



Trace Level Determination of Perchlorate in Various Water Matrices by Tandem Suppressed Conductivity and Mass Spectroscopy

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August 7th – 11th, 2017*

Presented by

Jay Gandhi, PhD

Today we will talk about....

- **Perchlorate**
 - Background and History
 - Ion Chromatography methods
 - Ion Chromatography with Hyphenated Methods
- **Summary**

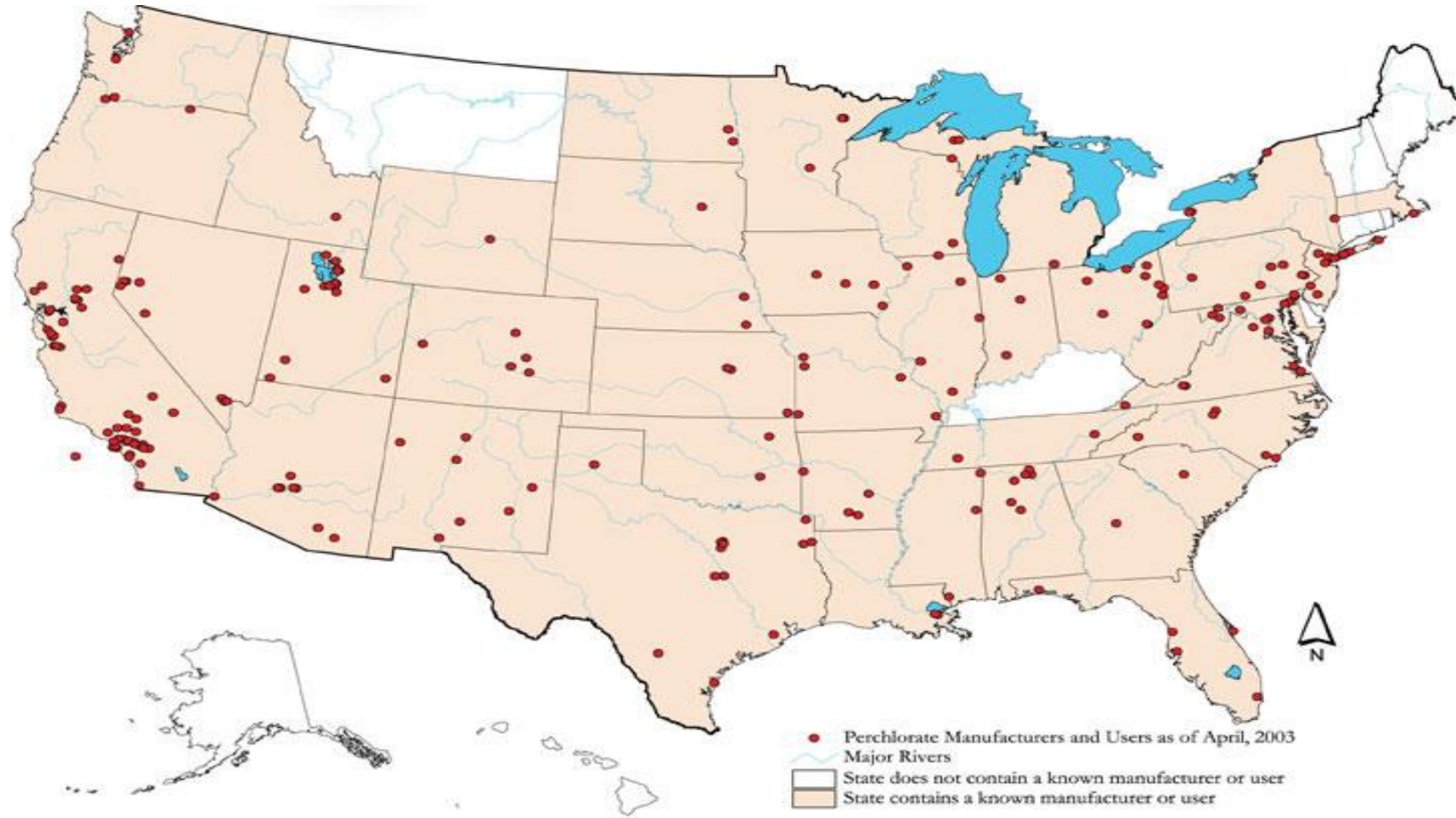
Perchlorate Background

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

Why Analyze?

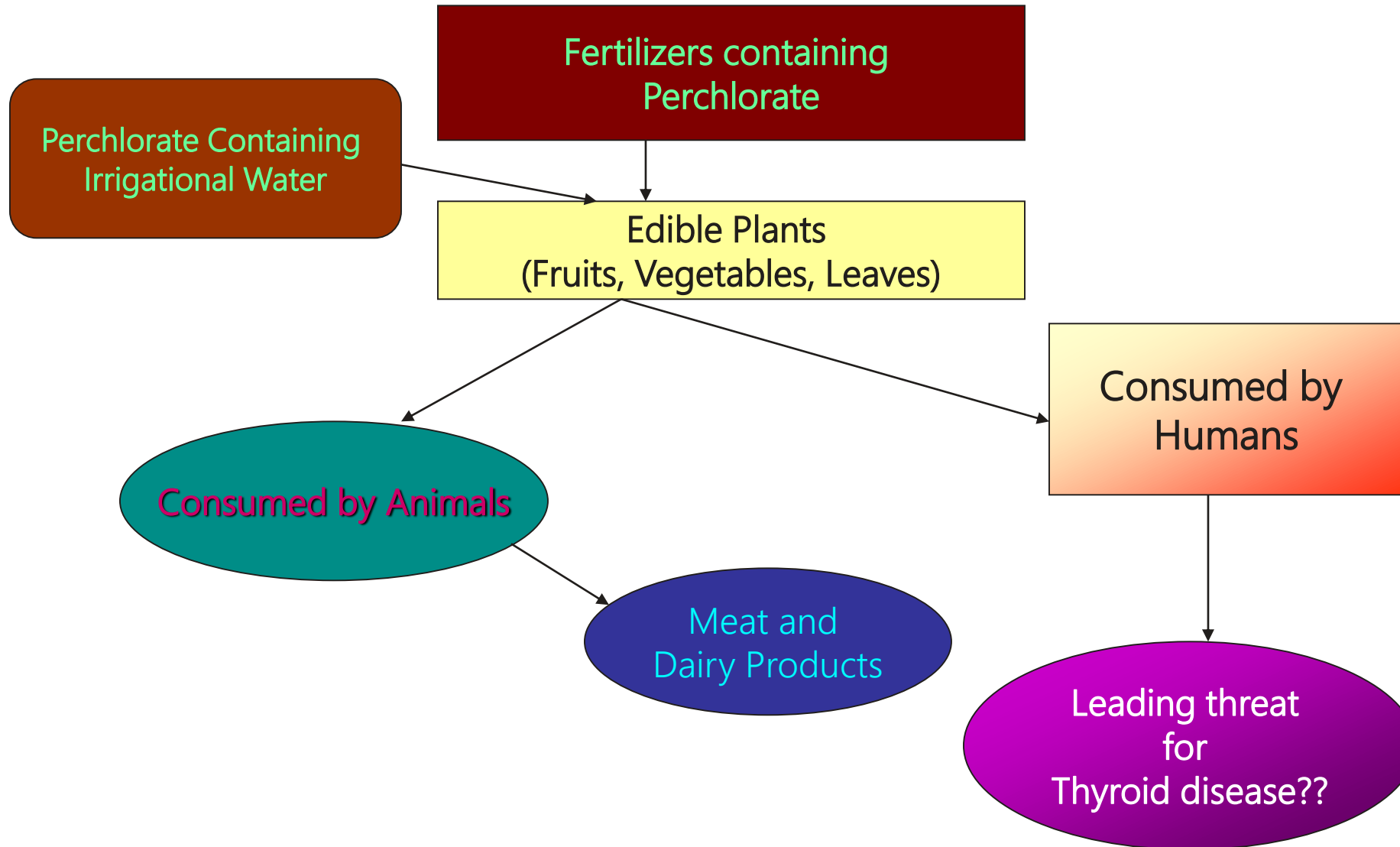
- It is persistent in environment
- It is believed to inhibit Iodine uptake in thyroid gland causing *hypo* thyroidism

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
- 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>

USEPA Methods

- **Perchlorate**

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

USEPA Methods

- Perchlorate

- ~~USEPA 314.2~~

- USEPA 314.0 enhanced

- USEPA 332.0 / SW846 6860

- USEPA 331.0 / SW846 6850

- ~~USEPA 314.1~~

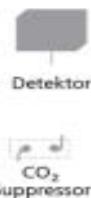
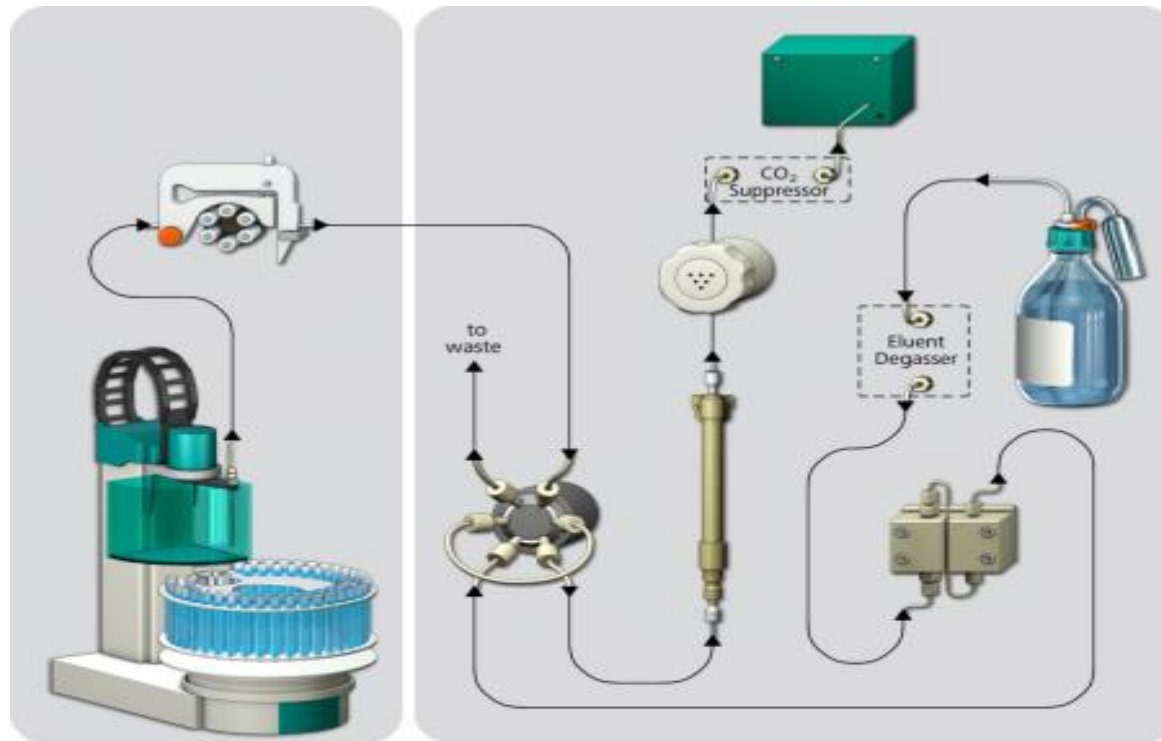
US EPA method
314.0 enhanced
Perchlorate
by Suppressed Conductivity

USEPA method 314.0 (enhanced)

AW US6-0071

AW US6-0241

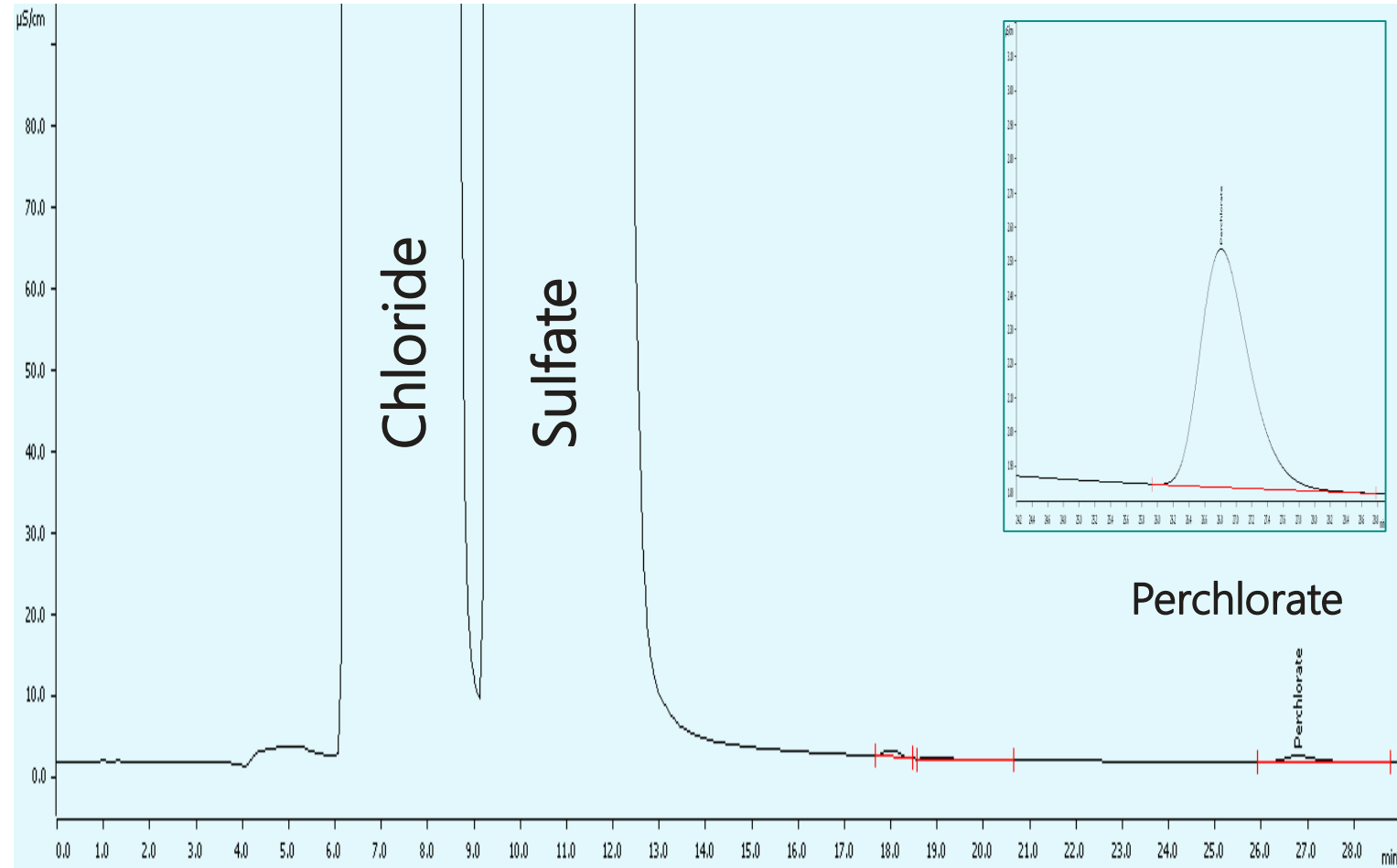
Using a Functionalized Monolithic Column or Anion Exchange Column



USEPA 314.0 - Perchlorate Standard in Matrix

Eluent flow	0.7 mL/min
Eluent	10.5mM Na ₂ CO 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

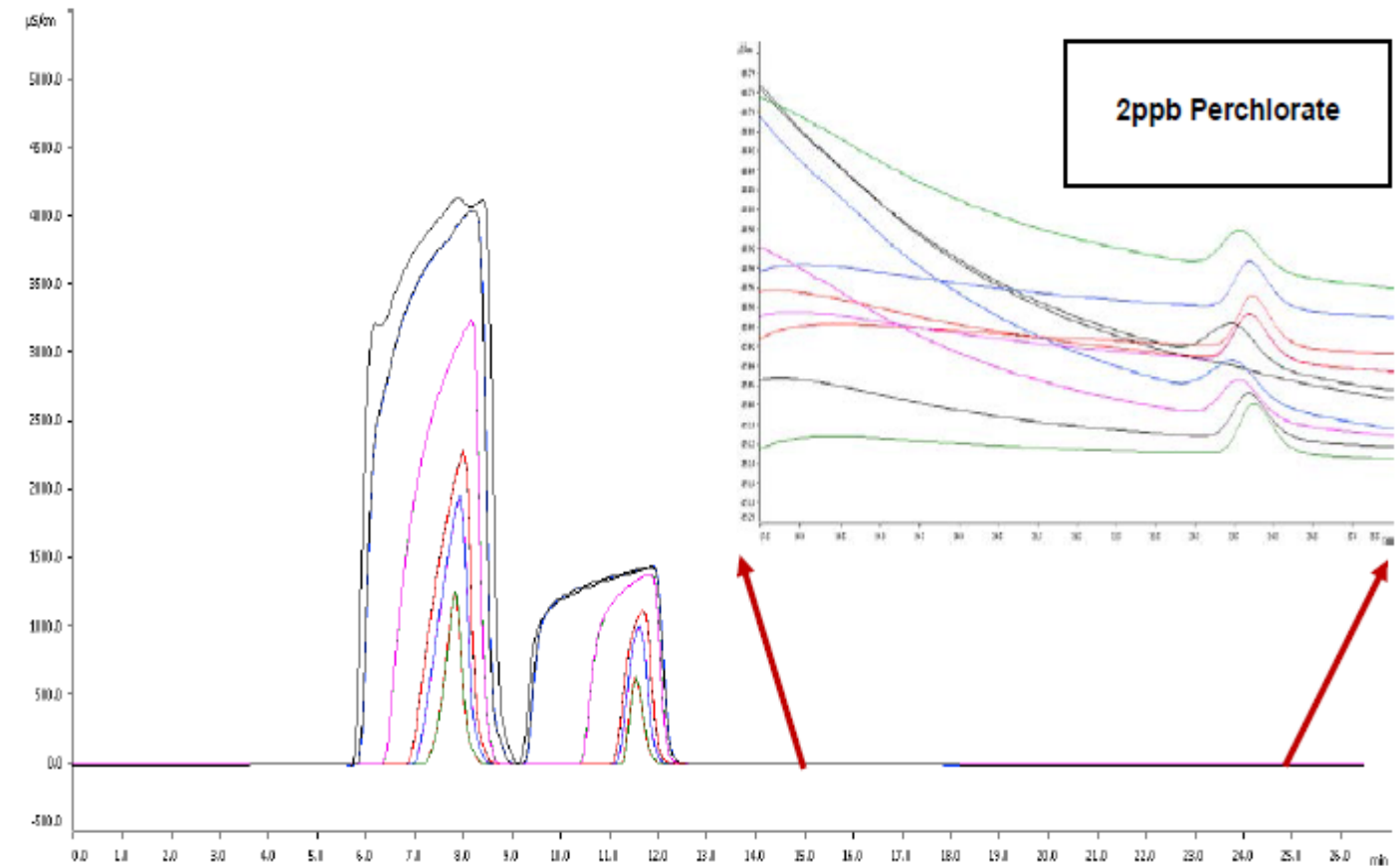


USEPA 314.0 MCT Study

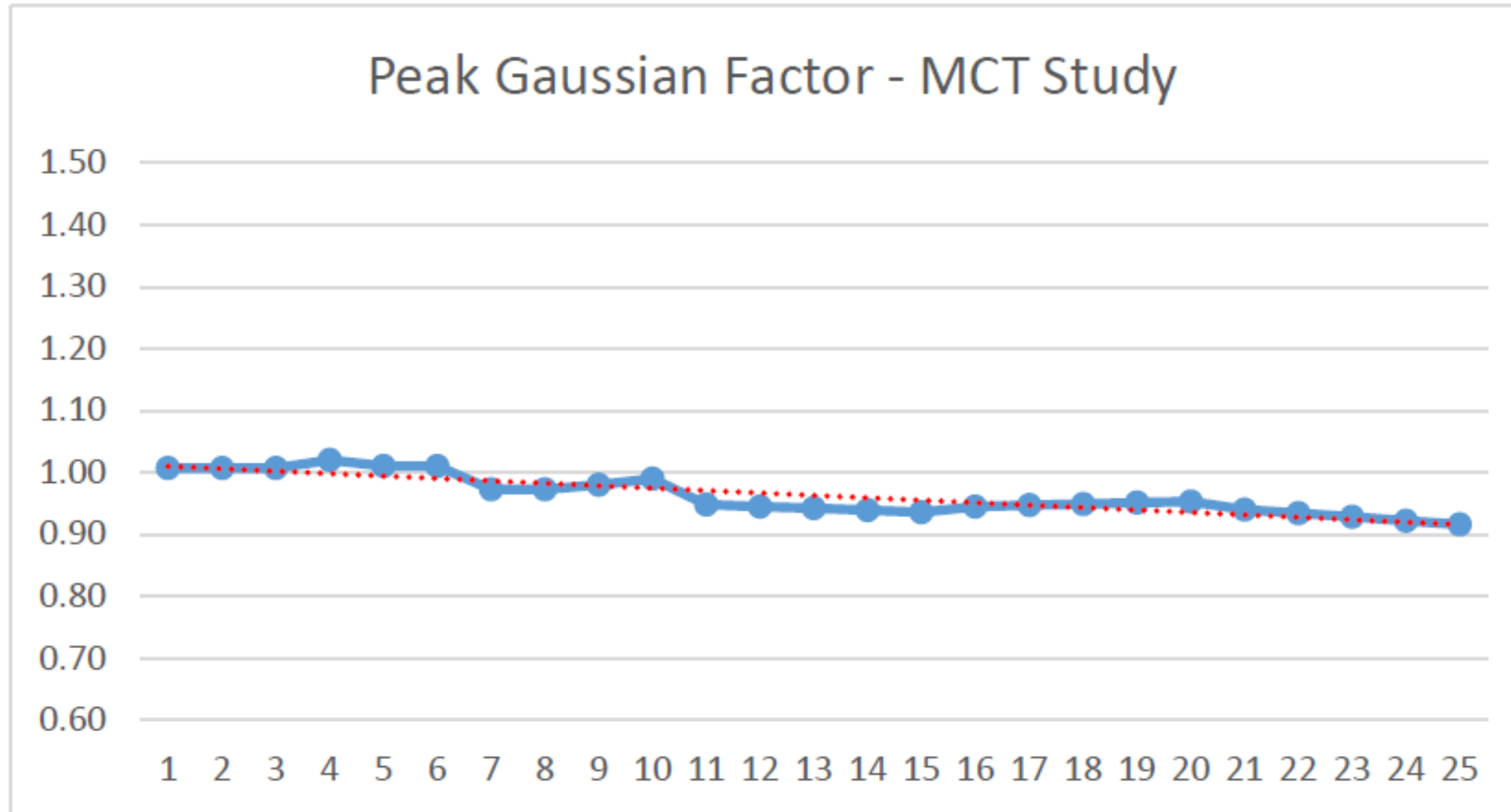
Eluent flow	0.7 mL/min
Eluent	10.5mM Na ₂ CO ₃ + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	1000 µL
Detector	Suppressed Conductivity

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)

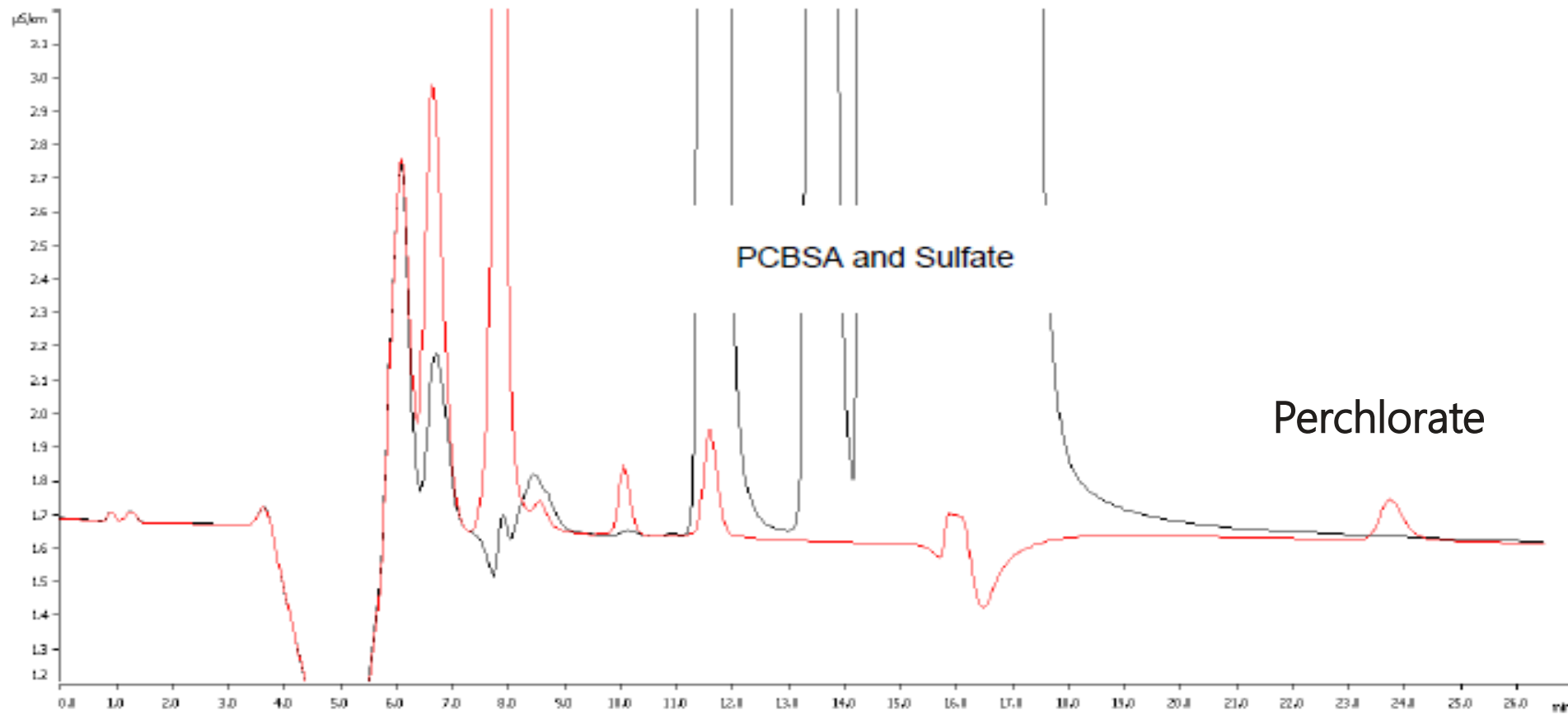


MCT Study Data (USEPA method 314.0, section 9)



No Interference – PCBSA

Interference



Black trace = 100ppm PCBSA and 1000ppm Sulfate followed by Red trace = Perchlorate 5ppb std

PCBSA = *para* – Chloro Benzene Sulfonic Acid

USEPA Method 332.0



+

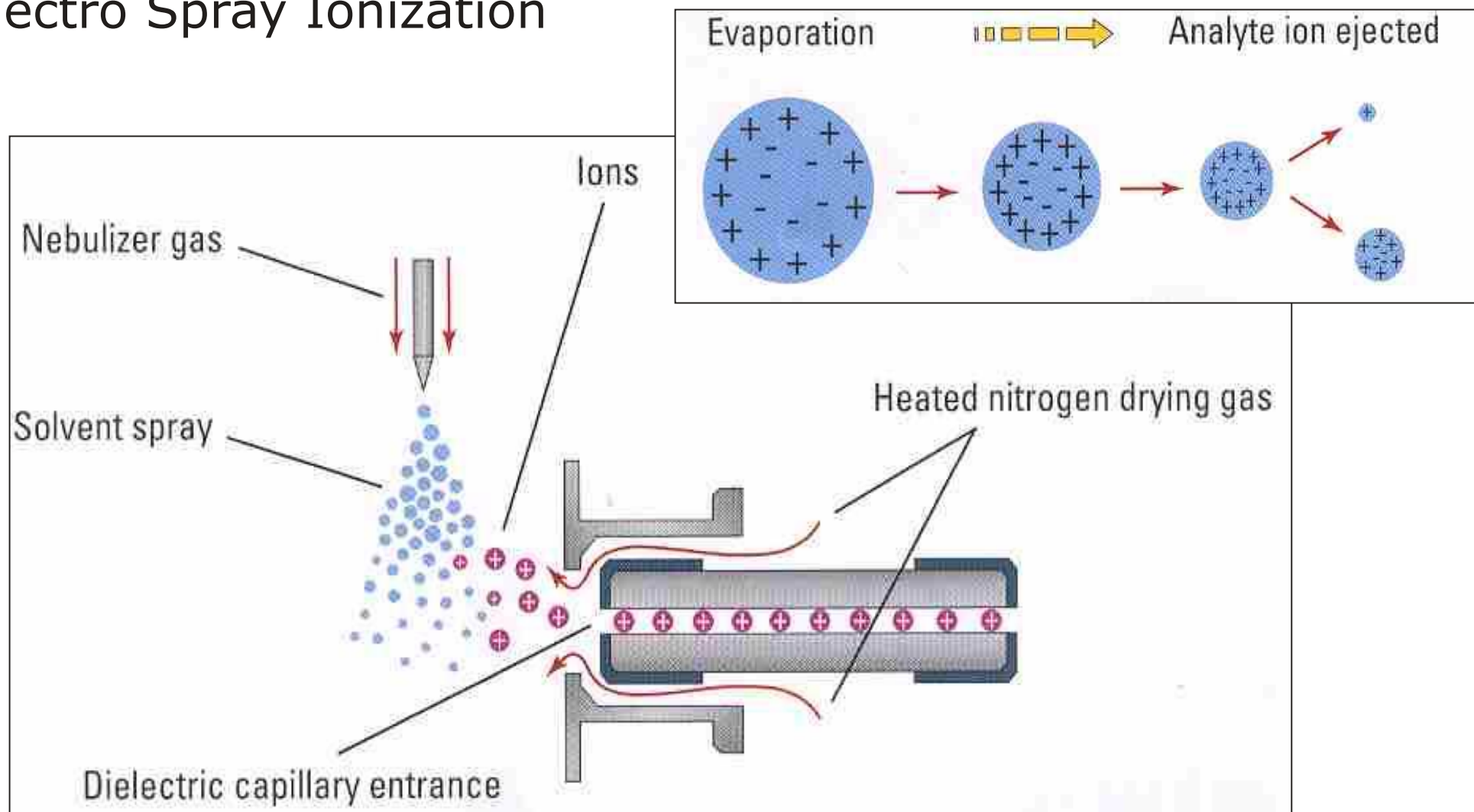


OR

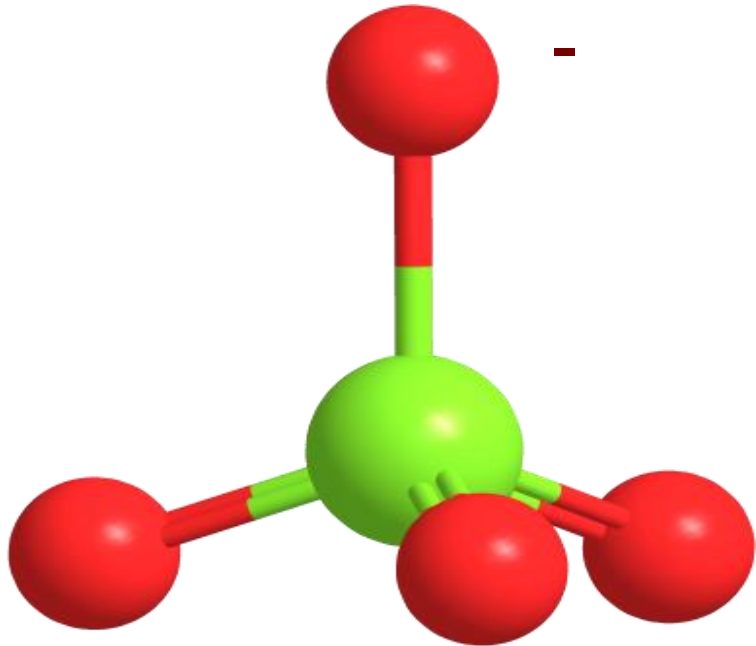


IC-MS

Electro Spray Ionization



Perchlorate Mass



Chlorine (Cl) = 35

+

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

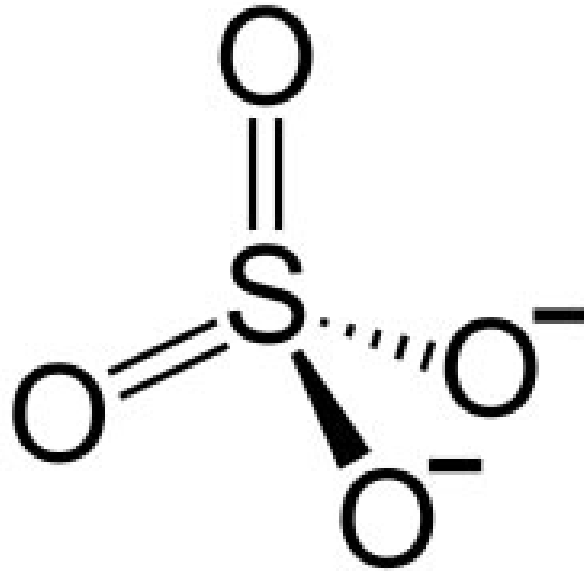
Perchlorate mass (Cl³⁵) =
35 + 64 = 99

→ 75%

Perchlorate mass (Cl³⁷) =
37 + 64 = 101

→ 25%

Perchlorate Mass / interference



Sulfate Ion

Sulfur (S) = 32

+

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

$$\text{HSO}_4^{-1} (\text{S}^{32}) = \\ 1 + 32 + 64 = 97$$

$$\text{HSO}_4^{-1} (\text{S}^{34}) = \\ 1 + 32 + 64 = 99$$

→ 4%

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

USEPA method
332.0 / SW846 6860
Perchlorate by ICMS / ICMSMS

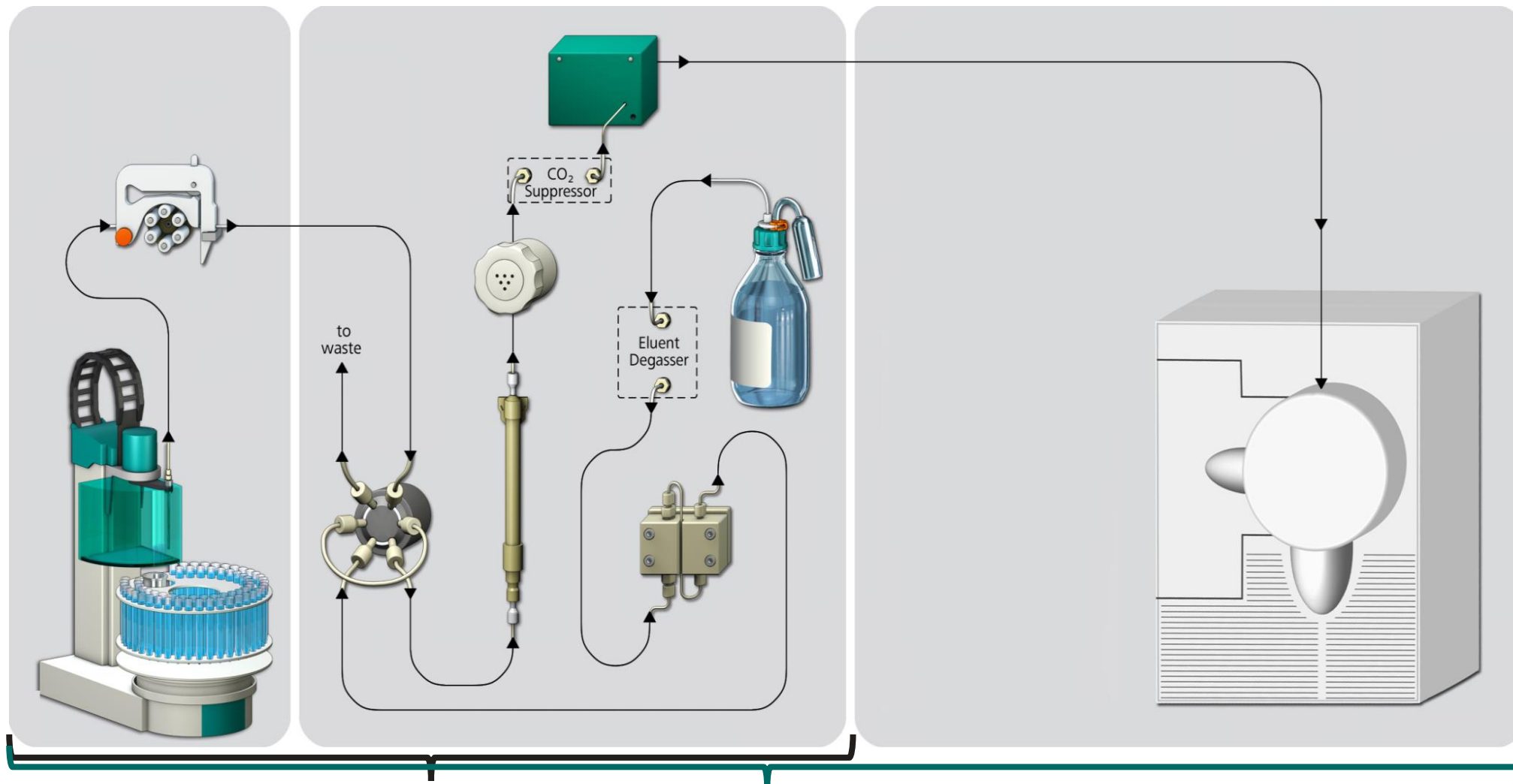
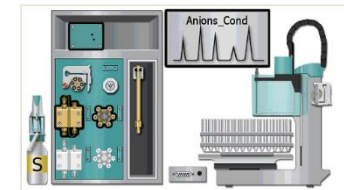
In Collaboration with
USEPA (ODW-OGW / OSW)



Metrohm Advanced IC – Agilent QQQ MSD



USEPA method 332 / SW846 6860



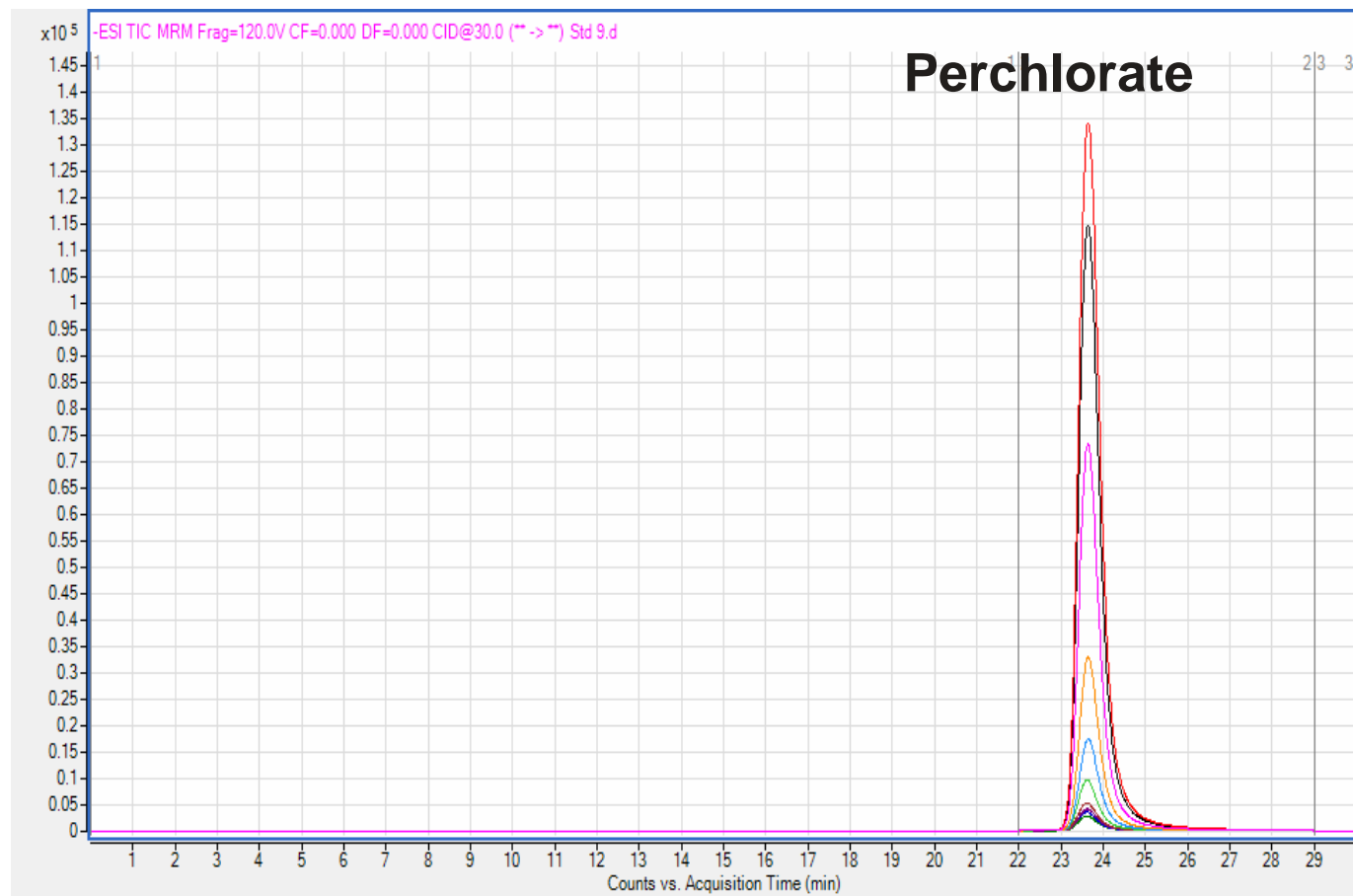
USEPA Method 314.0

USEPA Method 332.0

Chromatography

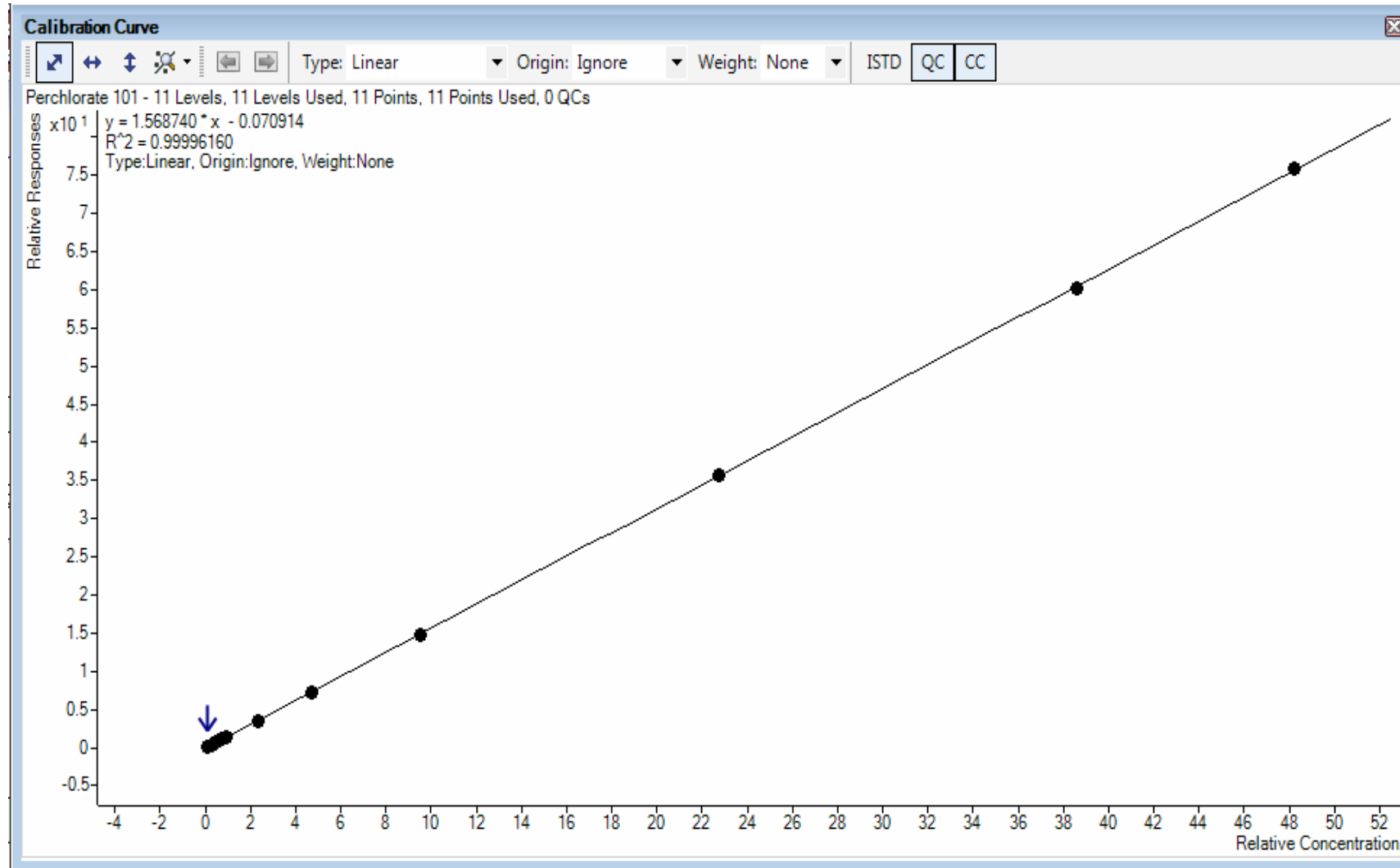
USEPA 332.0 – Perchlorate Calibration Overlay - ICMSMS

Eluent flow	0.7 mL/min
Eluent	10.5mM Na ₂ CO ₃ + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	100 µL
Detector	Agilent QQQ



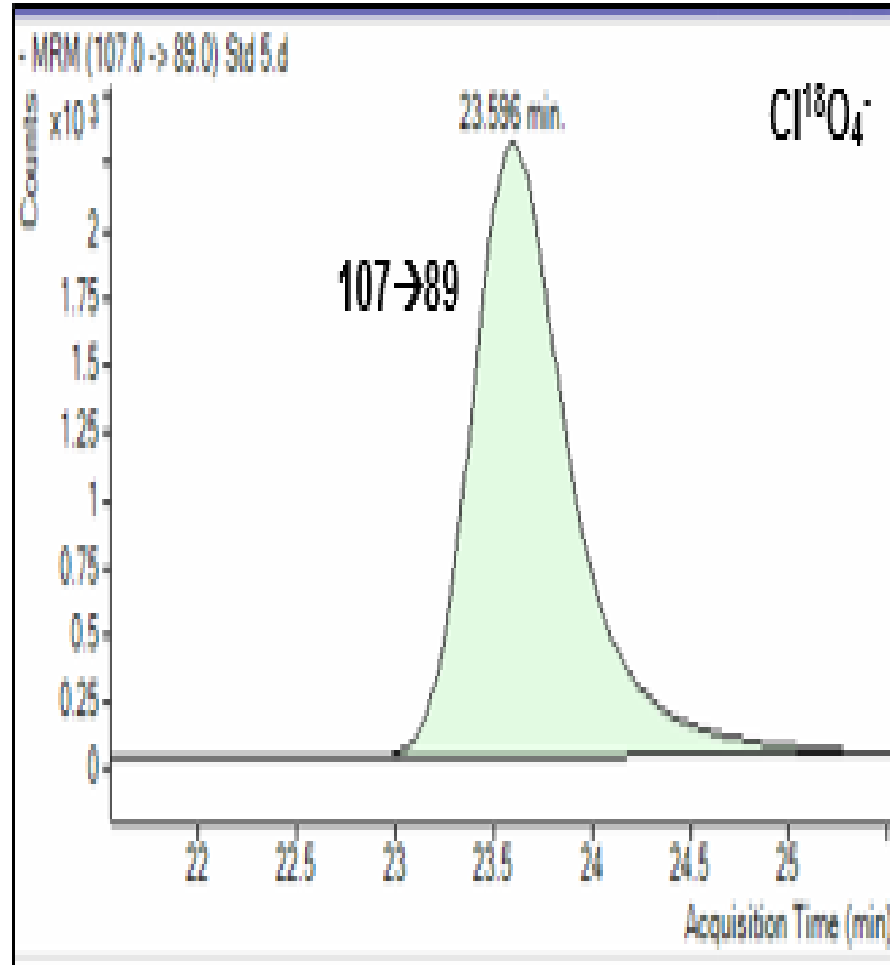
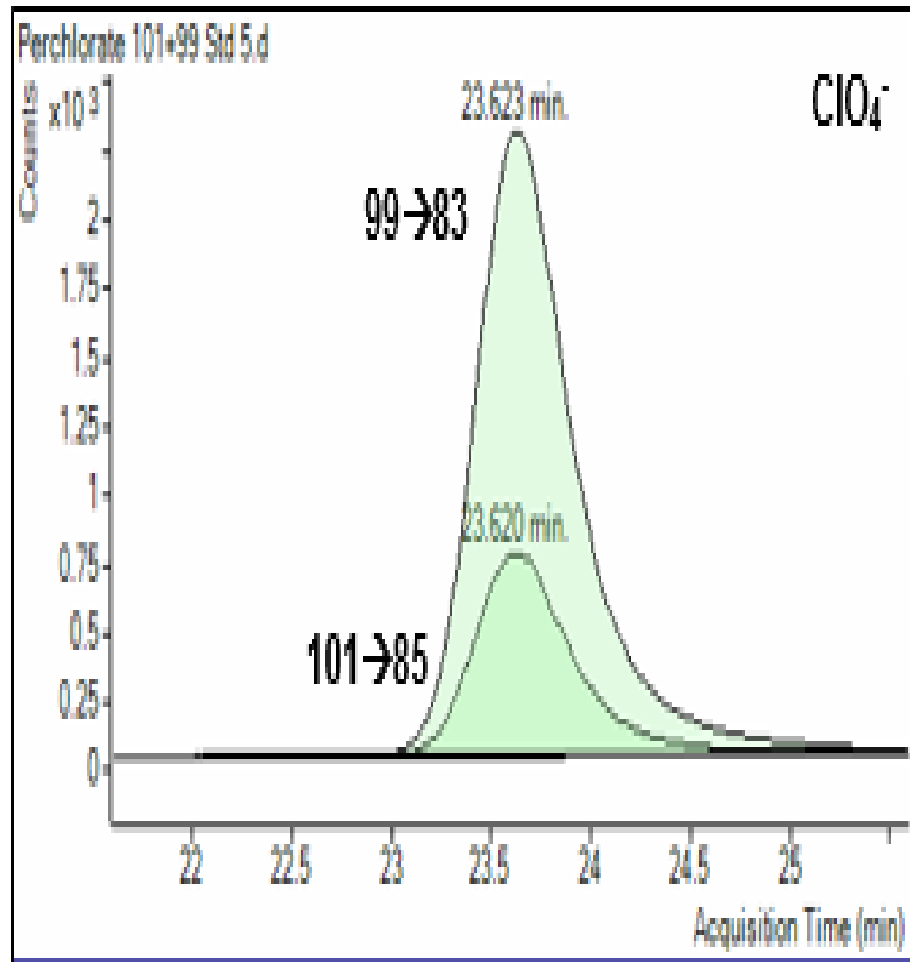
Perchlorate Calibration

AW IC US6-0240
AW IC US6-0244

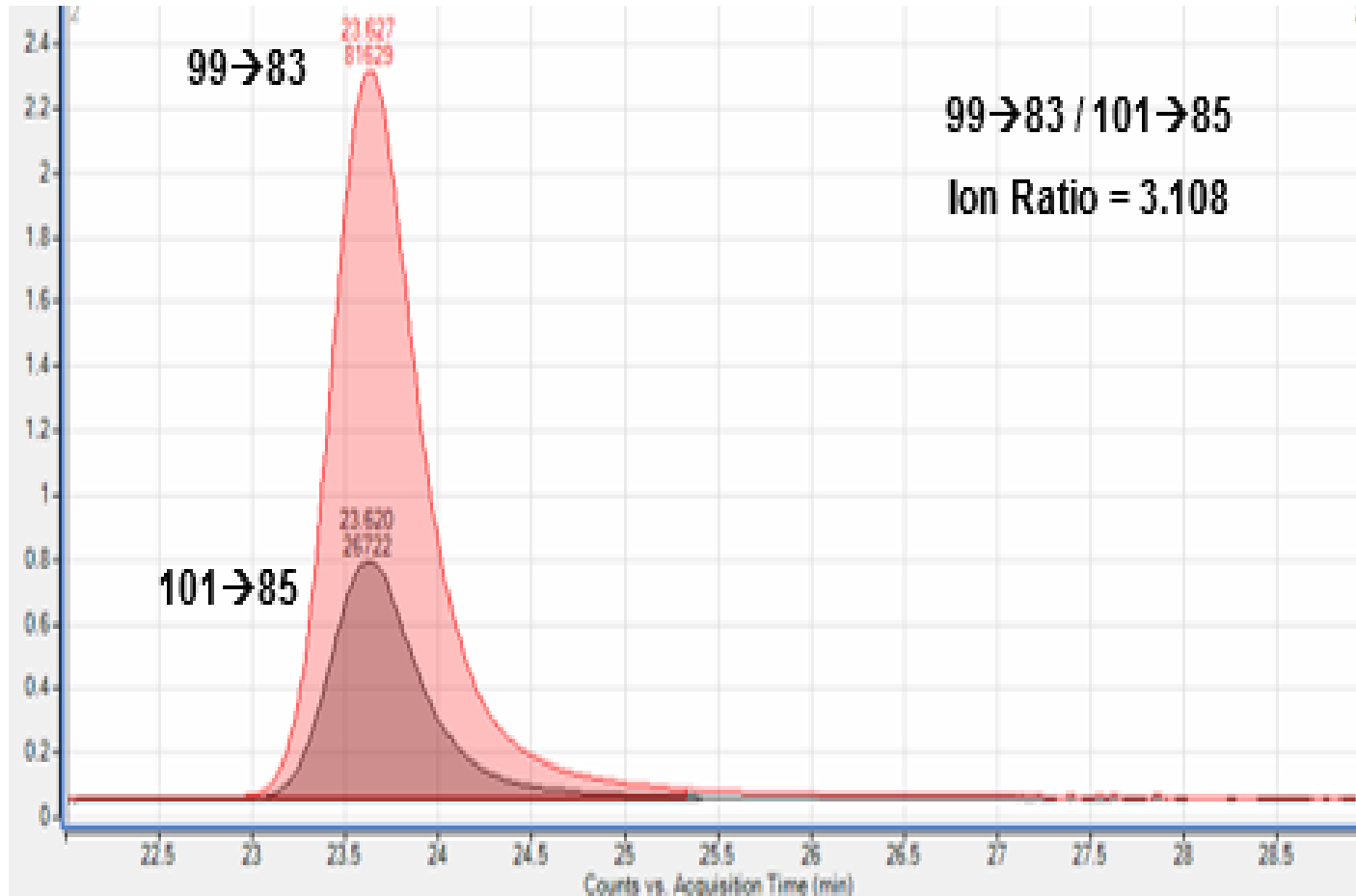


m/z 101
Range for
Calibration Standards
0.1ppb to 50ppb (ClO_4^{1-})

USEPA 332.0 – Perchlorate MRM and transitions



USEPA 332.0 – Perchlorate Ion Ratios



Average (150+ injections) Ion ratio for m/z 99/101 = 3.108

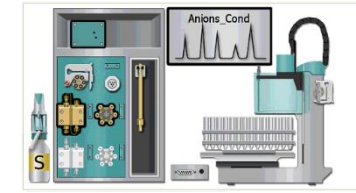
USEPA method acceptable value = 2.31 – 3.85

What is Ion Suppression



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

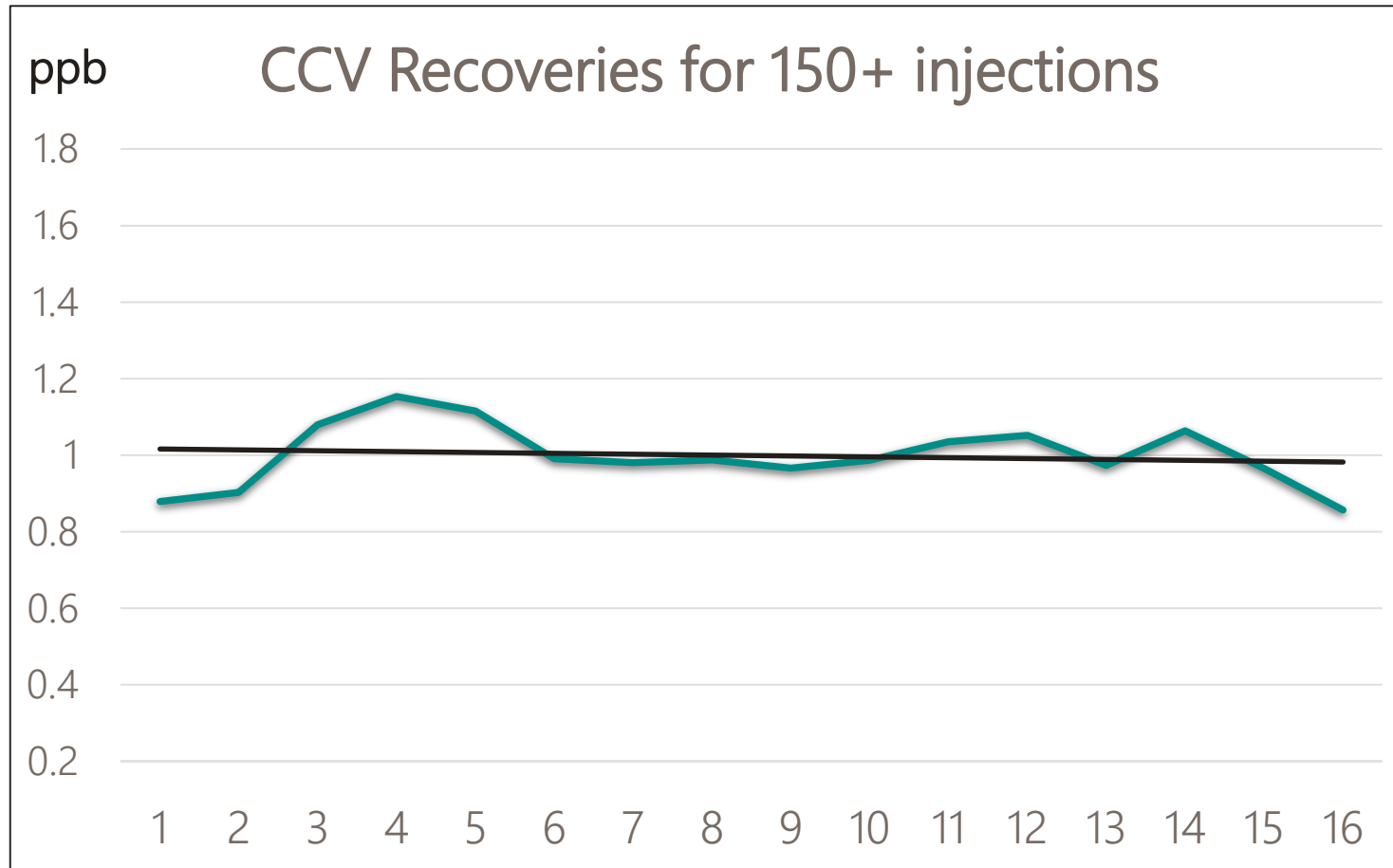
Effects of Ion Suppression



ISTD Response over 150 injections

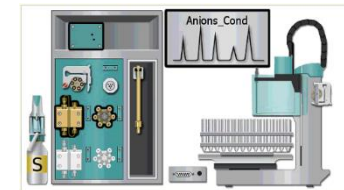


1 ppb Perchlorate CCV – Recoveries over 150+ injections

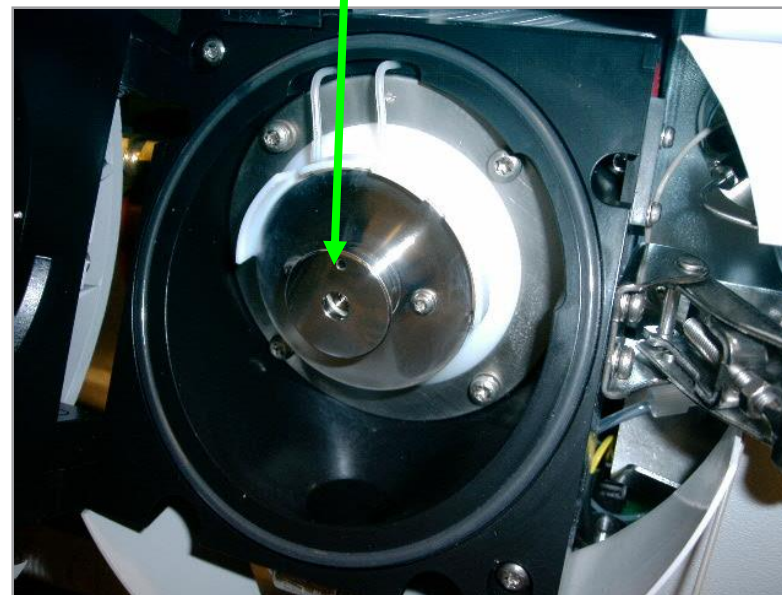


Average recovery = 99.9%

MSD Interface after 150 injections



No Salt deposition



Summary

- Metrohm Developed
 - 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)
 - No interference from industrial surfactant like p-Chloro Benzene Sulfonic Acid (PCBSA)
- 100% Solvent compatible IC hardware allowed to hyphenate with
 - Single Quad MSD
 - Triple Quad MSD

Use of appropriate loop and MSD connections

Adopting from method 314.0 to 332.0

Acknowledgements

- Ms. Shen Yi-Yang – USEPA OSW
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- Metrohm USA Applications Team
 - Mr. Jay Sheffer
- Agilent Technologies
 - Dr. Tarun Anumol
 - Mr. Craig Marvin

Thank you for listening

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