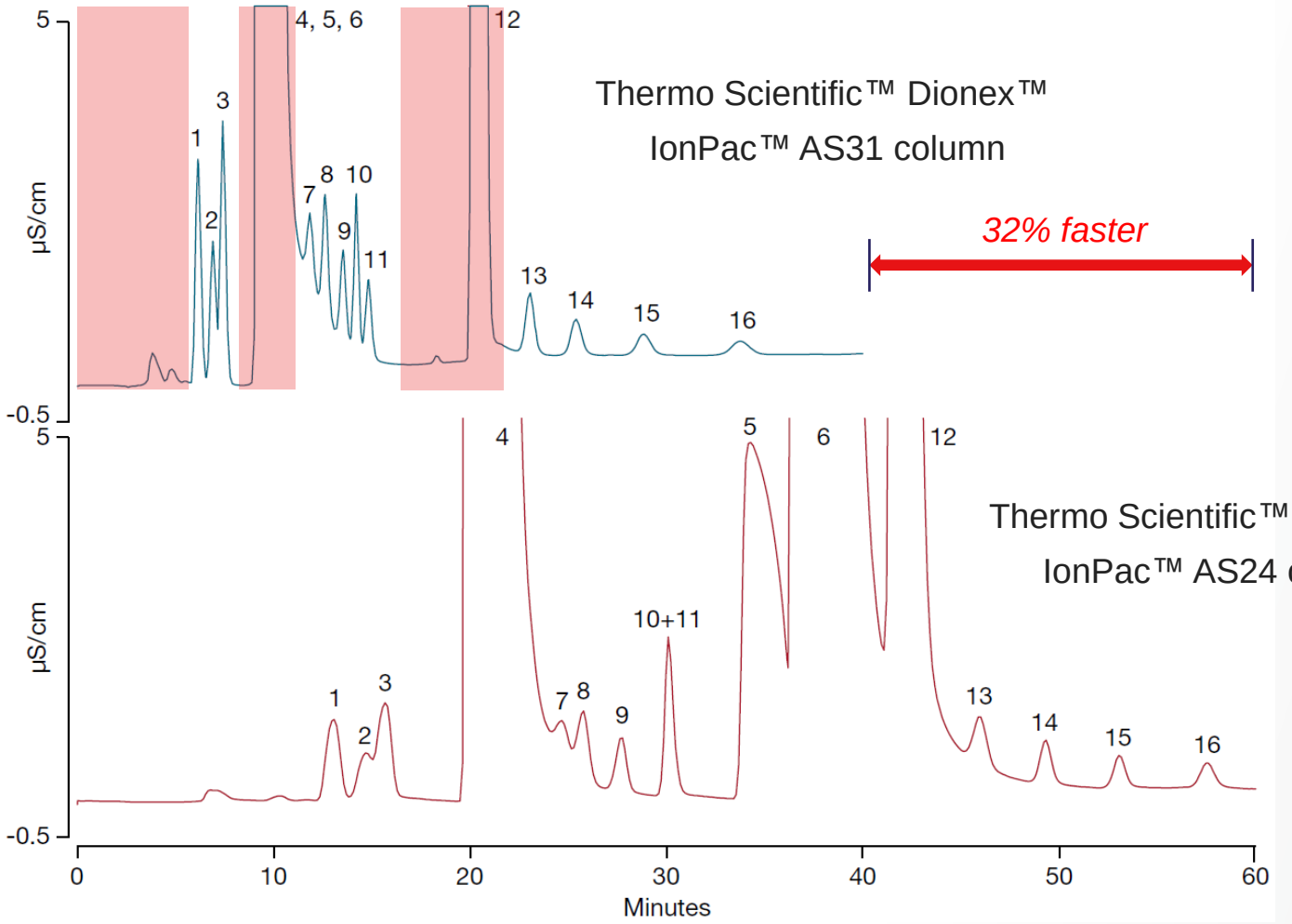
Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

Faster haloacetic acid determinations



Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

Faster haloacetic acid determinations



Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

Saving time by altering column specificity

Thermo Scientific Dionex ion chromatography family

Reagent-Free Ion Chromatography (RFIC)

High Pressure Ion Chromatography (HPIC)

Thermo Scientific™
Dionex™ Easion™
- 2 mm/4 mm IC
- Carbonate or MSA eluents
- **Chemical suppression**

Thermo Scientific™
Dionex™ Aquion™
- 2 mm/4 mm IC
- Carbonate or MSA eluents
- **Electrolytic suppression**

Thermo Scientific™
Dionex™ Integrion™
- 2 mm/4 mm HPIC
- Field upgradable options
- **RFIC** or manual eluents
- Tablet control
- Thermo Scientific ™ Viper™ fittings

Thermo Scientific™
Dionex™ ICS-6000
- 2 mm/4 mm HPIC
- RFIC, dual EGC and gradient pump
- **Flexible & modular** with tablet
- Versatile detection capabilities
- Performance monitoring/ tracking

Innovations in IC

- Reagent-free IC
  - Reproducibility
  - Ease of use
  - Reduced exposure to chemicals

- Column Chemistry
  - Capacity
    - Tolerance to matrix loading
  - Resolution
    - Reduced run times
  - Specificity

- Alternative detectors
  - Broaden the range of applications

Extended application range: optional detectors

Conductivity

- **Anions and cations**

Electrochemical

- **Electroactive compounds**
  (e.g. saccharides)

Mass spectrometry

- **Ionic and polar compounds**
  (e.g. Haloacetic acids (HAAs))

Spectrophotometric

- **UV and visible absorbing compounds**
- Post-column and pre-column derivatization techniques
  (e.g. Perchlorate)

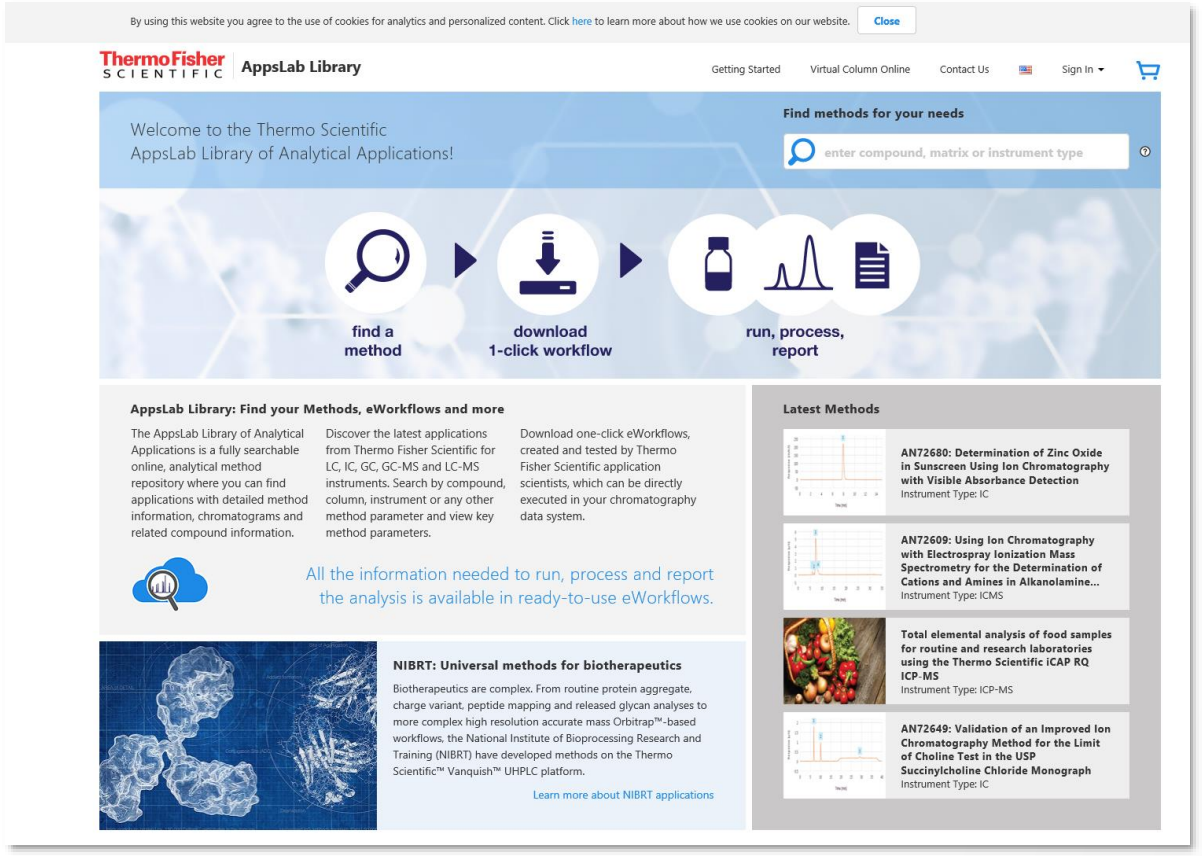
Inductively coupled plasma spectroscopy

- **Multiple elemental species**
  (e.g. Bromate, selenium)

Future directions in IC

- Columns
  - Selectivity, capacity, resolution
- Combining other systems with IC
  - Combustion IC; IC-MS
- Component layout
  - Unobstructed accessibly; tubing management
- Upgradability and customization
  - Base that can easily grow as needs expand
- Software
  - Usability; automation, diagnostics
- Online Support
  - Dedicated to post-sales resources

AppsLab: the latest applications



- Fully searchable online, analytical method repository
- Latest applications for **IC**, LC, GC, GC-MS, LC-MS, ICP-MS, ICP-OES and DIA instruments
- Download one-click eWorkflows for use with Thermo Scientific Chromeleon Chromatography Data System (CDS) software
- Ever-expanding database of field-tested workflows

www.appslab.com

Resources for IC information

IC Hub

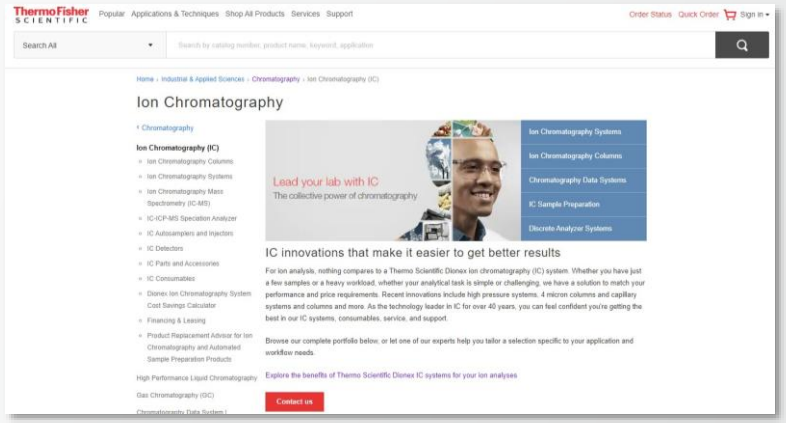
- What's new
- Best practices
- Tips and tricks

thermofisher.com/iceducation

Analyte Guru

- Scientific communities
- Community support
- Knowledgebase
- Blogs
- Events

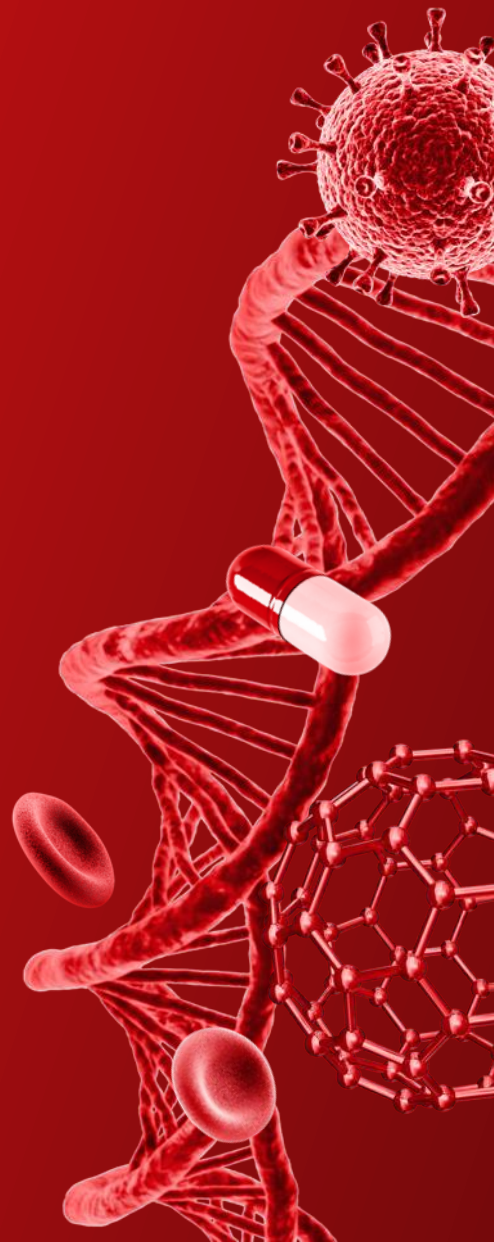
analyteguru.com



Dionex IC Products

- Systems
- Detectors
- Autosamplers
- Columns
- Consumables

thermofisher.com/IC

Thank you!

Any questions?