Kuehne
LABORATORY SERVICES

Ion Chromatography (IC) as the Right Tool

Learn about where to start with determining IC as the right tool, how it can replace more tedious methods, and what you'll need to get started.

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Agenda

- Industries: **Chemical Manufacturing**, Pharmaceuticals, Academia / Research
- What do you Value (CTQs, Tolerance Levels)
- HPLC-IC
- Method Development
- Problem Solving / Continuous Improvements

Industries

- Chemical Manufacturing
- Pharmaceuticals
- Academia / Research

Industries

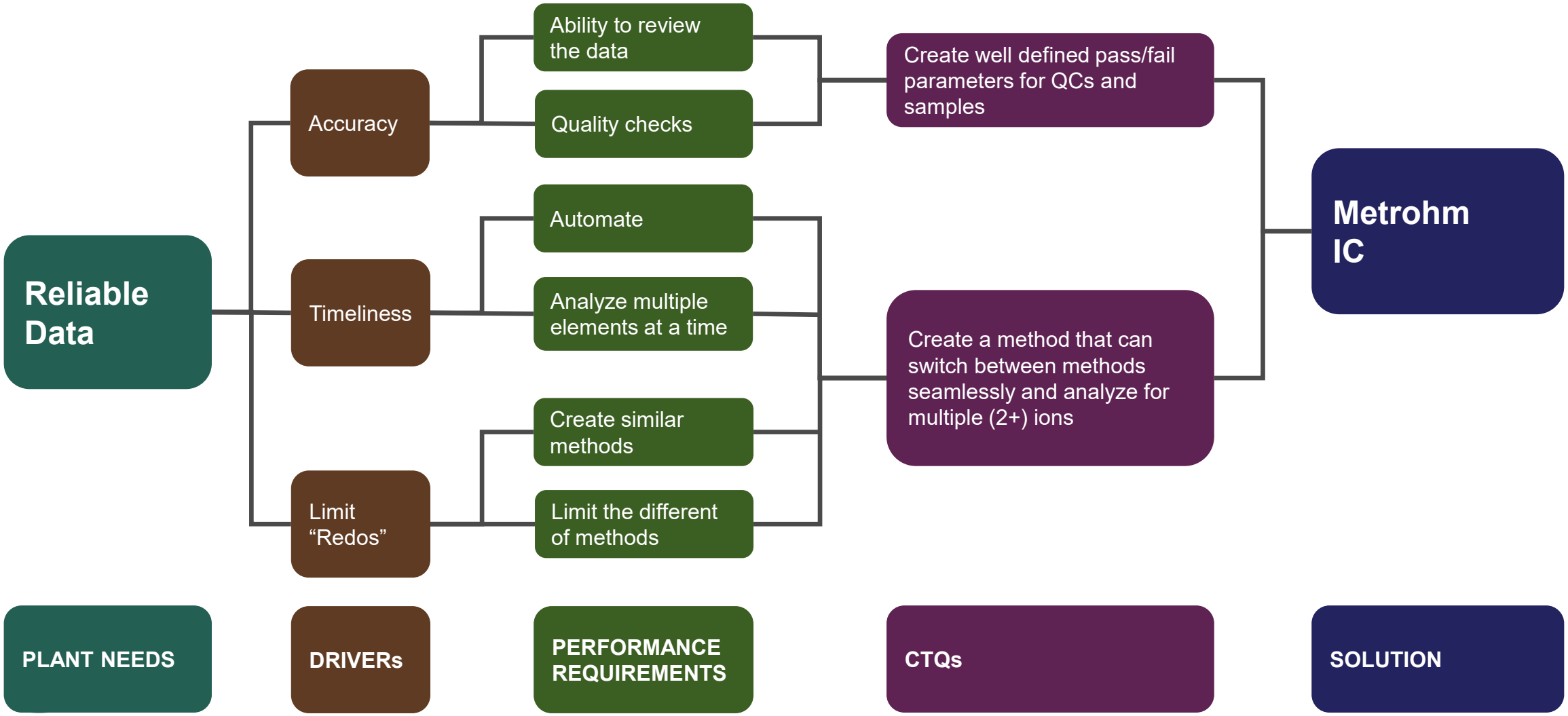
	Chemical Manufacturing	Pharmaceutical	Academia / Research
Focus	Robustness	Regulatory Compliance	Flexibility
Throughput	Moderate-High	Moderate-High	Low-Moderate
Sample Type	Known	Known, with more regulations	Diverse, often unknown

Determining Value

Determine

- What the parameters are
- What are the specifications for the parameters
- The tolerance levels of those specifications
- The cost to value. Both direct and indirect

Critical to Quality (CTQ) Example



Sulfate Analysis | Indirect Cost Example

	Gravimetric Method		IC	
Sample Prep	Carefully reduce pH to <4. Heat until a boil. Add BaCl2. Continue to let it boil.	45 - 60 Minutes	Turn Instrument on. Let it equilibrate	30 - 45 Minutes
	Let it cool.	30 Minutes	Make a 1000x dilution. Place sample in Vial.*	1 - 2 Minutes
	Weigh out a 0.47µ filter paper and weighing dish. Prepare the vacuum filter.	5 - 10 Minutes	Prepare the Sample Table and put sample on autosampler.	1 - 2 Minutes
Analysis	Using the filter vacuum, collect the precipitate.	5 - 10 Minutes	Run Calibration* Check	30 Minutes
	Dry Sample	60 - 120 Minutes	Run Sample*	30 Minutes
	Weight out Sample, Dish, Filer Paper.	1 - 2 Minutes		
Total Time		~ 230 Minutes		~ 110 Minutes (35 Minutes subsequent Runs)

Ion Chromatograph

Where to Start

Contact the manufacturer. Tell them what you are analyzing for, at what quantities and in what type of sample. Next you will want to tell them how many samples a day you will be analyzing.

A Chlor Alkali Example

- Manufacturer — Metrohm
- Ions of Interest — Bromide, Chlorate, Chloride, Sulfate, Perchlorate
- Sample Type(s) — Brine (NaCl), Sodium Hydroxide, Sodium Hypochlorite (Bleach)
- Range — 0.2 ppm – 300 ppm

Metrohm IC 940

Extension 942

Adds another pump. Able to add another mobile phase.

858 Professional Sample Processor

Metrosep A Supp 19 Column + Metrosep A Supp 19 Guard Column

Methods | Example

Three (3) Main Methods

- Routine Method
- High Salt – Routine Method
- Perchlorate

Prioritized

Simplicity, easy switching between methods

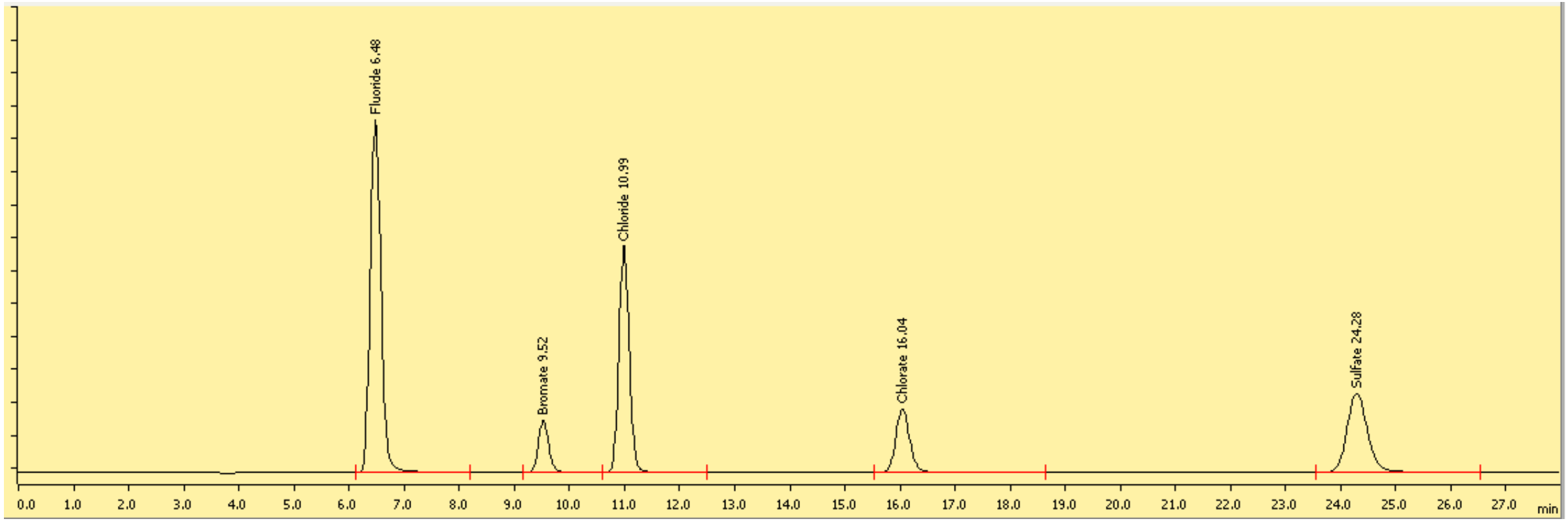
What to Consider

- Injection Size
- Temperature
- Flow Rate
- Mobile Phase
- Column (already discussed)

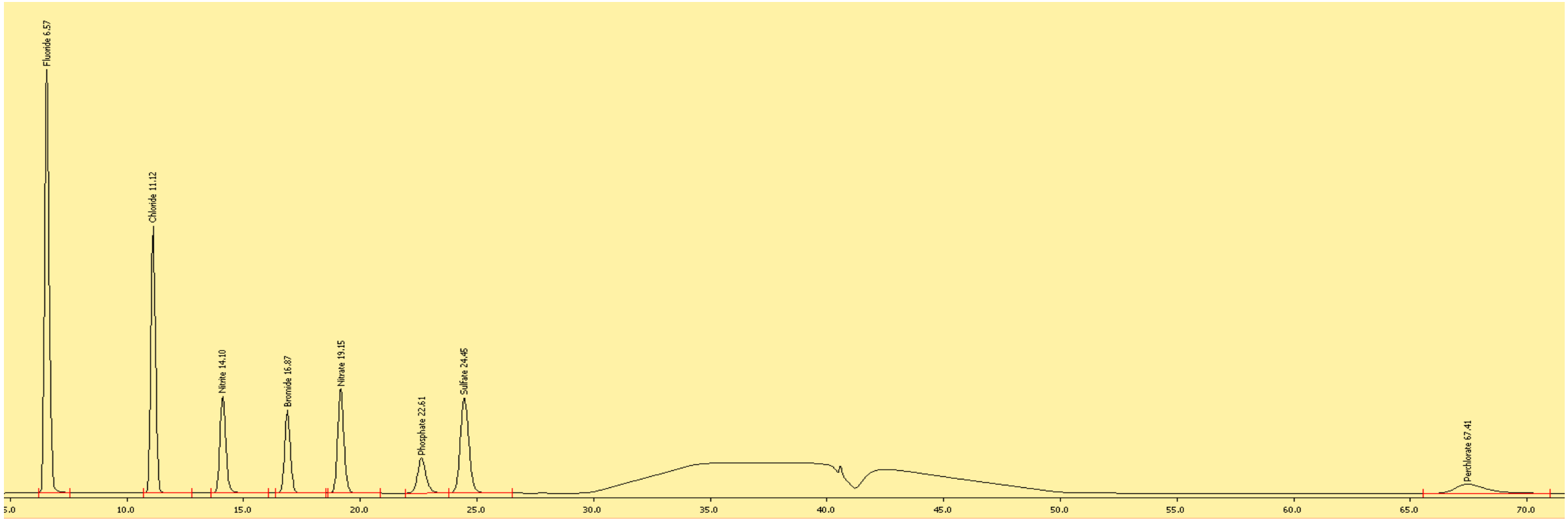
Methods | Value | SIMPLICITY

	Routine Method	Routine Method - High Cl	Perchlorate
Column	Metrosep A Supp 19 Column	Metrosep A Supp 19 Column	Metrosep A Supp 19 Column
Mobile Phase	Isocratic 3.6 mM	Isocratic 3.6 mM	Gradient (3 Steps) 1. 3.6 mM 2. 14.4 mM 3. 3.6 mM
Temperature	30°C	30°C	30°C
Suppression	Normal	Normal	1 Additional "Step"

Switching Between Methods – Routine Method



Switching Between Methods – Perchlorate



Clear Results

The data is only good if everyone can interpret it. Prioritize communicating the species and the units.

Our results need to be Sodium Chloride (NaCl) in grams per liter (g/L)

Results Example

Cl = 190 ppm | How to get results to NaCl in g/L

Change ppm to mg/L

190 mg/L

Multiply by any Dilution Factors

In this case we diluted the original sample 1 : 1000 with DI water

190 mg/L of Cl * 1000 = 190,000 mg/L of Cl

More Unit Conversion

190,000 mg/L = 190 mg/L of Cl

One More Factor

MM of Cl = 35.45 g/mol

MM of NaCl = 58.44 g/mol

58.44 / 35.45 = 1.65

Get the Result

190 * 1.65 = **313.5 g/L of NaCl**

Continuous Improvements

What to Change?

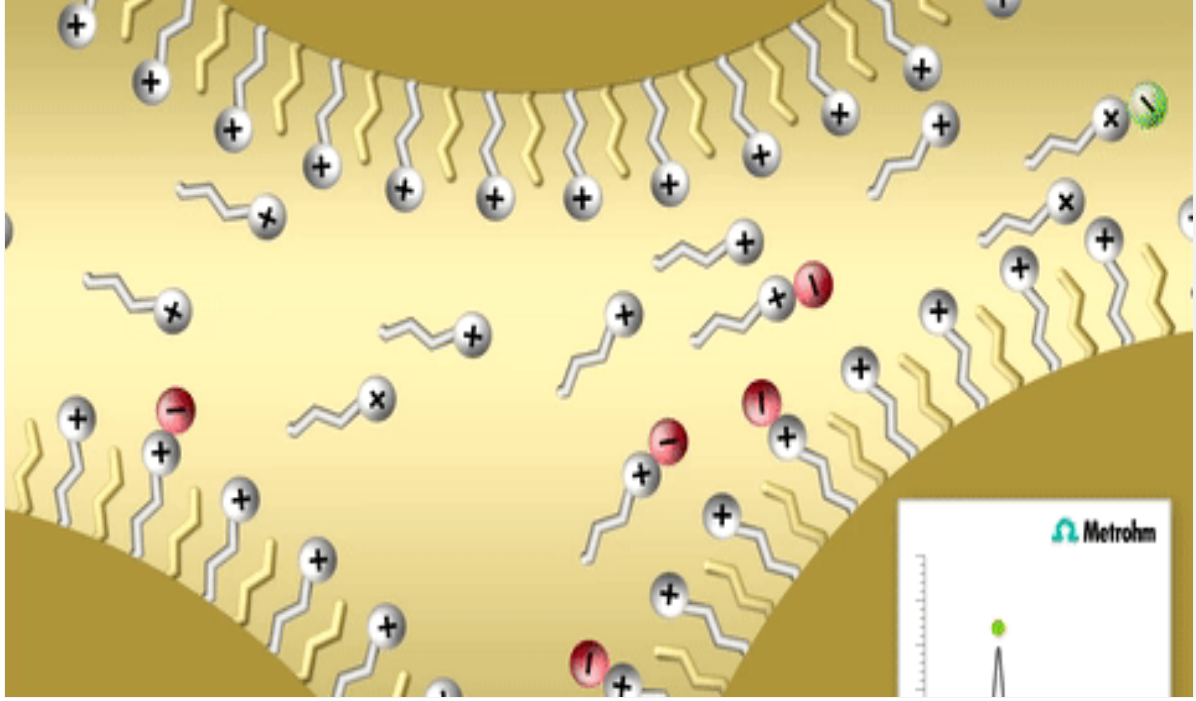
Mobile Phase

- Concentrations
- Additives?

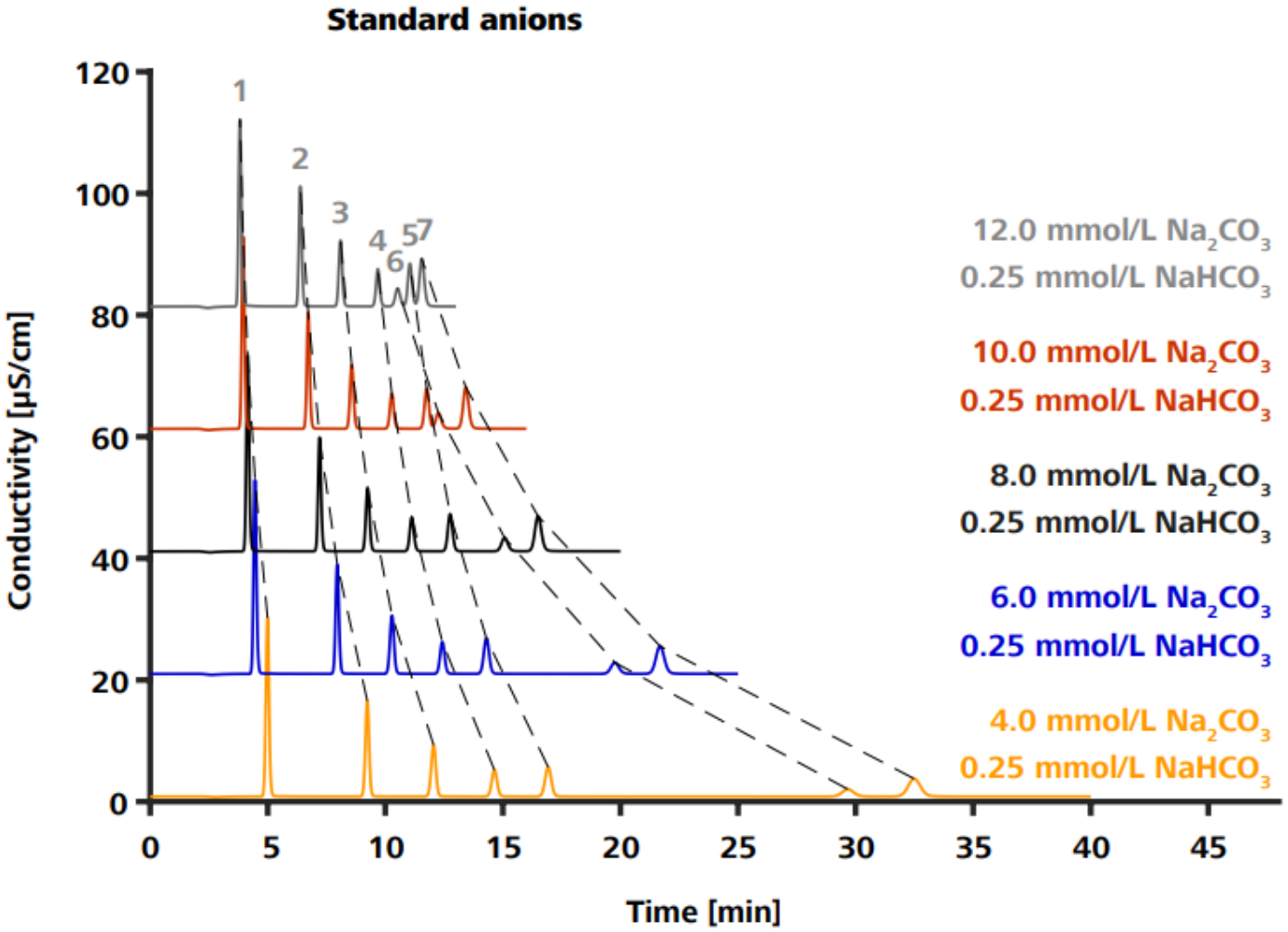
Temperature

Flowrate

Sample Preparation



Mobile Phase | Changing Concentrations

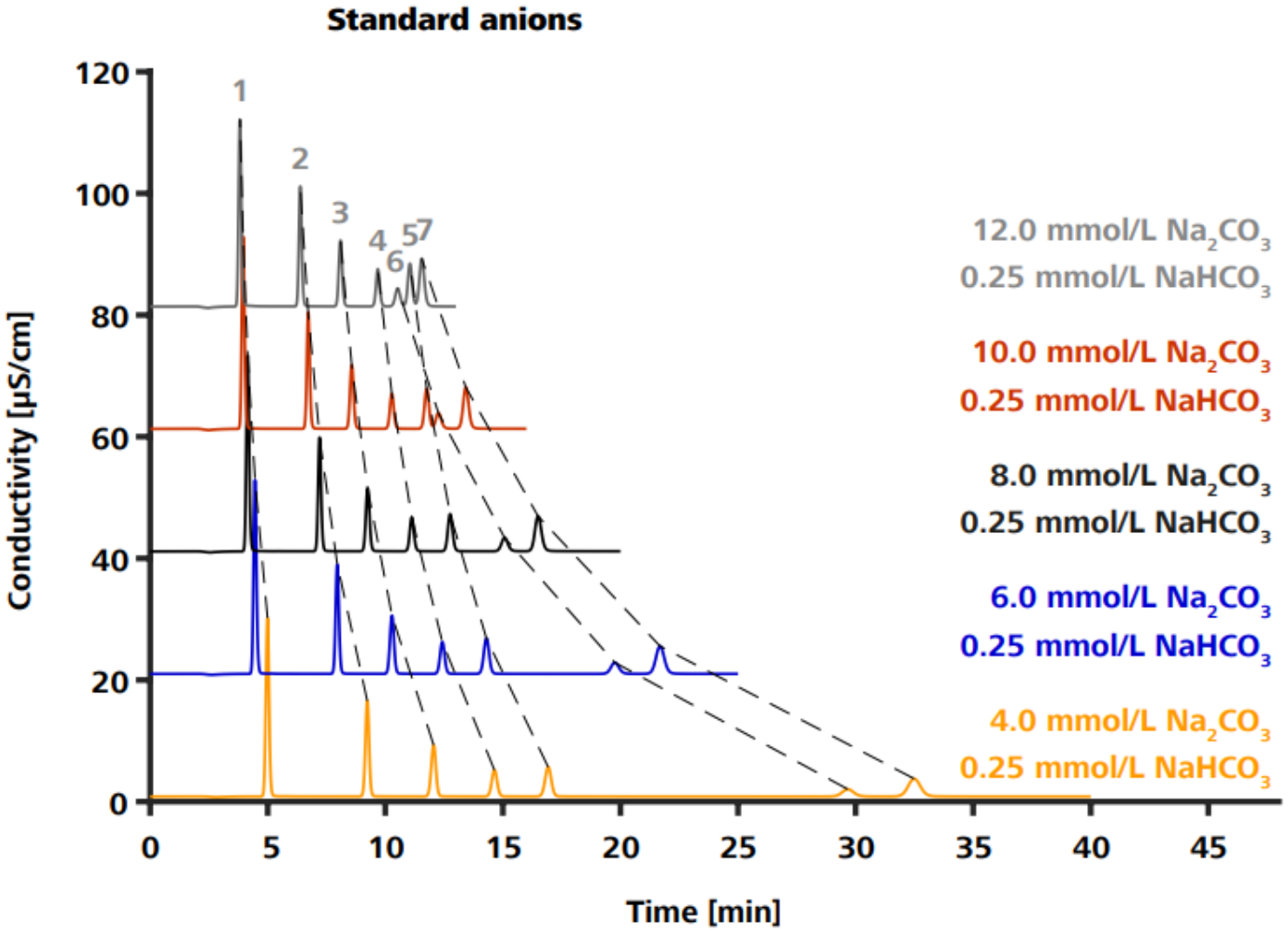


5.4.3 Na_2CO_3 variation at constant $NaHCO_3$

Column:	Metrosep A Supp 19 - 150/4.0
Sample preparation:	–
Detection:	Conductivity
Suppression:	Sequential suppression with MSM and MCS
Temperature:	30 °C
Loop:	20 µL
Flow rate:	0.7 mL/min
Eluent:	A) 0.25 mmol/L $NaHCO_3$, 4.0 mmol/L Na_2CO_3 B) 0.25 mmol/L $NaHCO_3$, 6.0 mmol/L Na_2CO_3 C) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3 D) 0.25 mmol/L $NaHCO_3$, 10.0 mmol/L Na_2CO_3 E) 0.25 mmol/L $NaHCO_3$, 12.0 mmol/L Na_2CO_3

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Fluoride	10
2	Chloride	10
3	Nitrite	10
4	Bromide	10
5	Nitrate	10
6	phosphate	10
7	Sulfate	10

Mobile Phase | Changing Concentrations

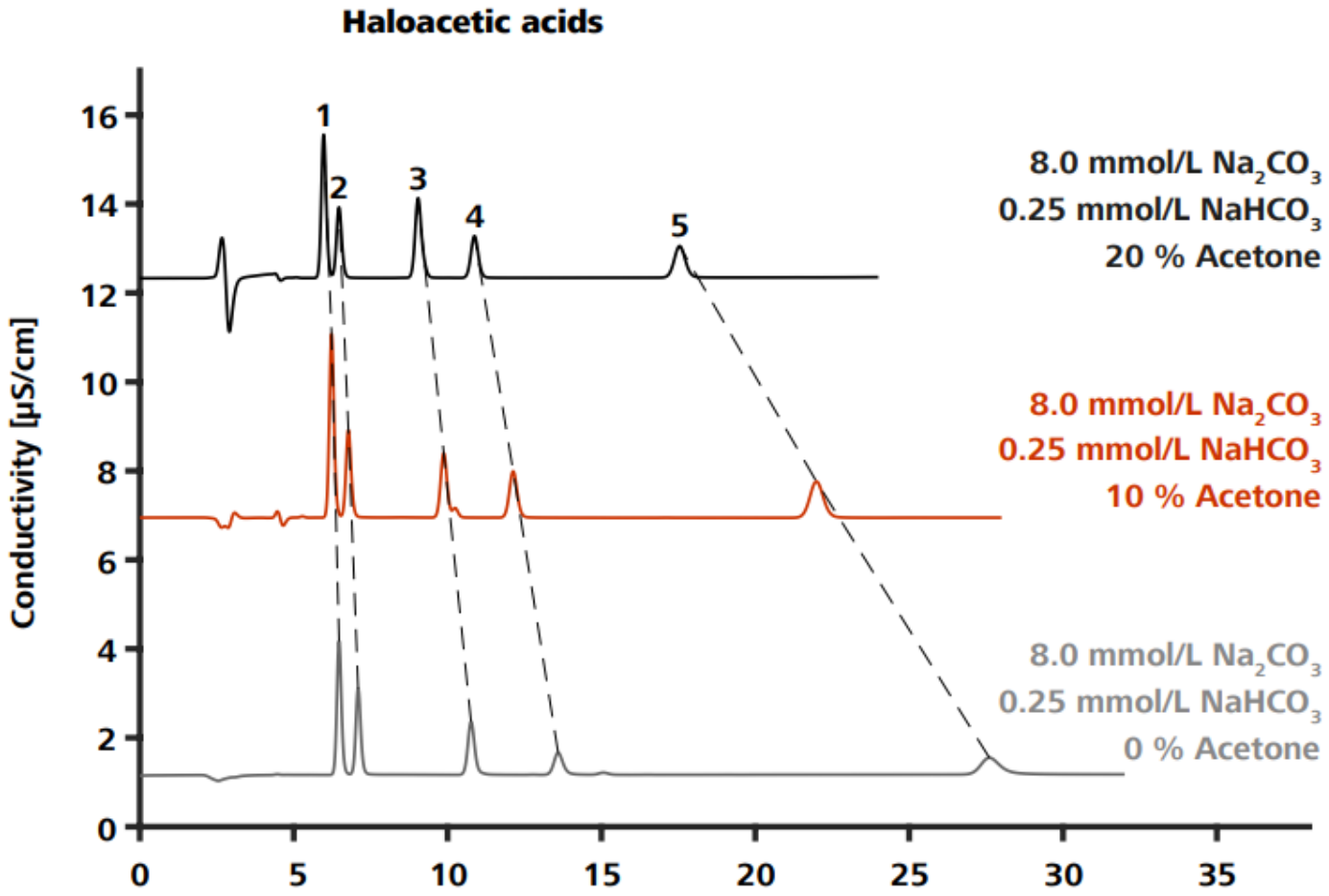


There is a strong relation between the sodium carbonate concentration and the retention times of the anions. But notice not all anions are affected the same.

This could be useful if time is an issue when analyzing for sulfate or nitrate.

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Fluoride	10
2	Chloride	10
3	Nitrite	10
4	Bromide	10
5	Nitrate	10
6	phosphate	10
7	Sulfate	10

Mobile Phase | Adding Acetone

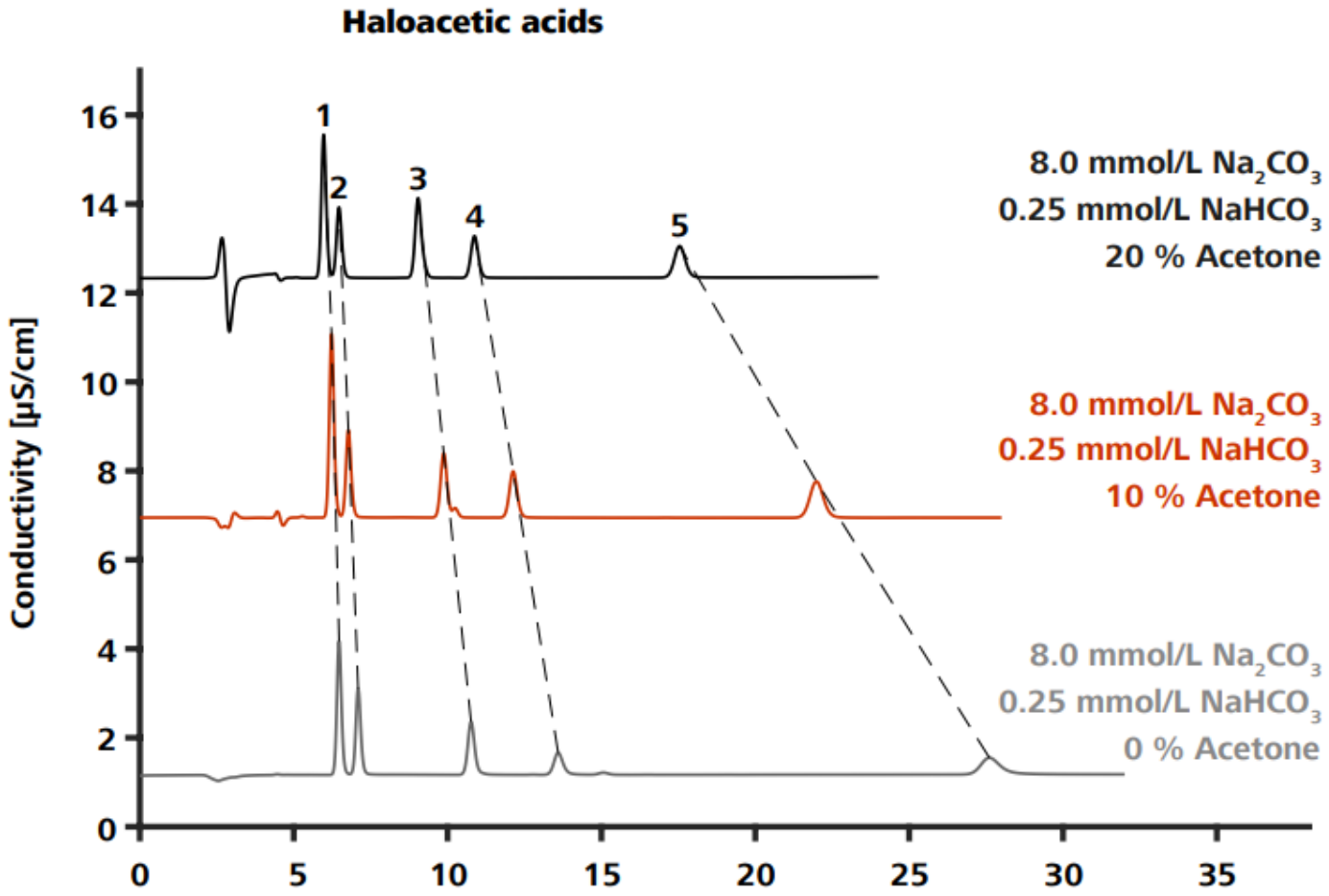


5.5.1 Variation of the acetone concentration

Column:	Metrosep A Supp 19 - 150/4.0
Sample preparation:	–
Detection:	Conductivity
Suppression:	Sequential suppression with MSM and MCS
Temperature:	30 °C
Loop:	20 µL
Flow rate:	0.7 mL/min
Eluent:	A) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 0% acetone B) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 10% acetone C) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 20% acetone

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Monochloroacetate	10
2	Monobromoacetate	10
3	Dichloracetate	10
4	Dibromacetate	10
5	Trichloroacetate	10

Mobile Phase | Adding Acetone

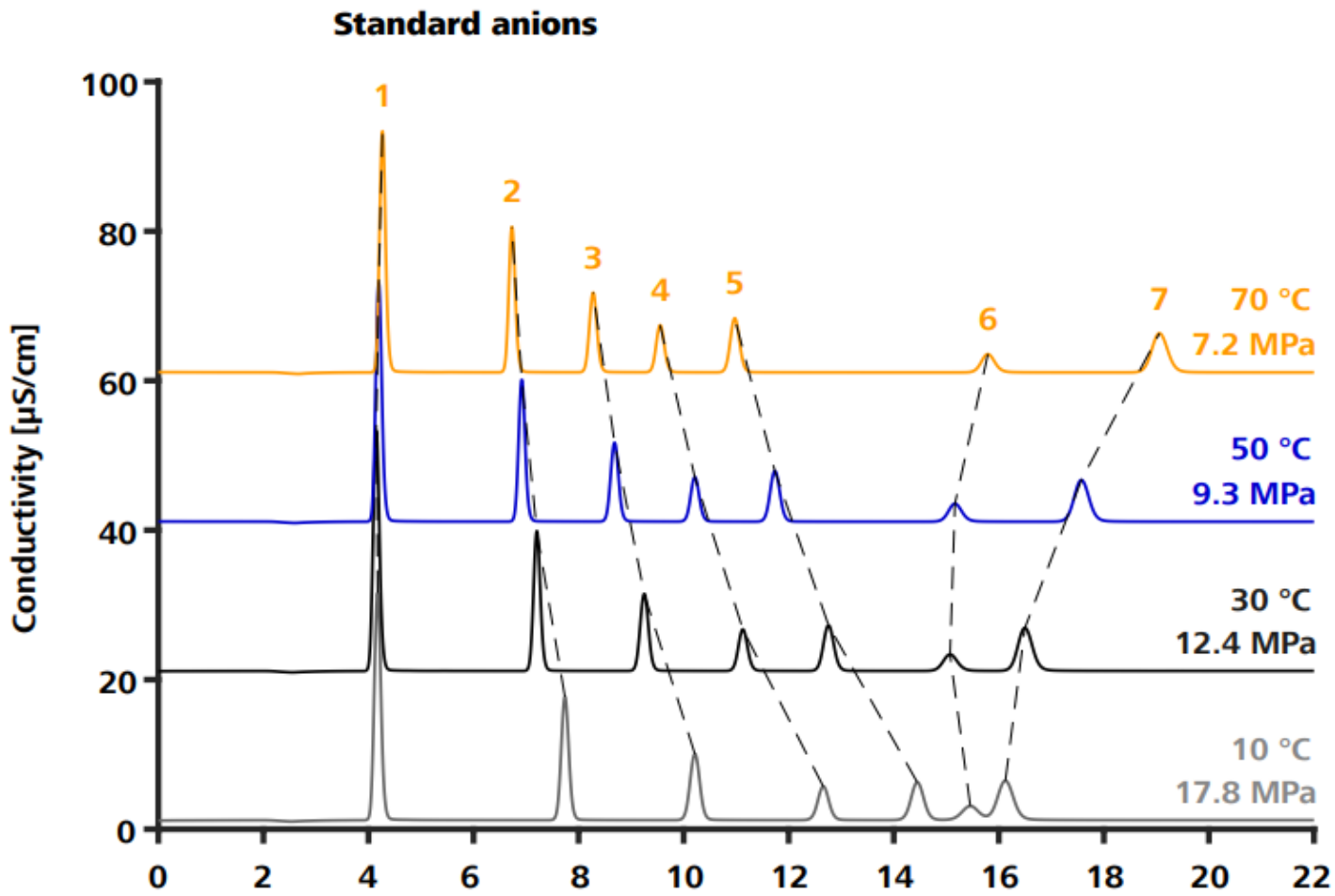


Adding acetone (or other organic solvents) could be useful especially when dealing with organic acids, hydrocarbons, etc.

The eluent will also be made more stable against bacterial contamination.

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Monochloroacetate	10
2	Monobromoacetate	10
3	Dichloracetate	10
4	Dibromacetate	10
5	Trichloroacetate	10

Change in Temperature



5.5.1 Variation of the acetone concentration

Column: Metrosep A Supp 19 - 150/4.0

Sample preparation: –

Detection: Conductivity

Suppression: Sequential suppression with MSM and MCS

Temperature: 30 °C

Loop: 20 µL

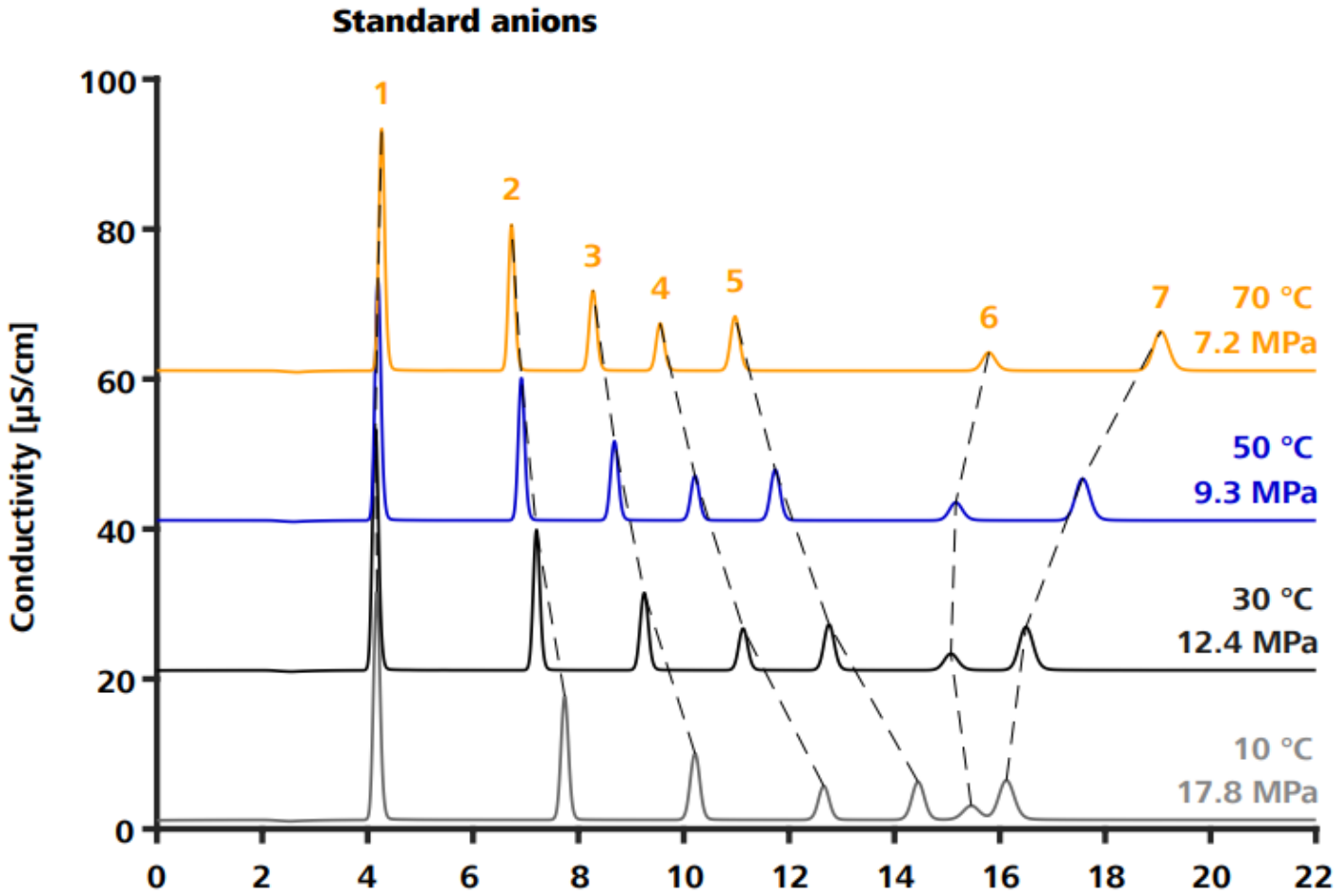
Flow rate: 0.7 mL/min

Eluent: A) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 0% acetone
B) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 10% acetone
C) 0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3, 20% acetone

Time [min]

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Monochloroacetate	10
2	Monobromoacetate	10
3	Dichloracetate	10
4	Dibromacetate	10
5	Trichloroacetate	10

Change in Temperature

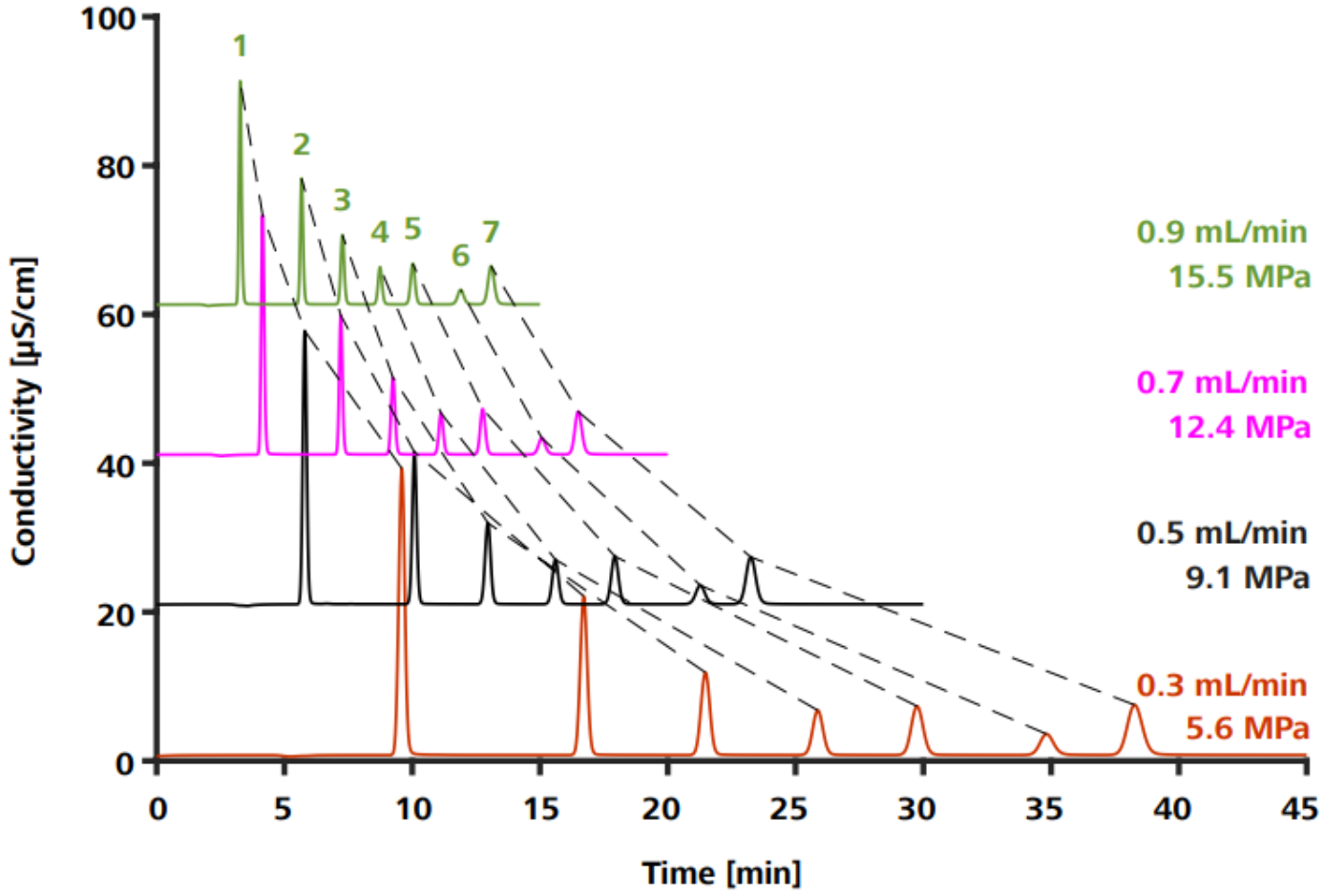


In the monovalent anions (F, Cl, NO2, Br, NO3) retention times (RT) decrease with the increase of temperatures, while the multivalent anion's RT increases.

Also, the Multivalent peaks become sharper.

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Monochloroacetate	10
2	Monobromoacetate	10
3	Dichloracetate	10
4	Dibromacetate	10
5	Trichloroacetate	10

Change in Flow Rate

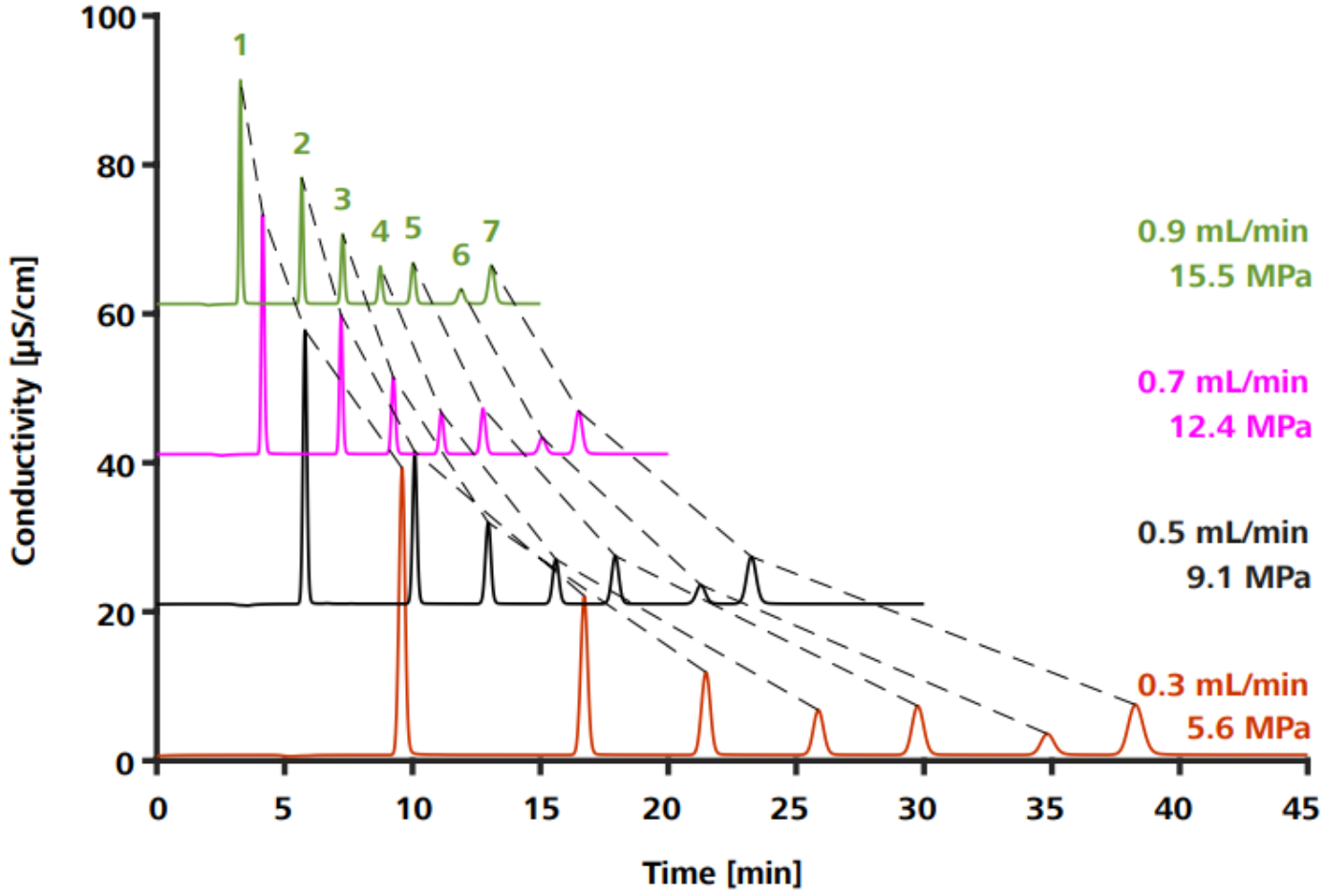


5.3 Variation of the eluent flow rate

Column:	Metrosep A Supp 19 - 150/4.0
Sample preparation:	–
Detection:	Conductivity
Suppression:	Sequential suppression with MSM and MCS
Temperature:	30 °C
Loop:	20 µL
Flow rate:	0.3–0.9 mL/min
Eluent:	0.25 mmol/L $NaHCO_3$, 8.0 mmol/L Na_2CO_3

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Fluoride	10
2	Chloride	10
3	Nitrite	10
4	Bromide	10
5	Nitrate	10
6	phosphate	10
7	Sulfate	10

Change in Flow Rate



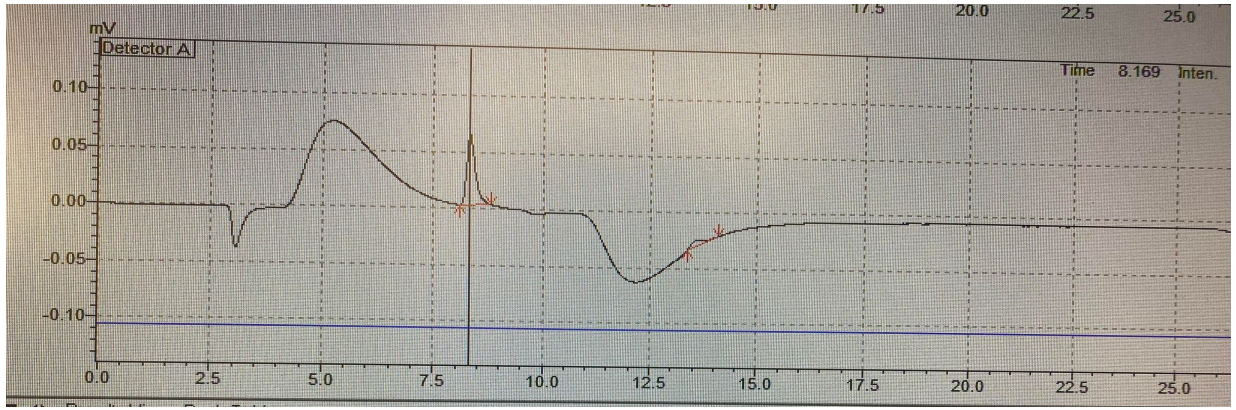
Increasing the flowrate will decrease the retention times for all the anions but at the expense of the peak's area / height.

	Metrosep A Supp 19 - 150/4.0	mg/L
1	Fluoride	10
2	Chloride	10
3	Nitrite	10
4	Bromide	10
5	Nitrate	10
6	phosphate	10
7	Sulfate	10

Sample Prep

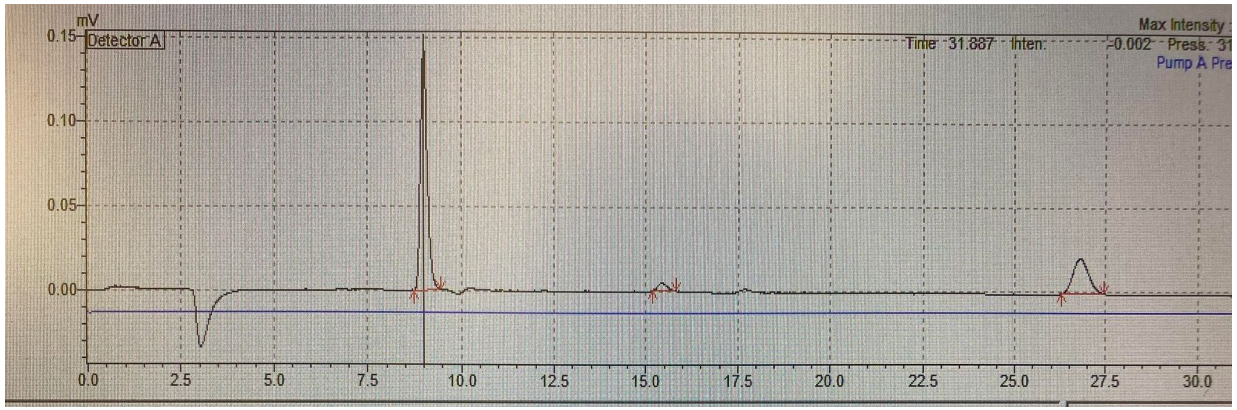
Top Example

Chromatogram of Sodium Hydroxide sample without pretreatment



Bottom Example

Results after passing the Sodium Hydroxide sample through a cartridge



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