Combining the Power of Mass Spectrometry with Ion Chromatography through a Single Software Solution

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Today we will talk about…..

- Perchlorate
  - Background and History
  - Ion Chromatography methods
  - Ion Chromatography with Hyphenated Methods
- What else can we analyze along with Perchlorate?
- Summary

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Perchlorate Background

- Used as rocket propellant
- Used in electroplating industry
- Used in fireworks
- There are also evidence of *"naturally occurring Perchlorate – Chilean fertilizer"*

Why Analyze?

- It is persistent in environment
- It is believed to inhibit Iodine uptake in thyroid gland causing *hypo* thyroidism

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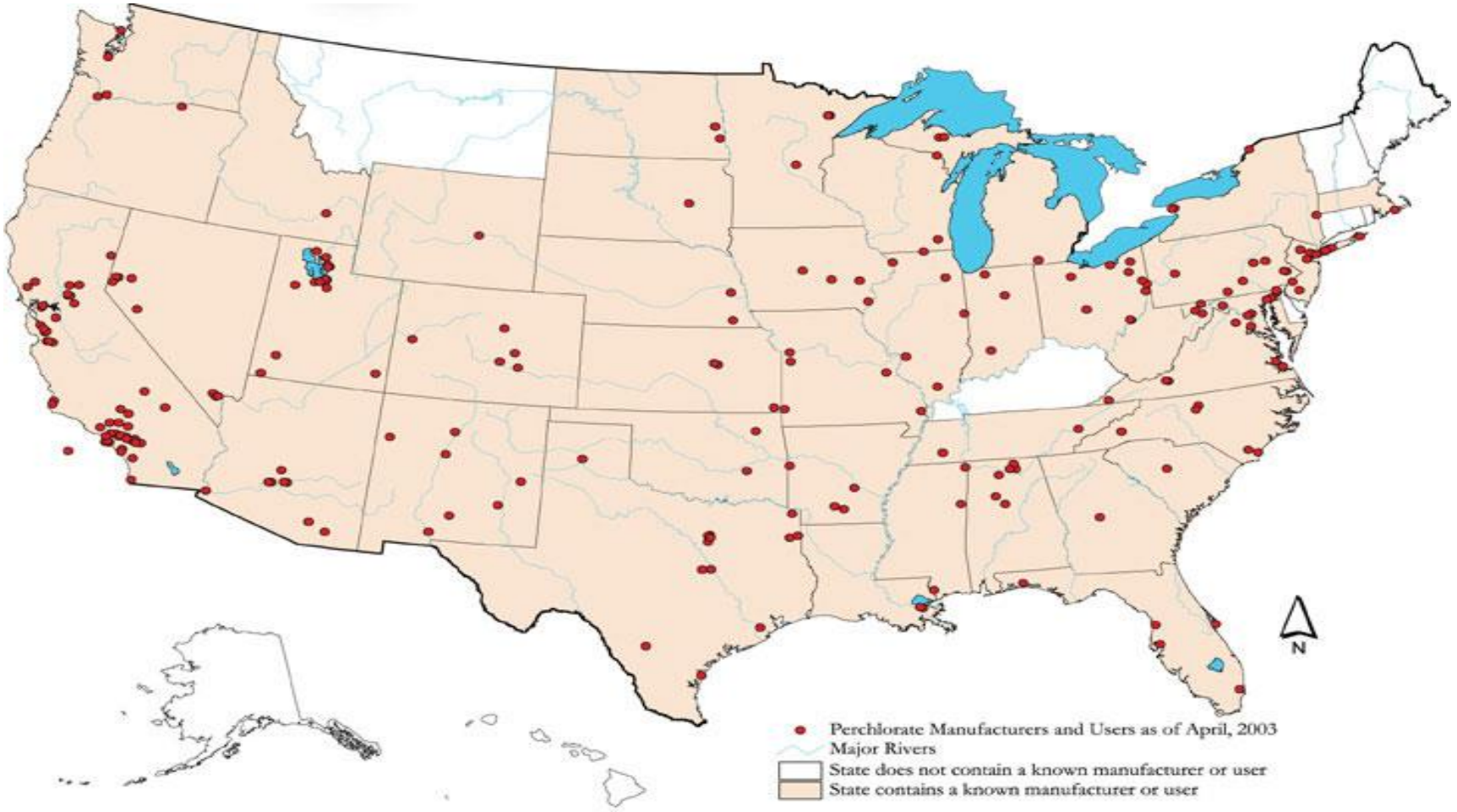
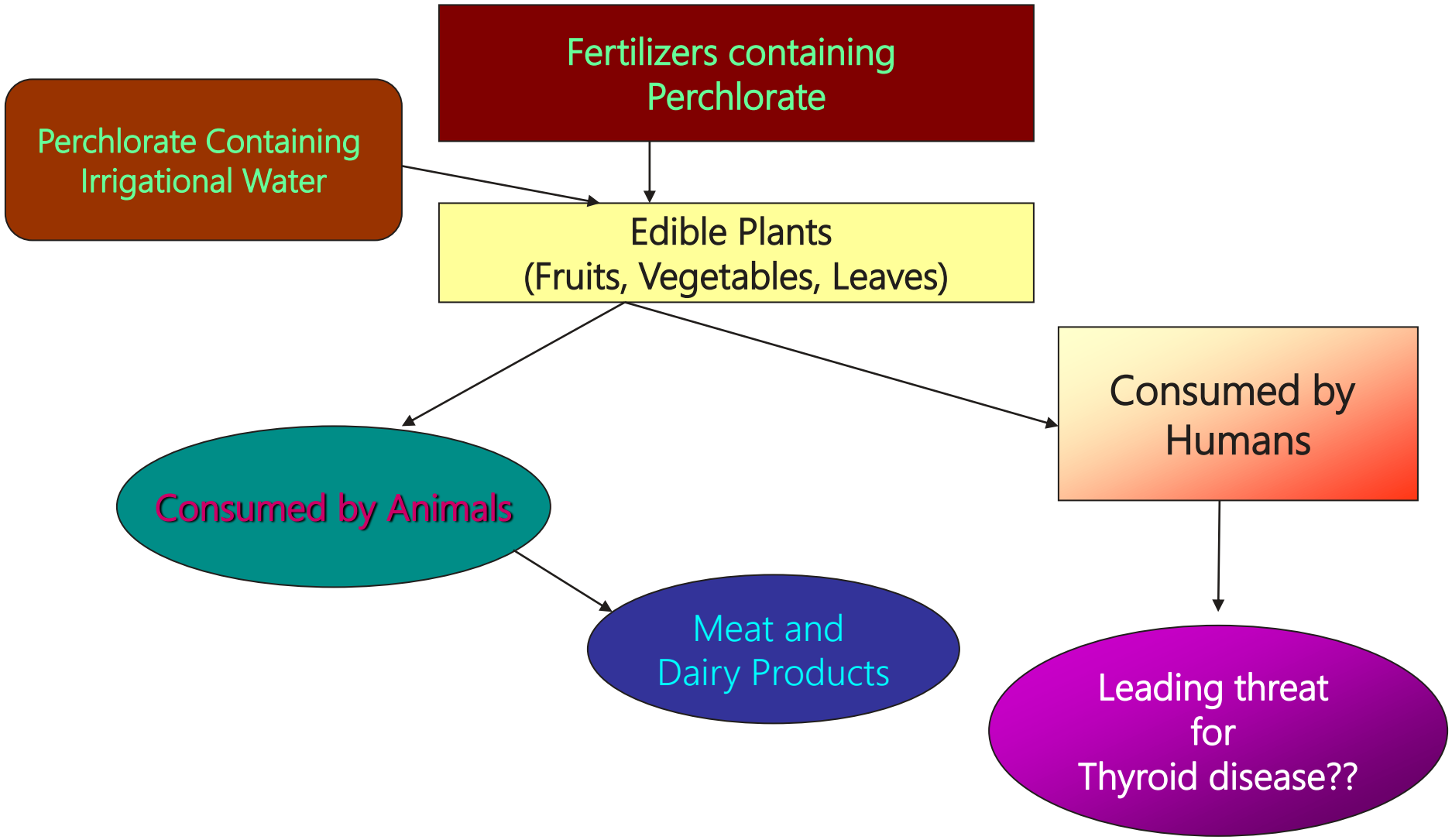
Perchlorate Background



Map provided as public information on USEPA website - 2005

Possible Perchlorate Pathway



Regulatory Timelines

- Under SDWA, USEPA determines which chemical contaminant to regulate (CCL – Contaminant Candidate List)
- Perchlorate was part of
  - CCL1 – 1998
  - CCL2 – 2005
  - CCL3 – 2009
  - UCMR 1 – 2005
  - USEPA decision to regulate – Feb 2011
- In 2006 – State of Massachusetts regulates at 2ppb
- In 2007 – State of California promulgated at 6ppb
  - *Most recent news – State of CA moving to regulate at 1ppb levels*
- 12 Other states has adopted non-enforceable levels

Reference document: https://www.regulations.gov/document?D=EPA-HQ-OW-2009-0297-0685
https://www.epa.gov/dwstandardsregulations/perchlorate-drinking-water

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USEPA Methods

- **Perchlorate**
  - USEPA 314.0 enhanced
  - USEPA 314.1
  - USEPA 314.2
  - USEPA 332.0 / SW846 6860
  - USEPA 331.0 / SW846 6850

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USEPA Methods

- Perchlorate
  - USEPA 314.0 enhanced
  - ~~USEPA 314.1~~
  - ~~USEPA 314.2~~
  - USEPA 332.0 / SW846 6860
  - ~~USEPA 331.0 / SW846 6850~~

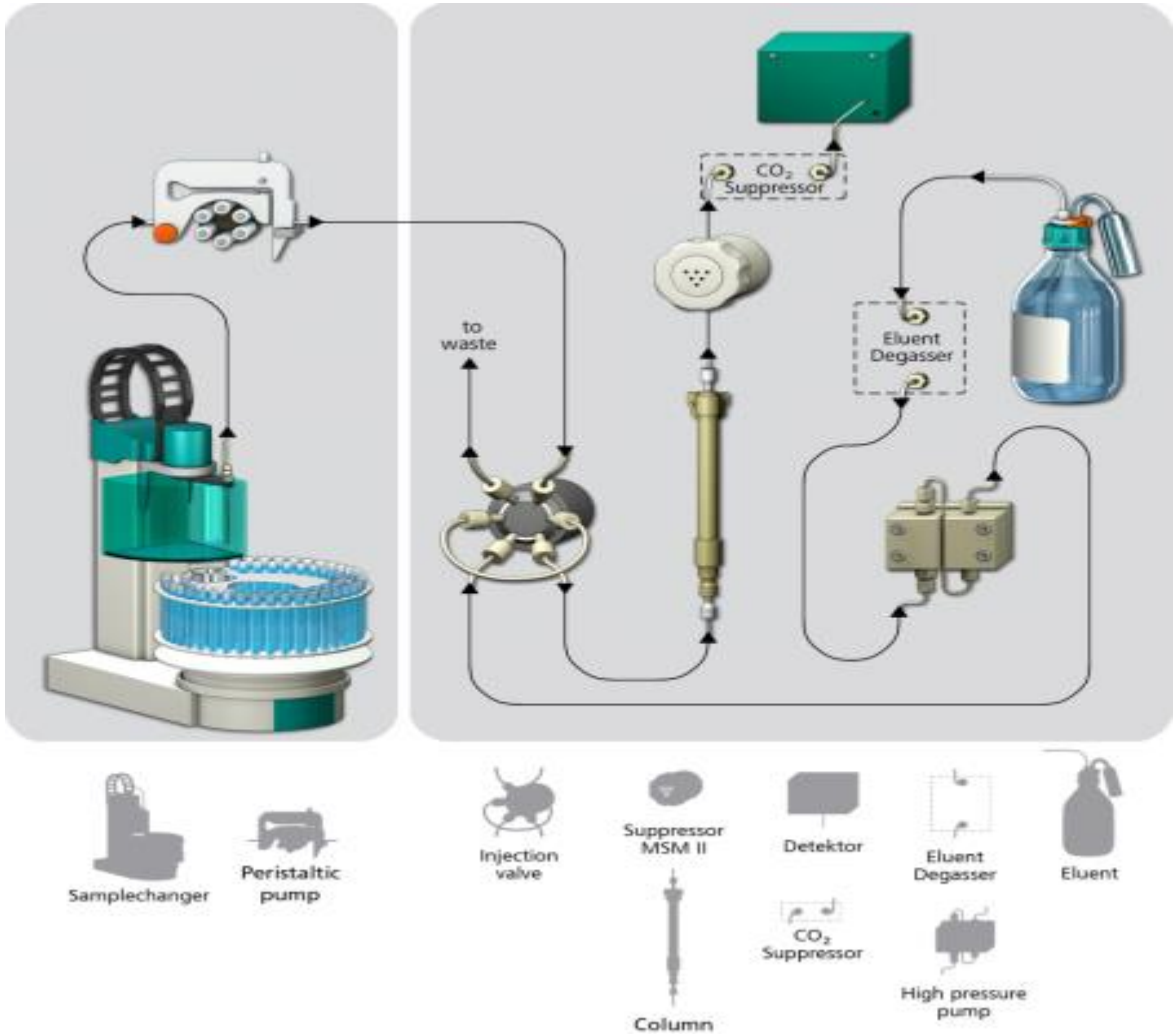
US EPA method 314.0 enhanced

Perchlorate by Suppressed Conductivity

AW US6-0071
AW US6-0241

USEPA method 314.0 (enhanced)

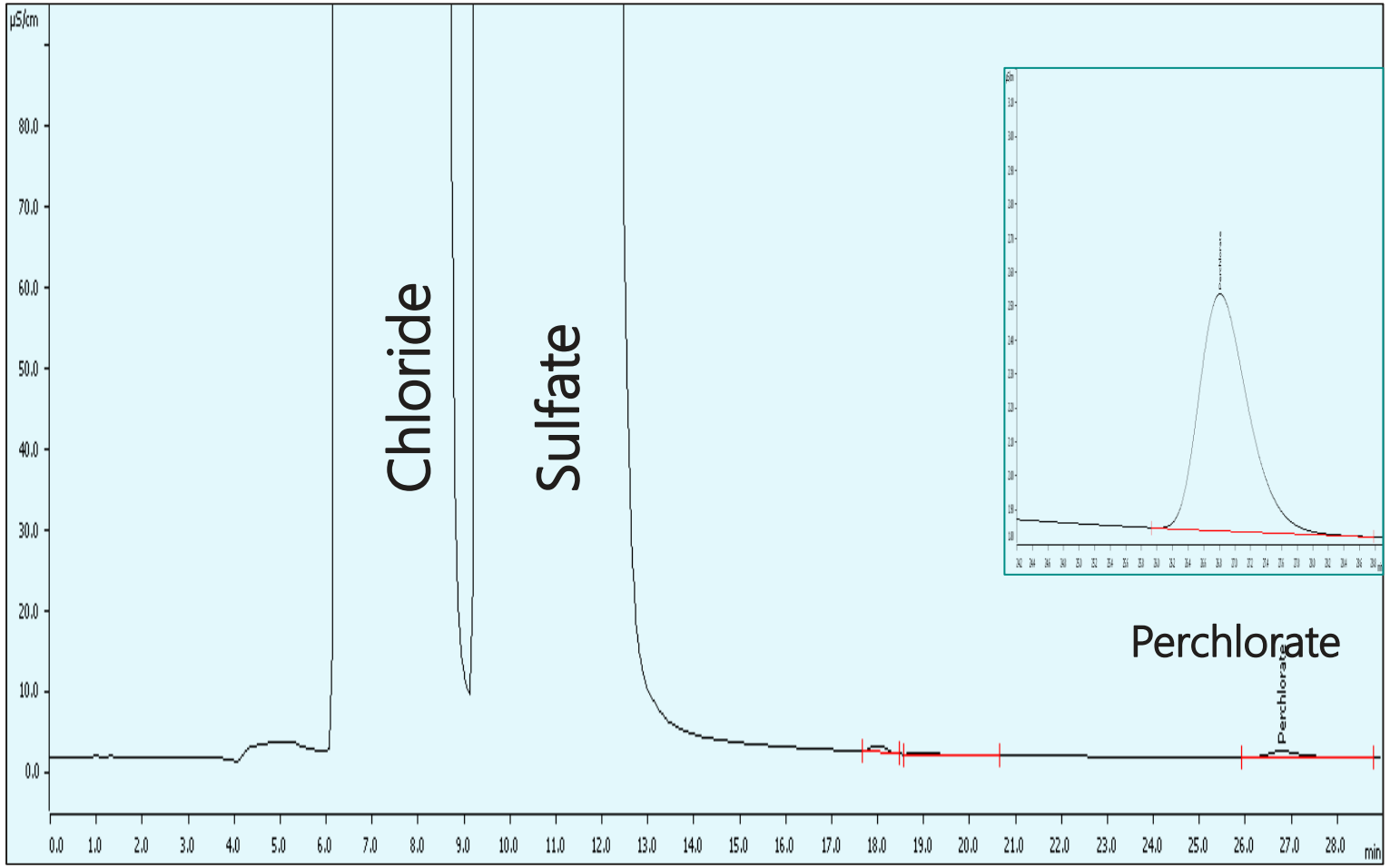
Using a Functionalized Monolithic Column or Anion Exchanger Column



USEPA 314.0 - Perchlorate Standard in Matrix

Eluent flow	0.7 mL/min
Eluent	10.5mM Na_2CO_3 + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	1000 µL
Detector	Suppressed Conductivity

Component Name	Retention Time, mins	Concentration, mg/L
Chloride	7.5	1000
Sulfate	11.5	1000
Perchlorate	26.8	0.005

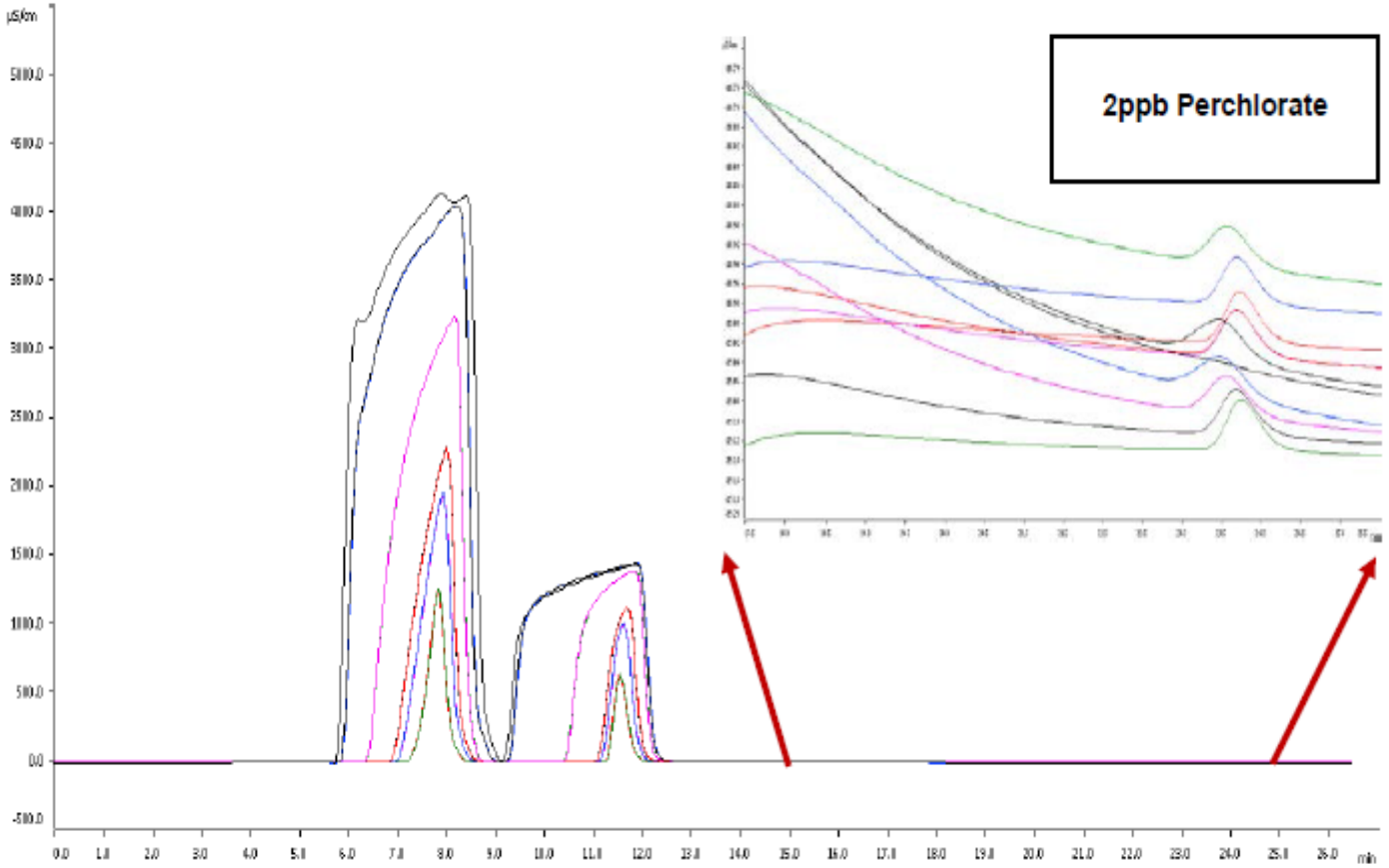


USEPA 314.0 MCT Study

Eluent flow	0.7 mL/min
Eluent	10.5mM Na_2CO_3 + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	1000 µL
Detector	Suppressed Conductivity

Component Name	Retention Time, mins	Concentration, mg/L
Chloride	9.28	50 - 1000
Sulfate	19.7	50 - 1000
Perchlorate	24.8	0.002

Maximum Conductivity Threshold Study (MCT Study)



MCT Study Data (USEPA method 314.0, section 9)

MCT Study Data	
	Perchlorate, PGF
3000ppm TDS Matrix (n=5)	1.01
1500ppm TDS Matrix (n=5)	0.98
750ppm TDS Matrix (n=5)	0.94
300ppm TDS Matrix (n=5)	0.95
150ppm TDS Matrix (n=5)	0.93
50ppm TDS Matrix (n=5)	0.96

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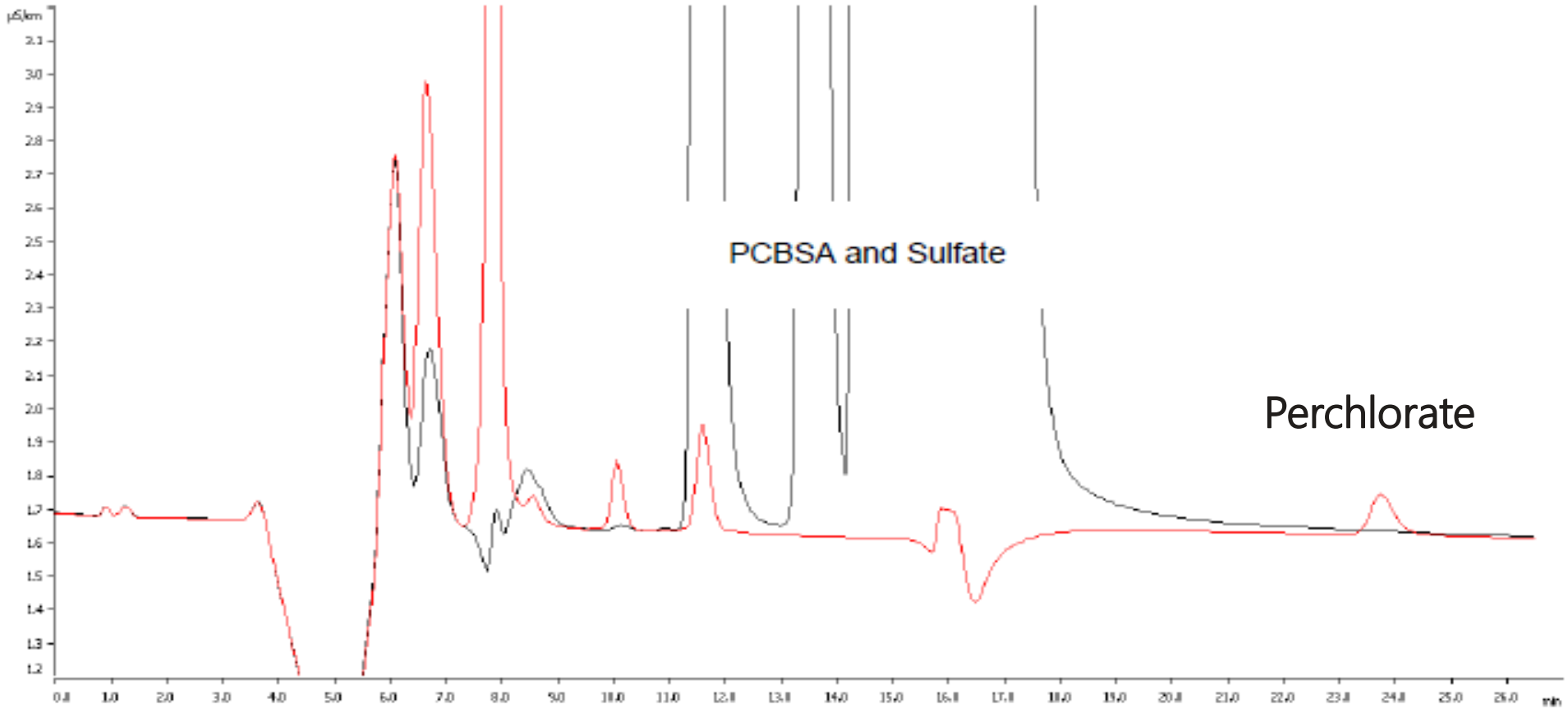
Major Interference – PCBSA



USEPA Method 332.0

+

OR

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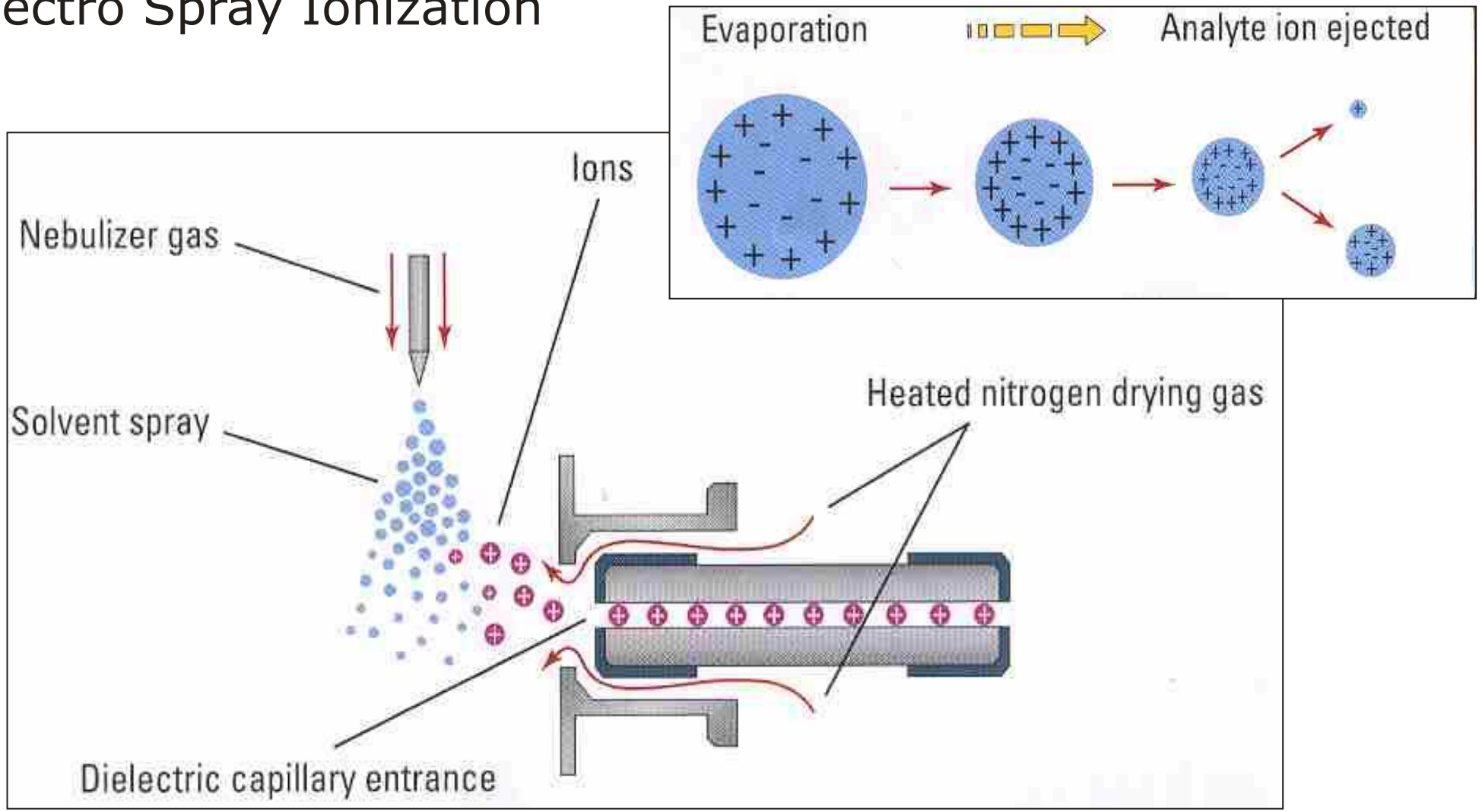
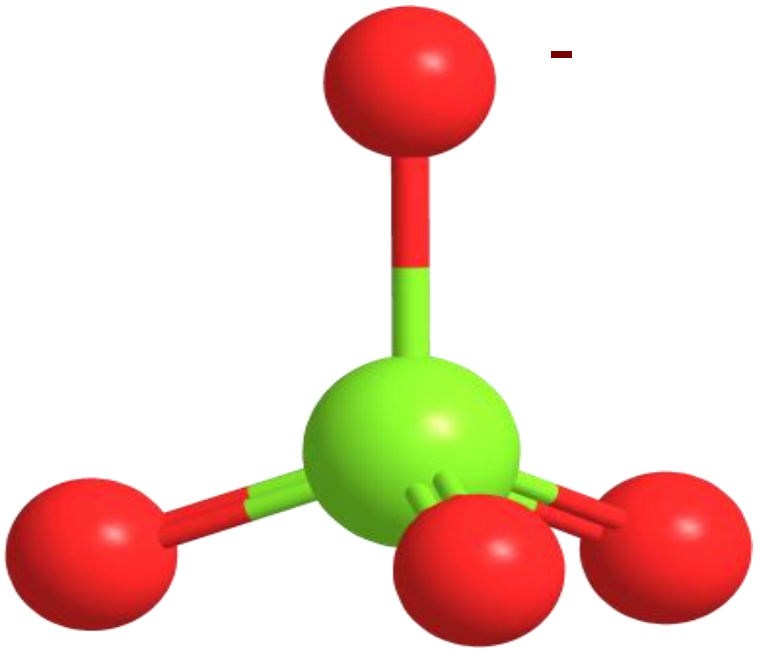
IC-MS

Electro Spray Ionization



Perchlorate Mass



Chlorine (Cl) = 35

+

4 x Oxygen (O) = 4 x 16 = 64

Perchlorate mass (Cl^{35}) = 35 + 64 = 99	→ 75%
Perchlorate mass (Cl^{37}) = 37 + 64 = 101	→ 25%

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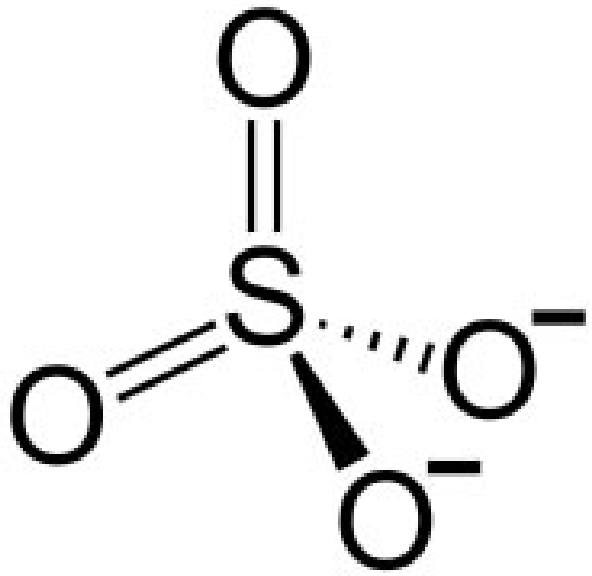
Perchlorate Mass / interference



Sulfate Ion

Sulfur (S) = 32

+

4 x Oxygen (O) = 4 x 16 = 64

HSO_4^{-1} (S^{32}) =
1+32 + 64 = 97

HSO_4^{-1} (S^{34}) =
1+32 + 64 = 99

→ 4%

4% of 1000 parts per million = 40 parts per million OR
40,000 parts per billion

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USEPA method 332.0 / SW846 6860

Perchlorate by ICMS / ICMSMS

In Collaboration with
USEPA (ODW-OGW / OSW)

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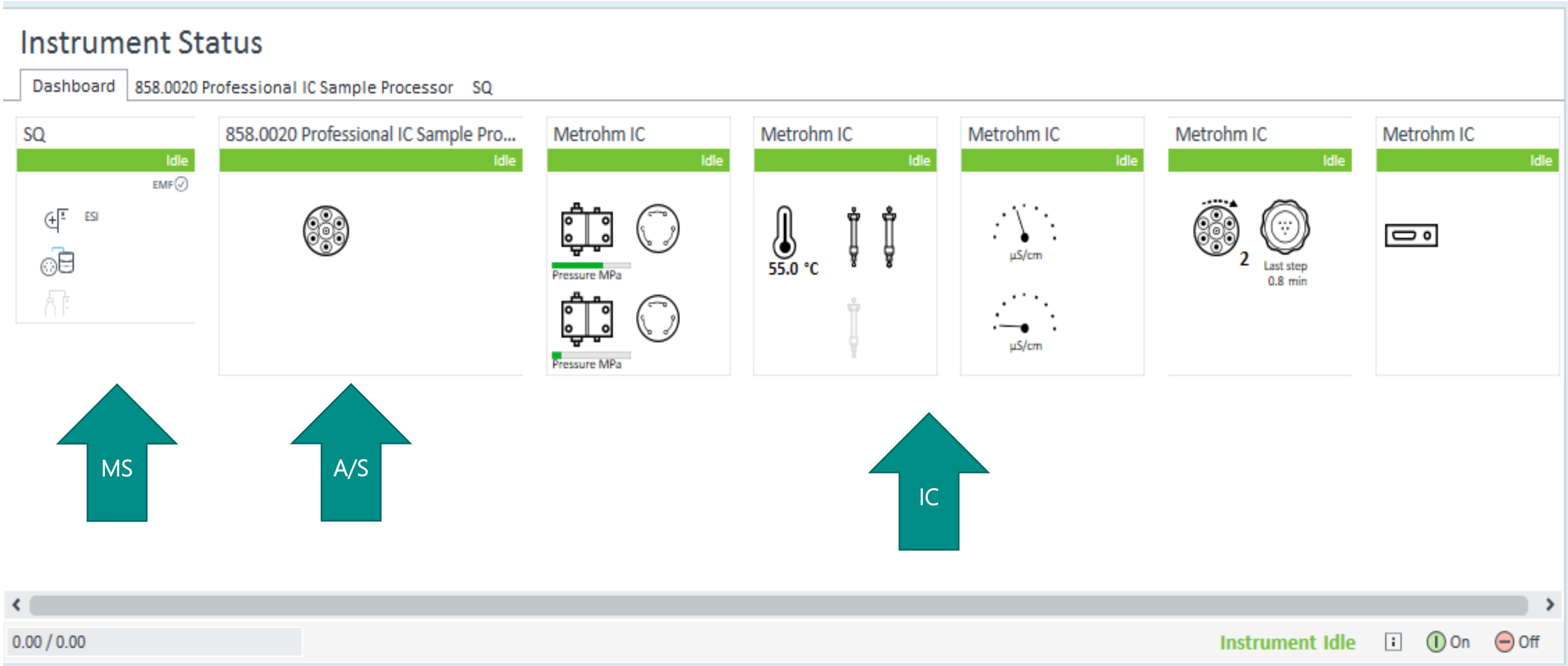
Metrohm Advanced IC – Agilent iQMSD

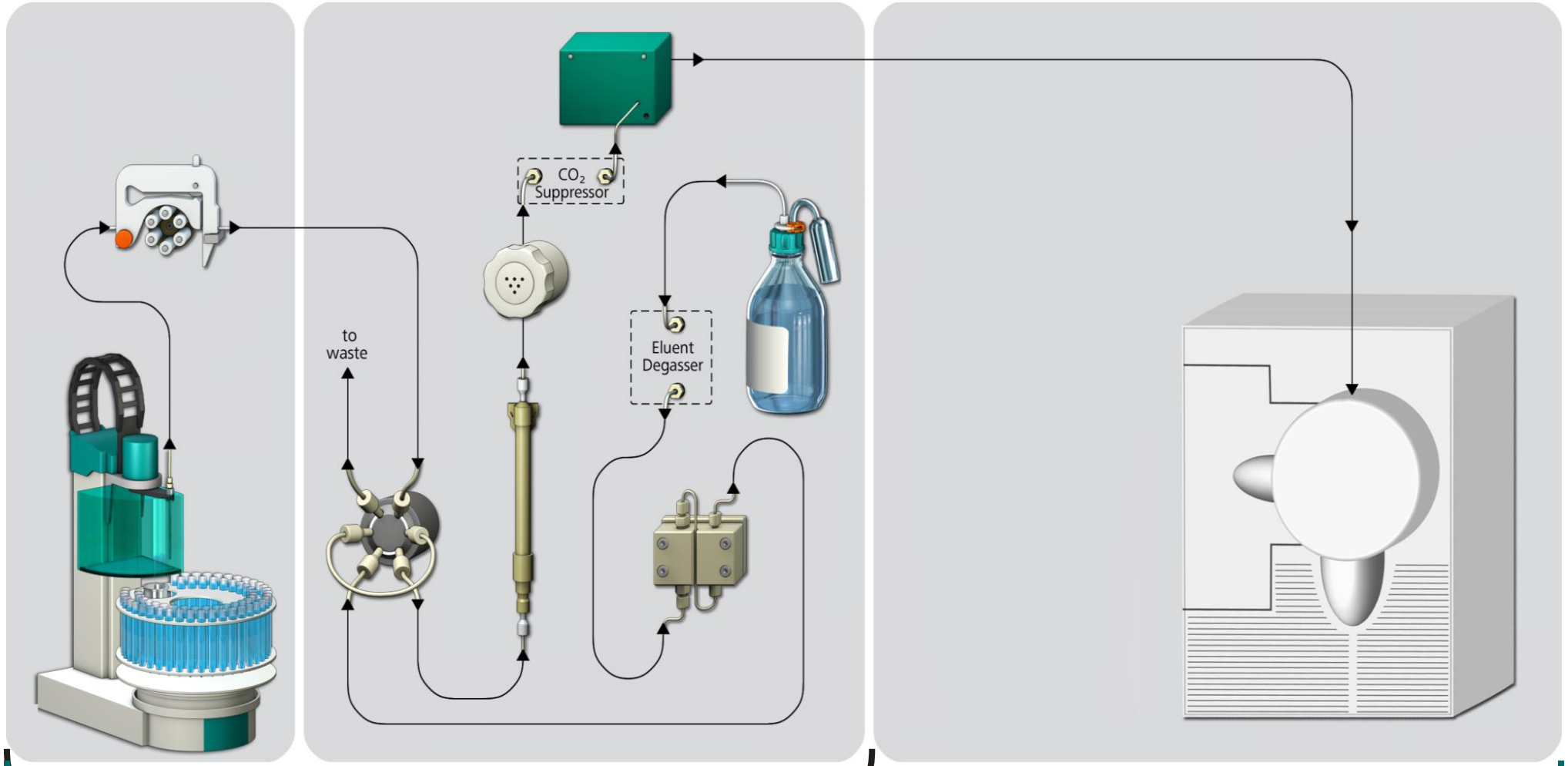
Features

- Advanced Metrohm IC
  - Inline Cross flow filtration (optional)
  - Variable Volume Injection (optional)
- Agilent iQMSD
  - Standard ESI
- Open Lab CDS software for IC and MS control

Agilent Open Lab CDS



USEPA method 332 / SW846 6860



USEPA Method 314.0

USEPA Method 332.0

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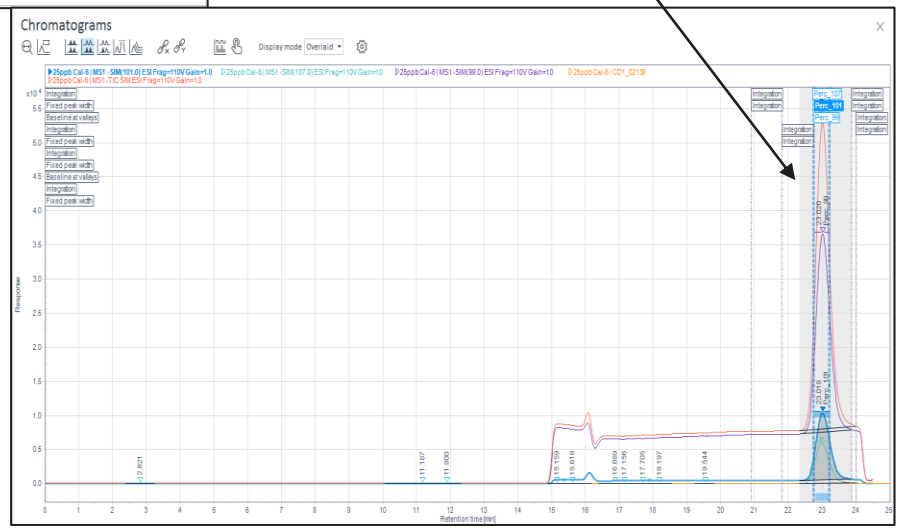
Chromatography

USEPA 332.0 –Calibration 0.5ppb & 25ppb - ICMS

Eluent flow	0.7 mL/min
Eluent	10.5mM Na_2CO_3 + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	100 µL
Detector	Agilent iQ MSD

Perchlorate



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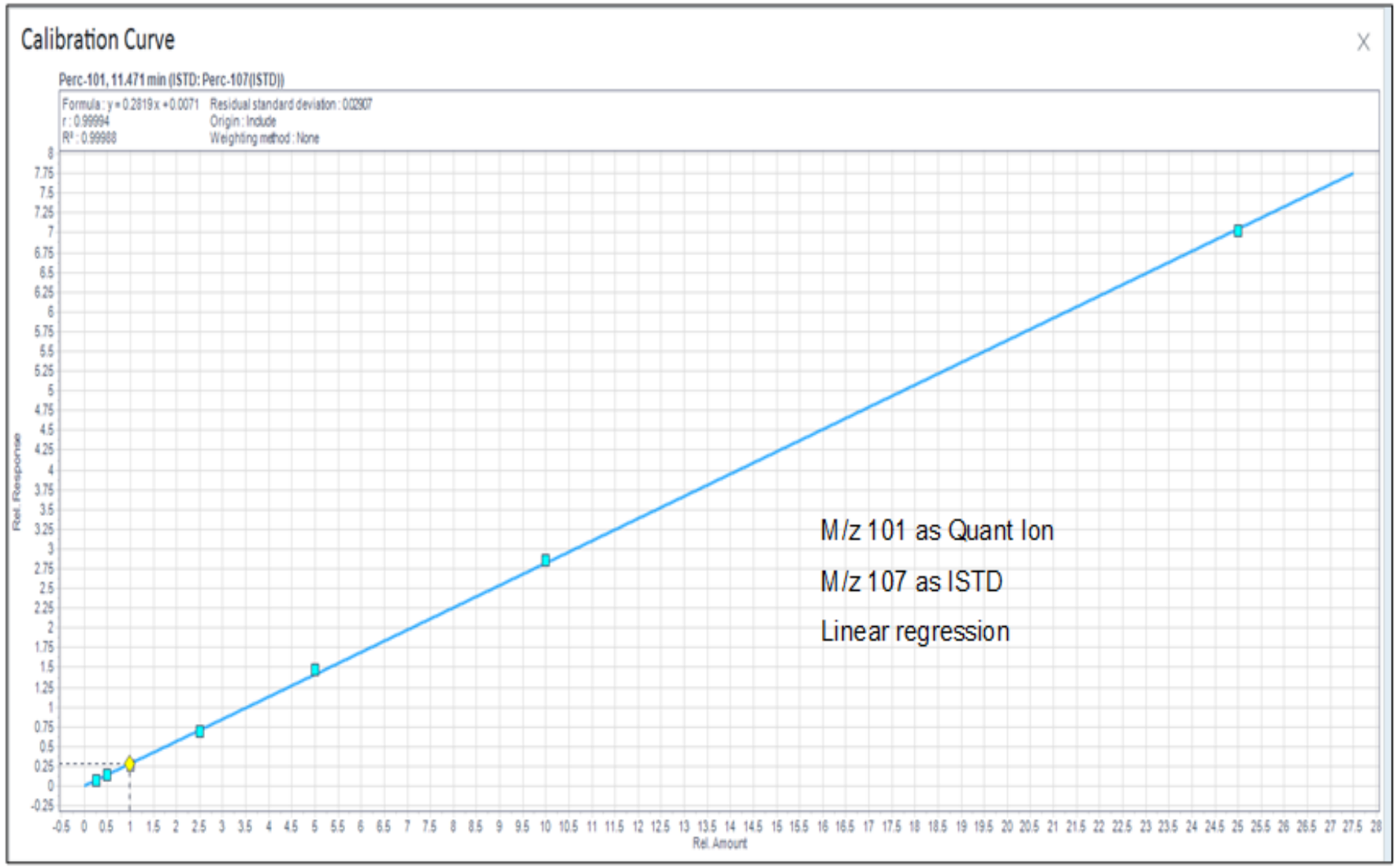
Perchlorate Calibration

AW IC US6-0240
AW IC US6-0244
AW IC US6-0291



m/z 101
Range for
Calibration Standards
0.25ppb to 25ppb (ClO_4^{1-})

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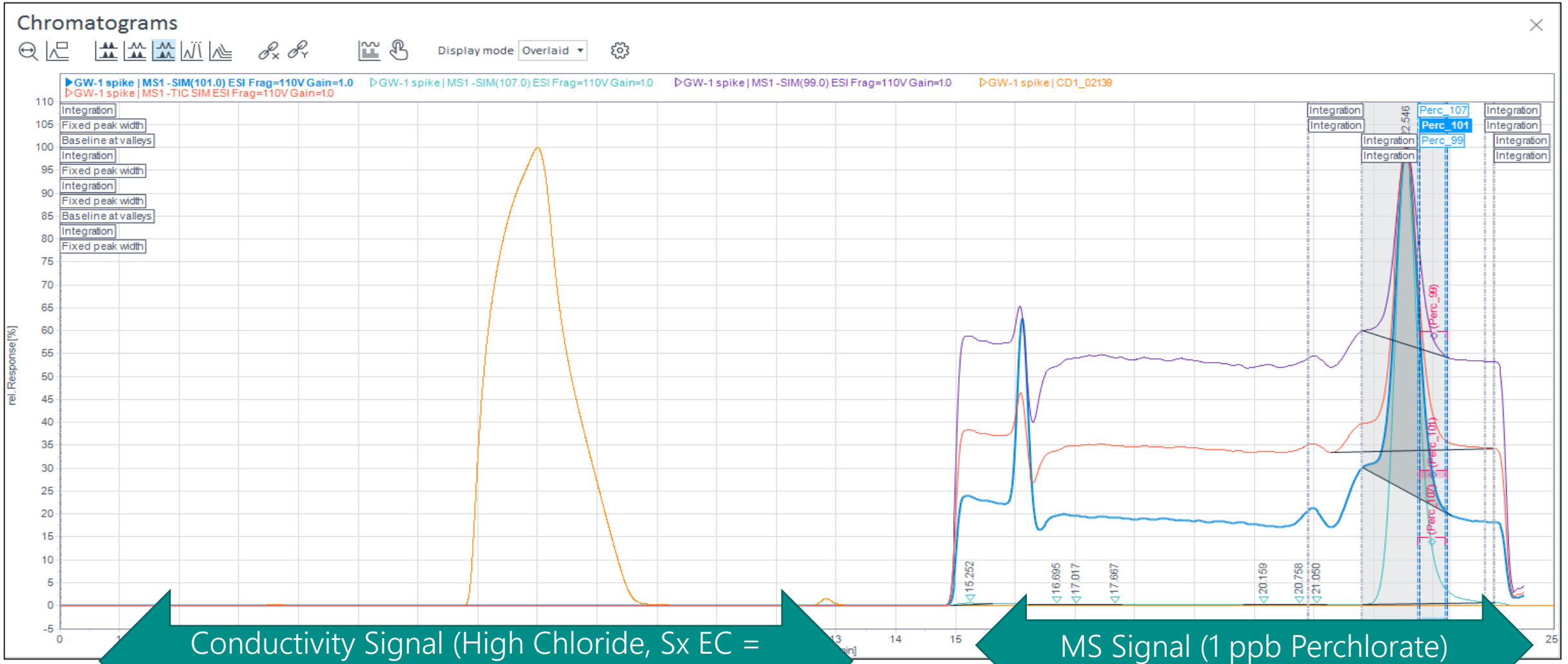
Real World Samples (example of Samples from CA)



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Real World Samples (example of Samples from Houston, TX)

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Reproducibility Data

Sample ID	m/z 99	m/z 101
0.5 µg/L standard	0.475	0.448
0.5 µg/L standard	0.468	0.472
0.5 µg/L standard	0.459	0.506
0.5 µg/L standard	0.463	0.483
0.5 µg/L standard	0.473	0.483
0.5 µg/L standard	0.475	0.495
0.5 µg/L standard	0.486	0.495
Average	0.4713	0.4831
Std. Dev	0.01784	0.01899
Calculated MDL (µg/L)	0.056	0.060

Sample ID	m/z 99	m/z 101
3000ppm Matrix + 1µg/L ClO_4	0.96	1.08
3000ppm Matrix + 1µg/L ClO_4	1.01	0.98
3000ppm Matrix + 1µg/L ClO_4	1.01	0.99
3000ppm Matrix + 1µg/L ClO_4	0.93	0.95
3000ppm Matrix + 1µg/L ClO_4	1.08	0.96
3000ppm Matrix + 1µg/L ClO_4	1.02	0.98
3000ppm Matrix + 1µg/L ClO_4	0.97	0.92
Average	0.9971	0.9800
Std. Dev	0.04889	0.05000
Calculated MDL (µg/L)	0.154	0.157

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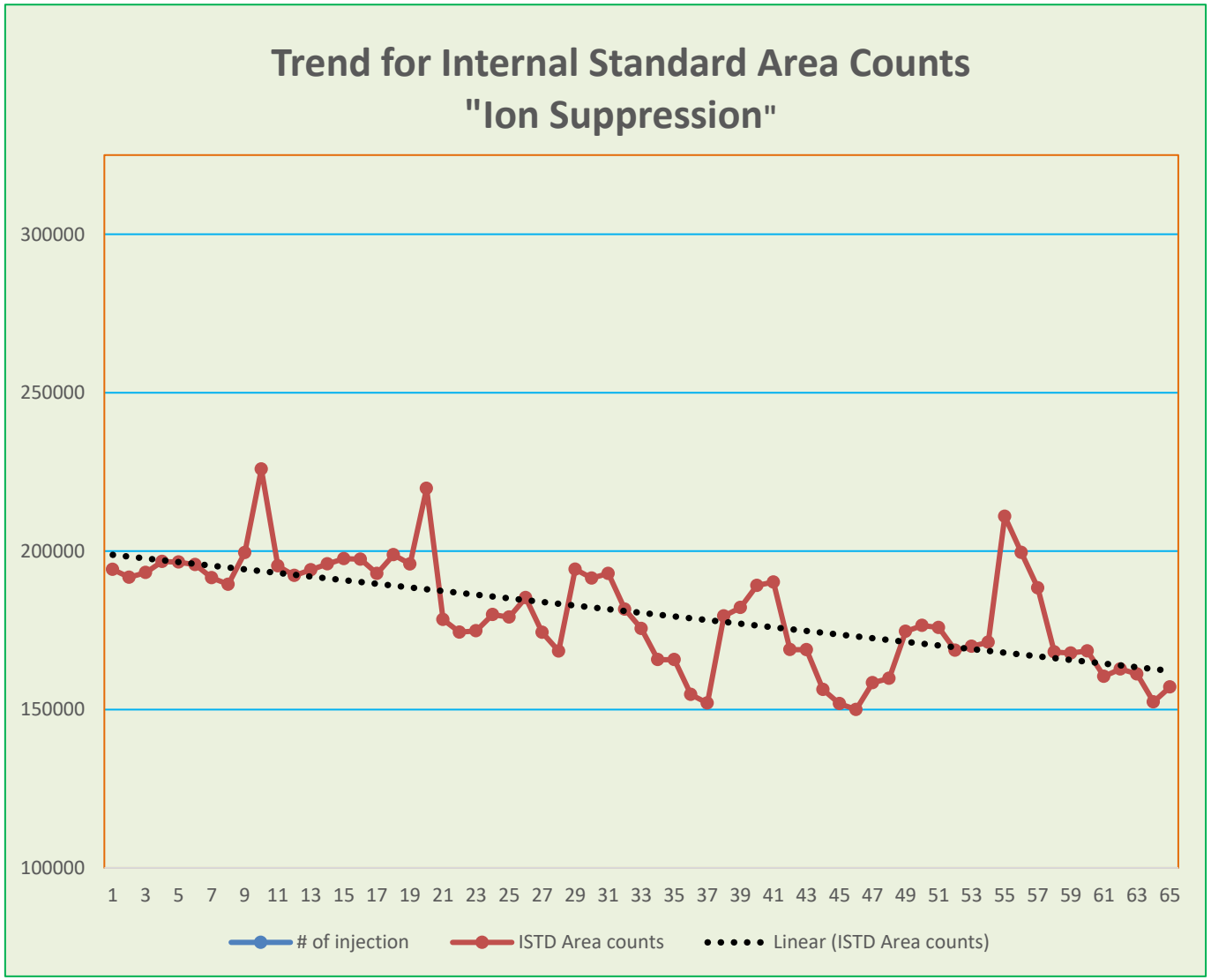
What is Ion Suppression

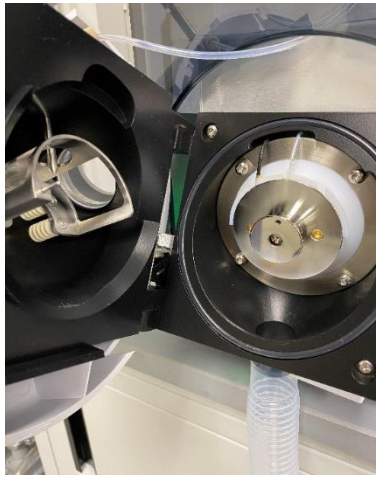
- In LCMS / ICMS world, this is commonly known term
- Explanation of “ion suppression”

Effects of Ion Suppression



- Trendline indicates and demonstrates the "ionic suppression"
- However, "ionic suppression" has no significant loss in ESI performance

Before analysis



After 150+ injections

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Summary

- Metrohm and Agilent Developed
  - Single software platform for ICMS analysis
  - Simple, rugged and isocratic analysis for Perchlorate
  - Environment friendly Carbonate chemistry for analytical column
  - Chromatographically resolved challenging matrices and interferences like
    - 3000 parts per million TDS (1000ppm each of Chloride, Carbonate and Sulfate)
    - Industrial surfactant like p-Chloro Benzene Sulfonic Acid (PCBSA)
- 100% Solvent compatible IC hardware allowed to hyphenate with
  - Single Quad MSD

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Thank You

Be one of the forward thinking organizations that have experienced our full product portfolio

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