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

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Today we will talk about…..

- Perchlorate, Bromate and HAA
  - Background and History
  - Ion Chromatography methods
  - Ion Chromatography with Hyphenated Methods
- 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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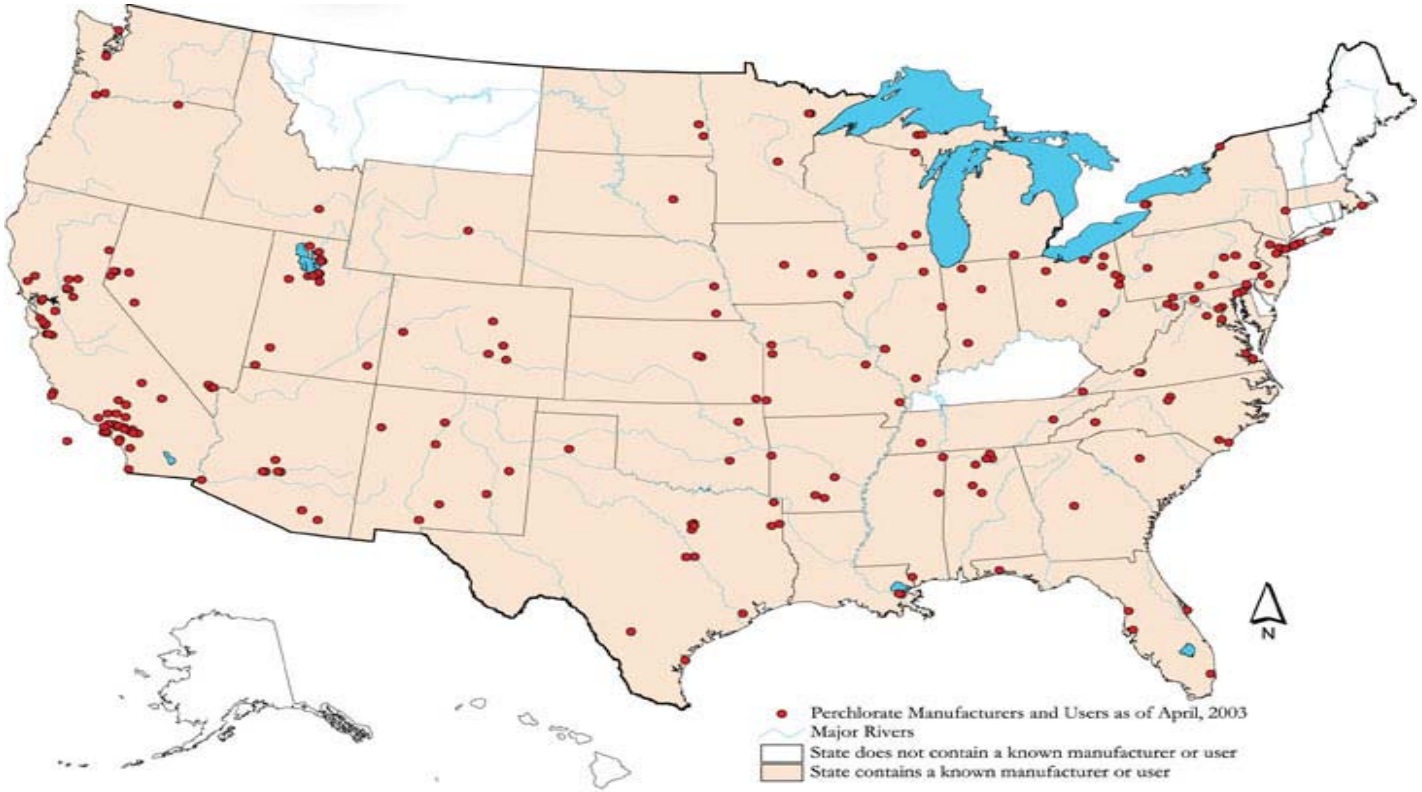
Perchlorate Background



Map provided as public information on USEPA website - 2005

USEPA Methods

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

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USEPA Methods

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

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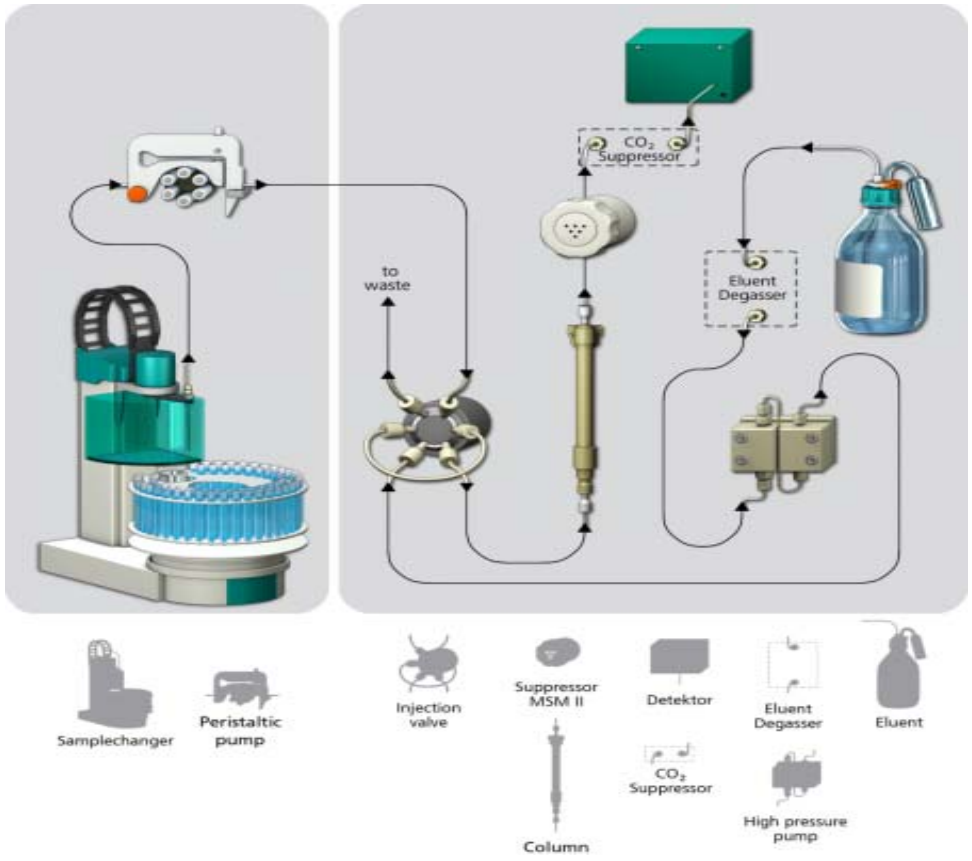
US EPA method 314.0 enhanced

Perchlorate by Suppressed Conductivity

AW US6-0071
AW US6-0241

USEPA method 314.0 (enhanced)

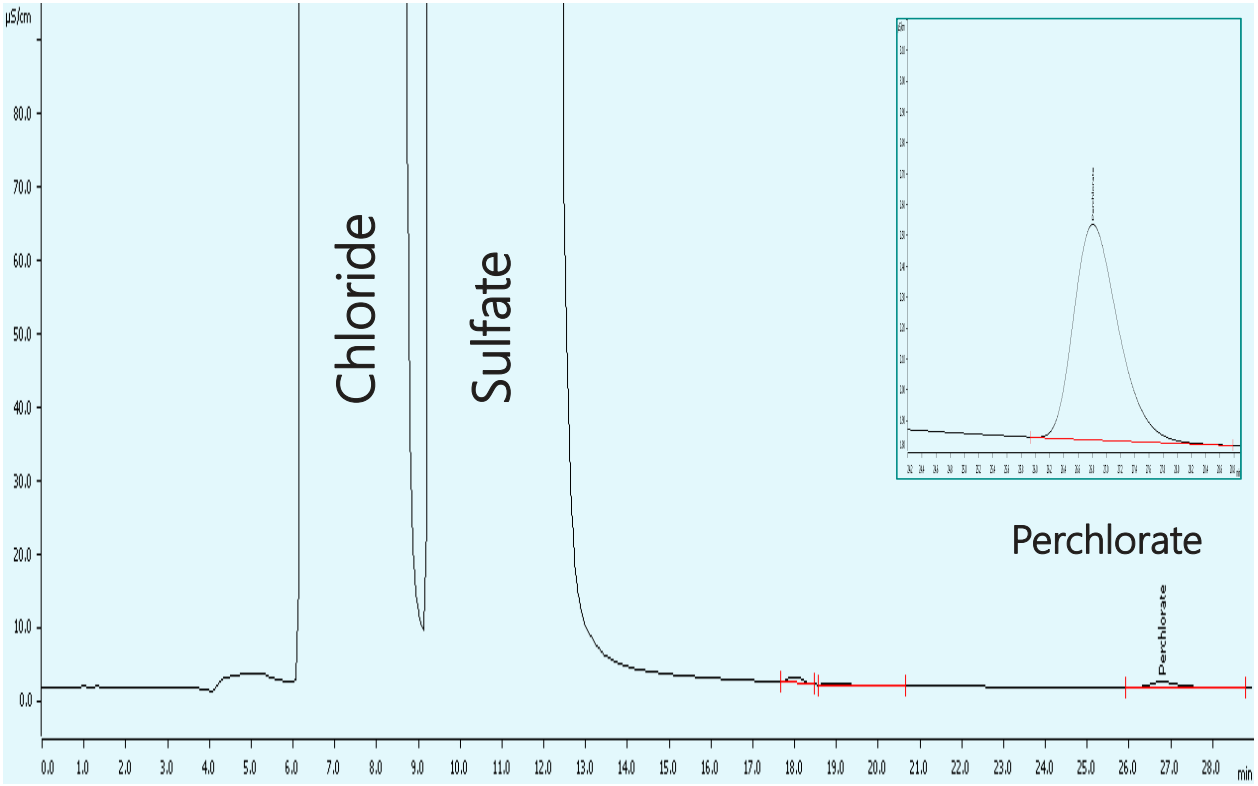
Using a Functionalized Monolithic Column or Anion Exchanger Column



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



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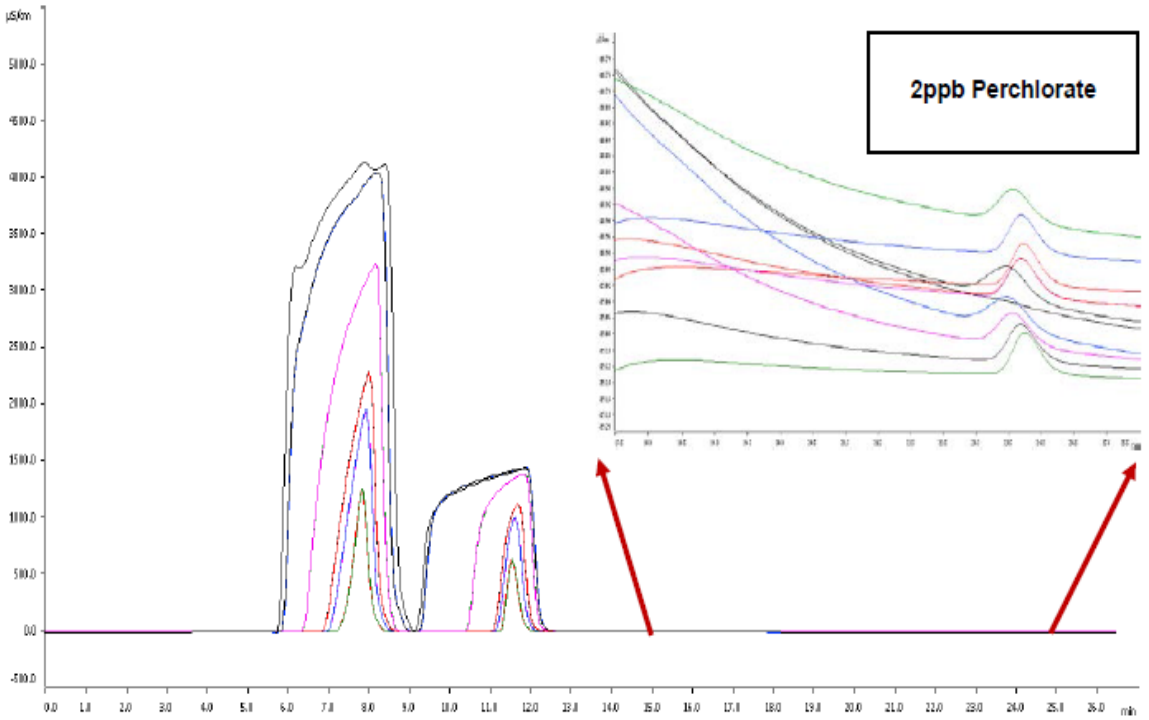
USEPA 314.0 MCT Study

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)



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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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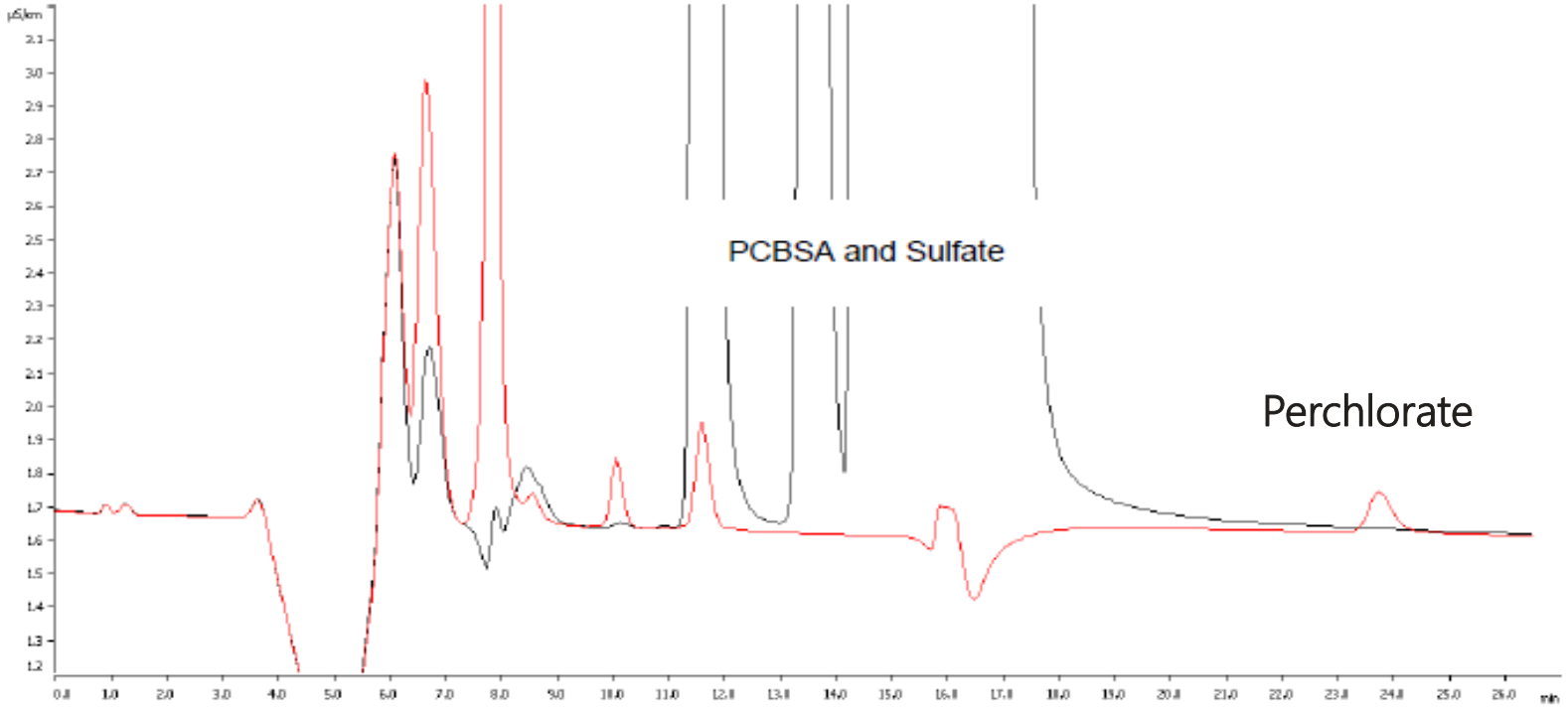
Major Interference – PCBSA

Interference



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

PCBSA = *para* – Chloro Benzene Sulfonic Acid

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USEPA Method 332.0 / 557.0

+

OR

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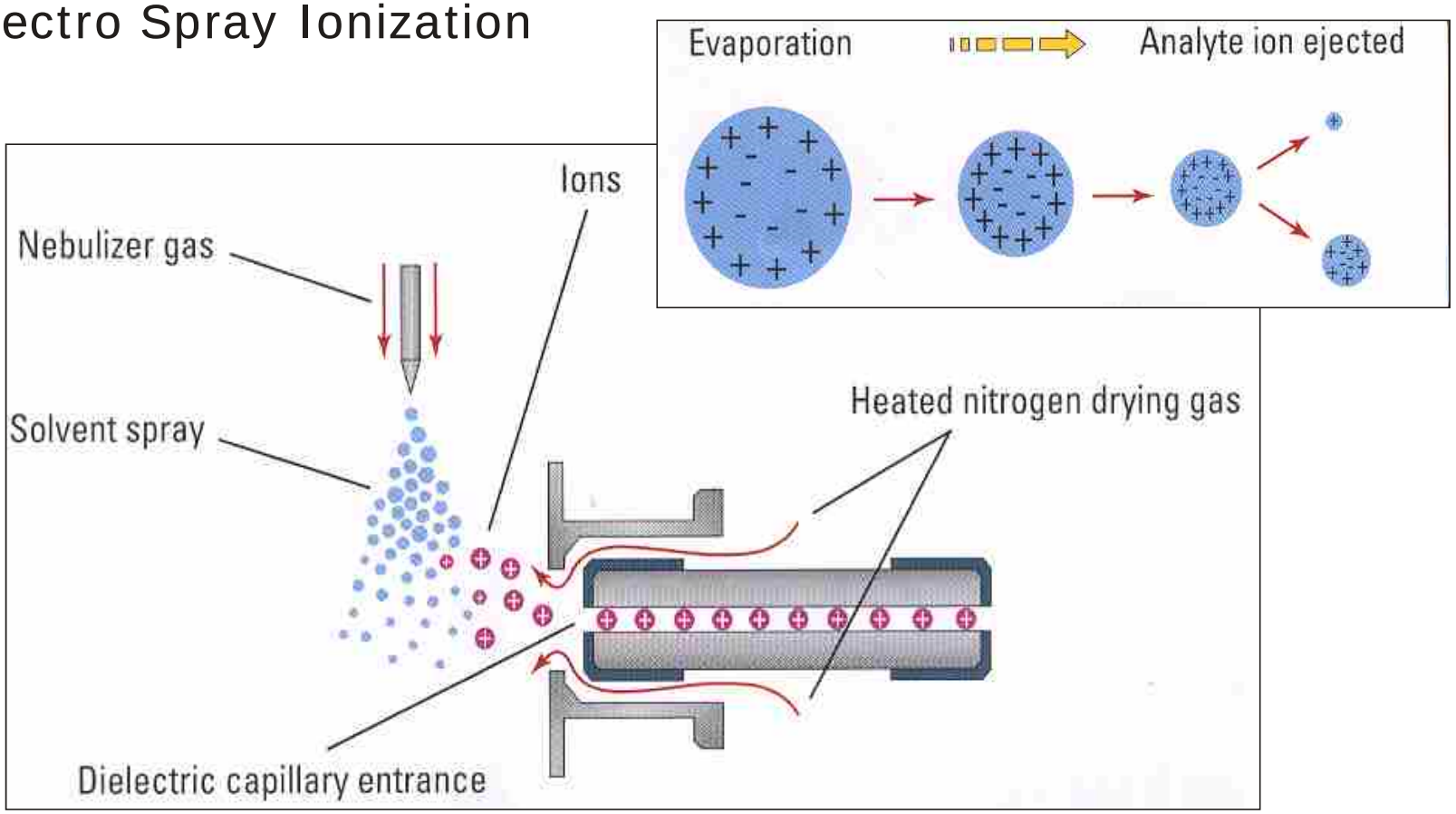
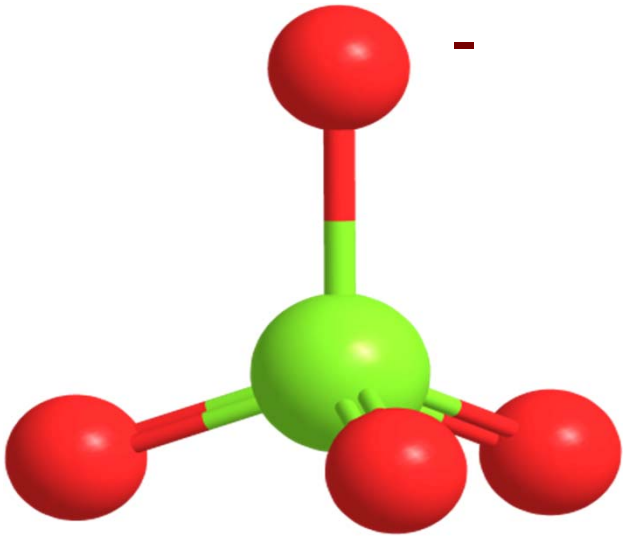
IC-MS

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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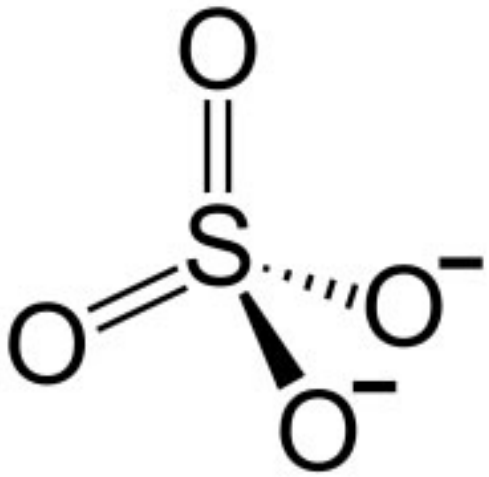
Perchlorate Mass / interference



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

USEPA method 332.0 / SW846 6860

Perchlorate by ICMS / ICMSMS

In Collaboration with
USEPA (ODW-OGW / OSW)

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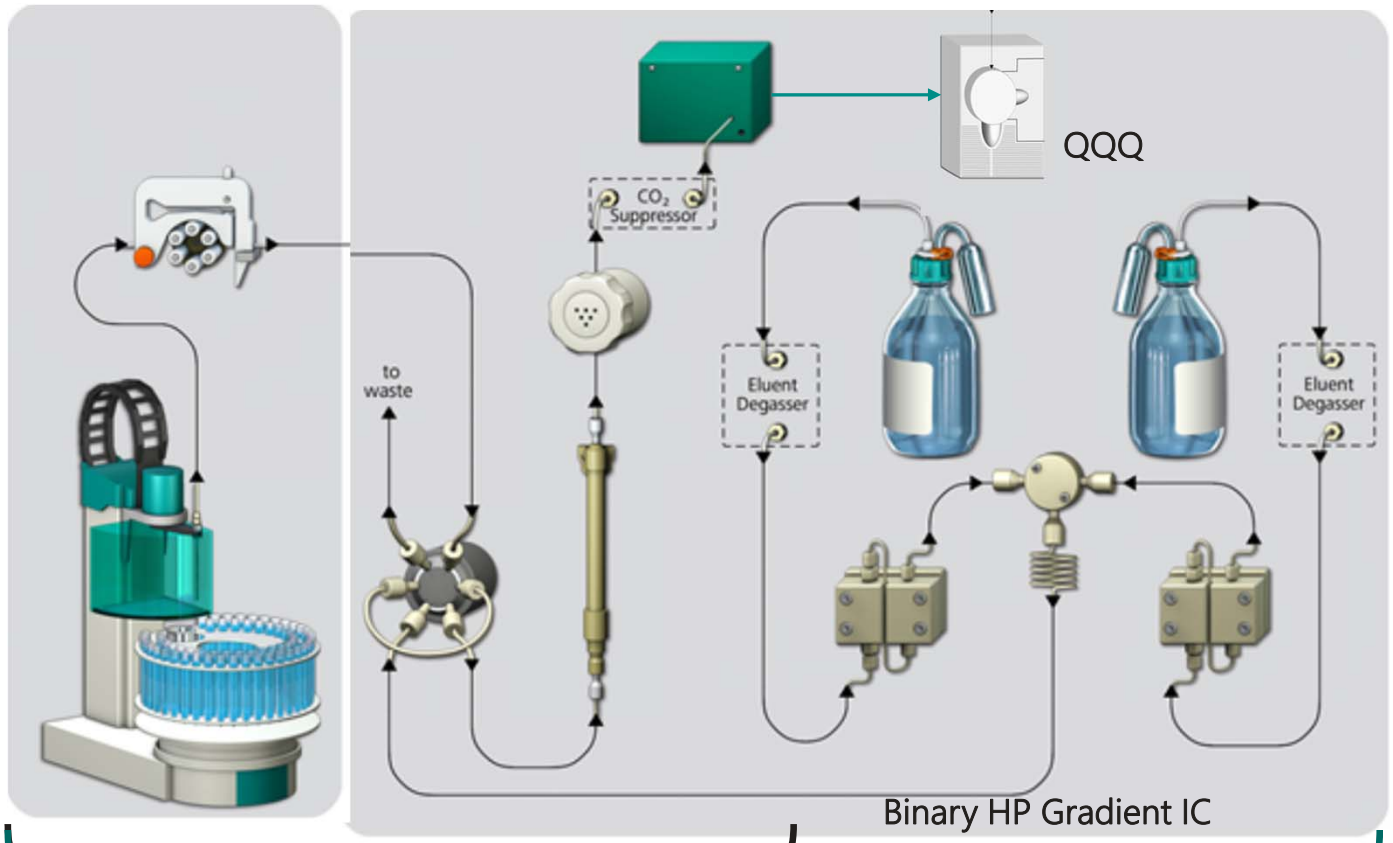
Metrohm Advanced IC – Agilent QQQ MSD

IC/MSMS Configuration



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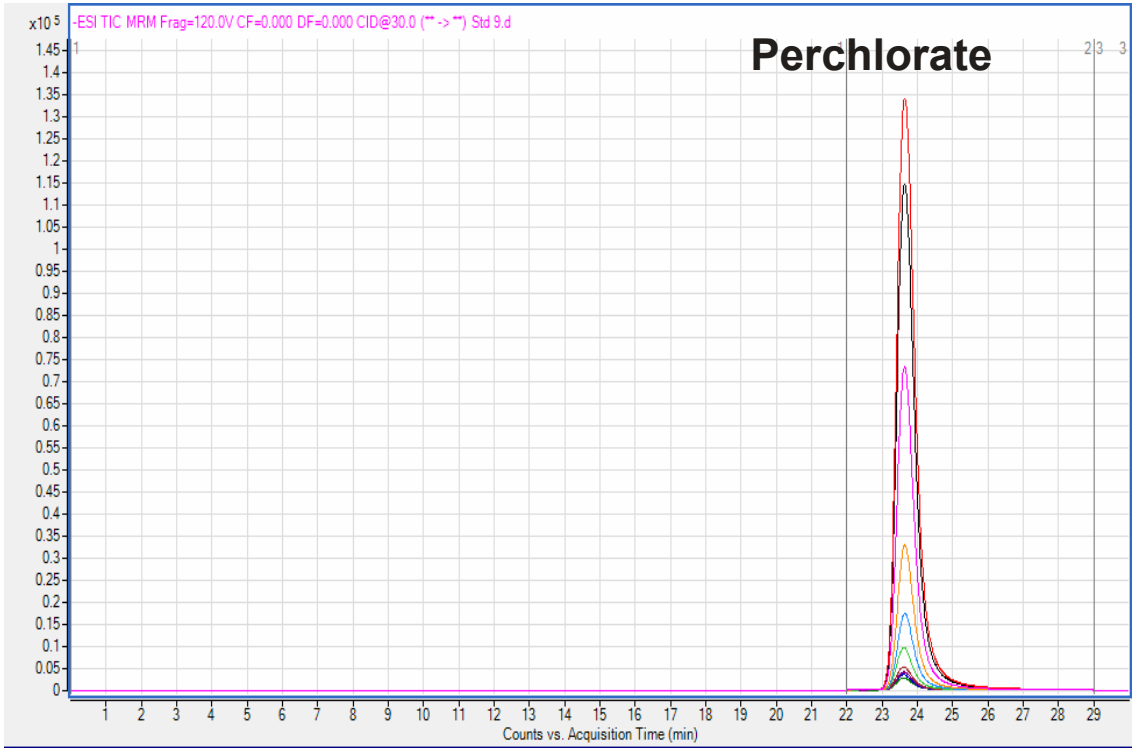
Chromatography

USEPA 332.0 – Perchlorate Calibration Overlay - ICMSMS

Eluent flow	0.7 mL/min
Eluent	10.6mM Na_2CO_3 + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	100 µL
Detector	Agilent QQQ



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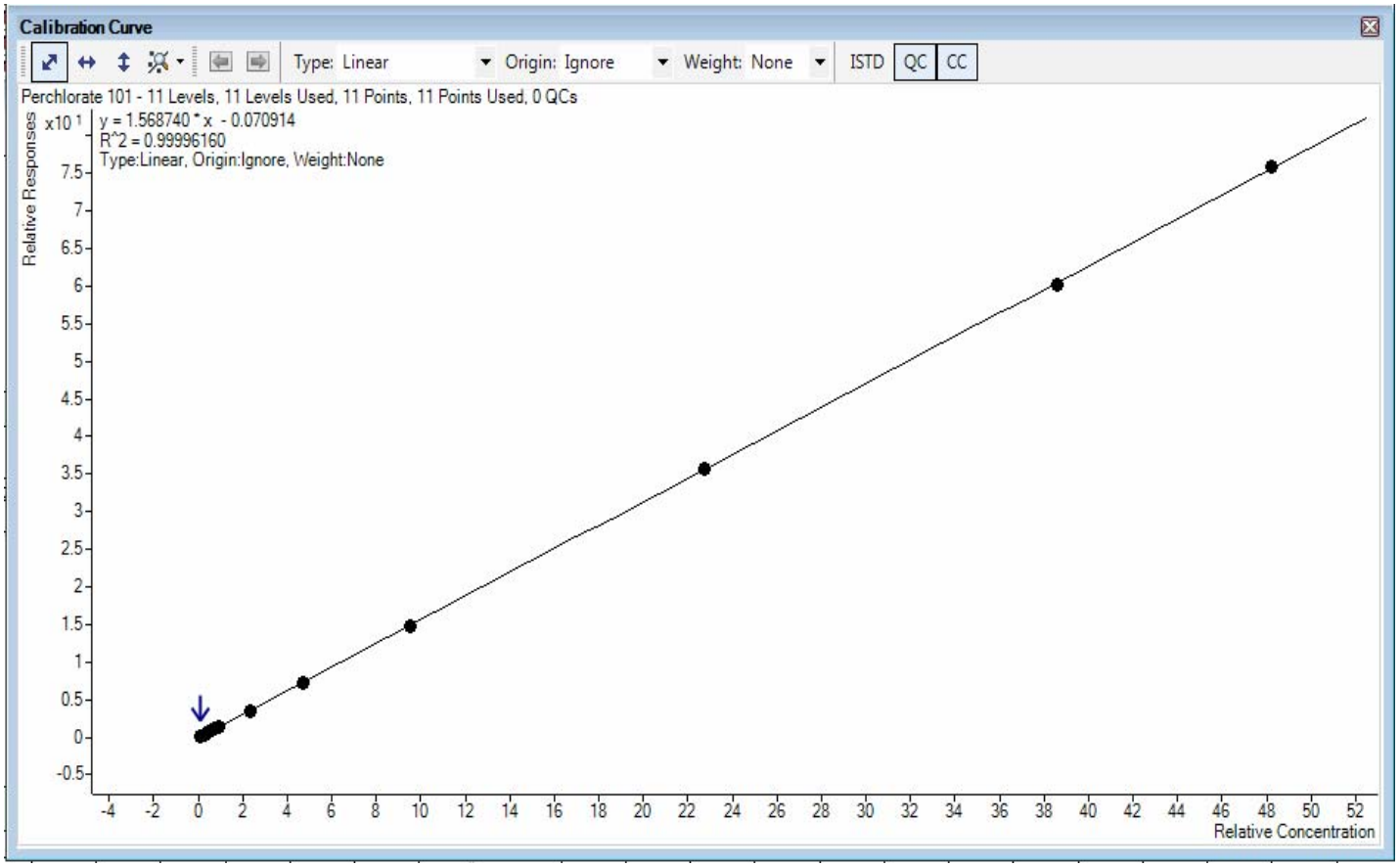
Perchlorate Calibration

AW IC US6-0240
AW IC US6-0244



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

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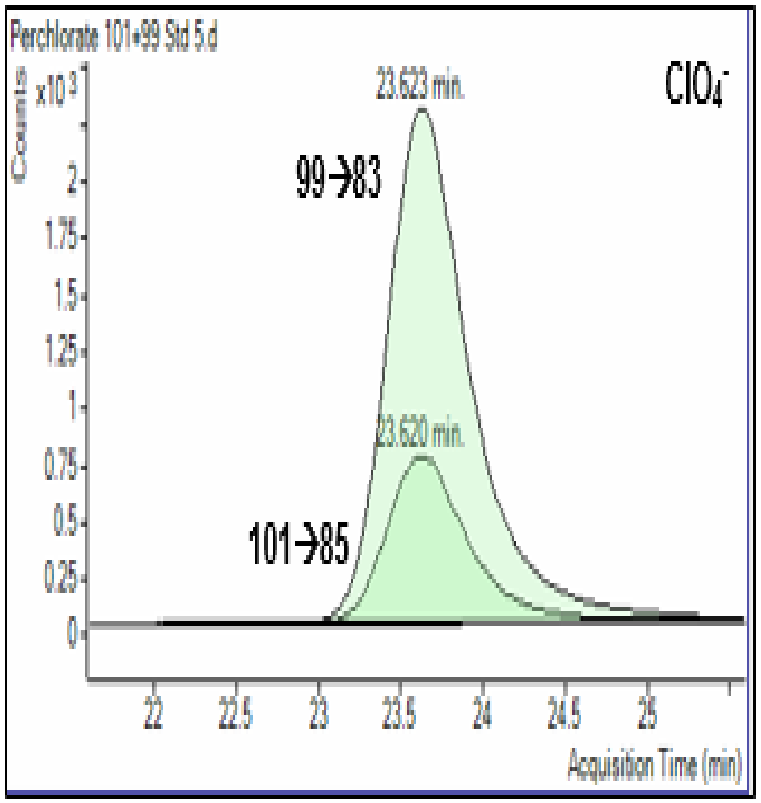
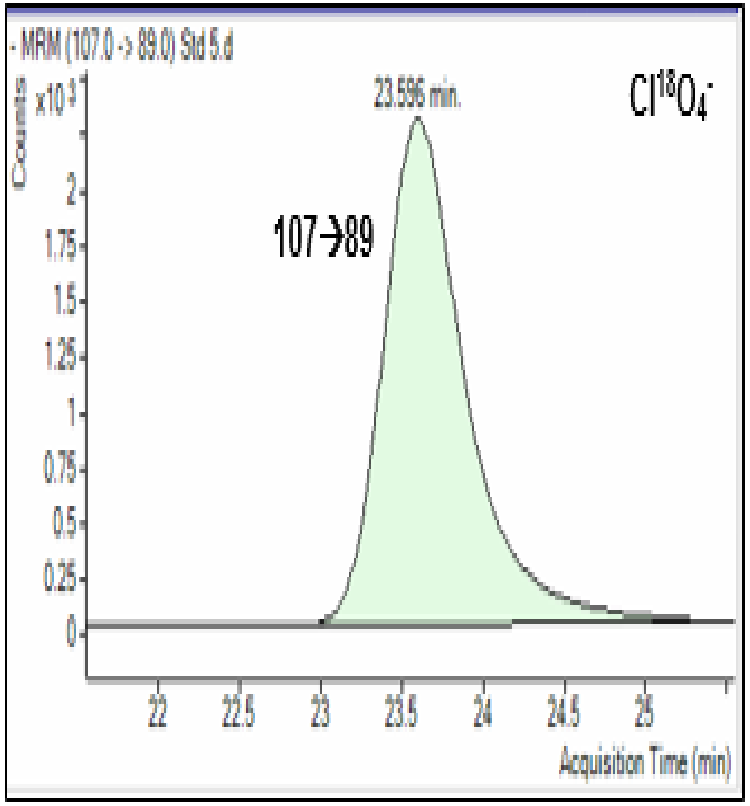
USEPA 332.0 – Perchlorate MRM and transitions





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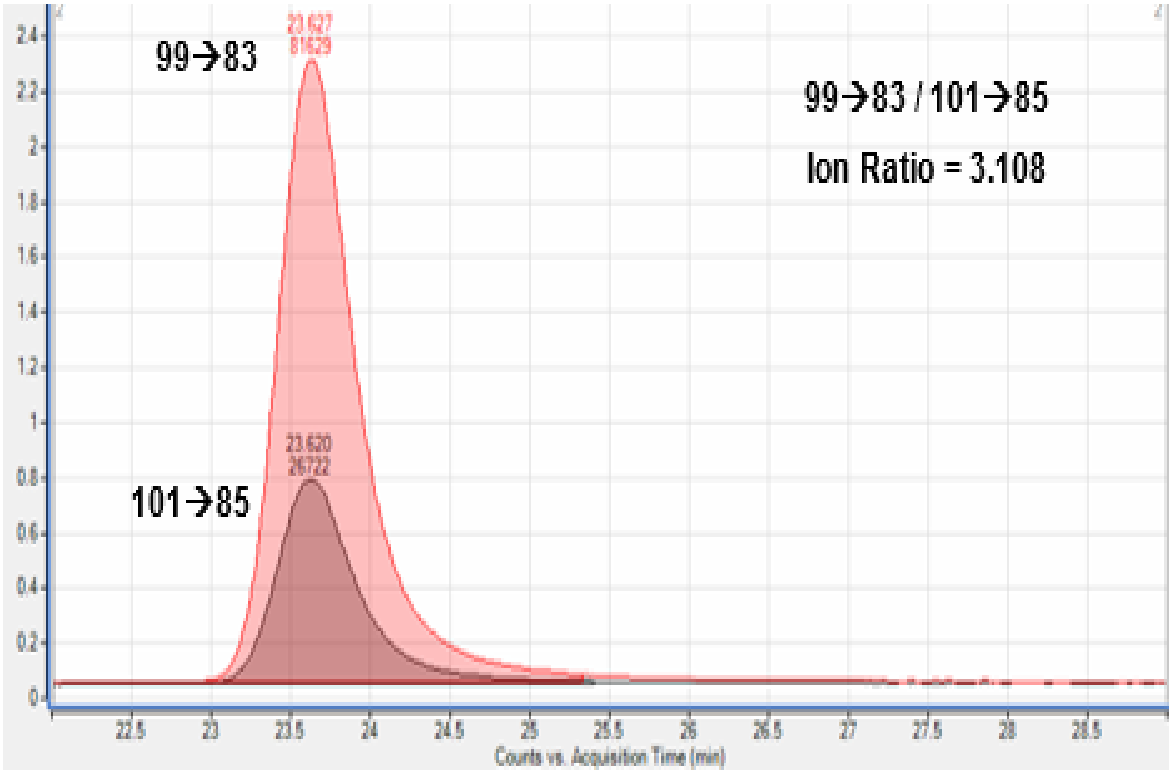
USEPA 332.0 – Perchlorate Ion Ratios



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

USEPA method acceptable value = 2.31 – 3.85

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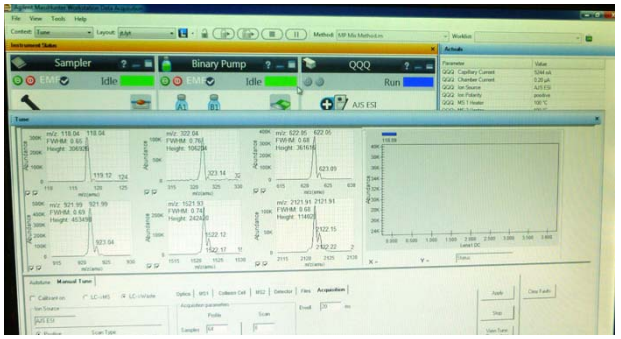
Direct inject of Water Samples to analyze HAAs using IC/MSMS

Haloacetic acids

Class	Compound	Acronym	MCL (ug/L)
Carcinogen	Bromate	BrO_3^-	10
HAA_5	Monochloroacetic acid	MCAA	60
	Dichloroacetic acid	DCAA	
	Trichloroacetic acid	TCAA	
	Monobromoacetic acid	MBAA	
	Dibromoacetic acid	DBAA	
HAA_9	Bromochloroacetic acid	BCAA	-
	Bromodichloracetic acid	BDCAA	
	Dibromochloroacetic acid	DBCAA	
	Tribromoacetic acid	TBAA	
Emerging HAAs	Monoiodoacetic acid	MIAA	-
	Chloroiodoacetic acid	CIAA	
	Bromoiodoacetic acid	BIAA	
	Diiodoacetic acid	DIAA	
Herbicide degradate	Dalopon	Dal	

IC-MS/MS Interface



Metrohm to Agilent interface

Agilent MassHunter Platform

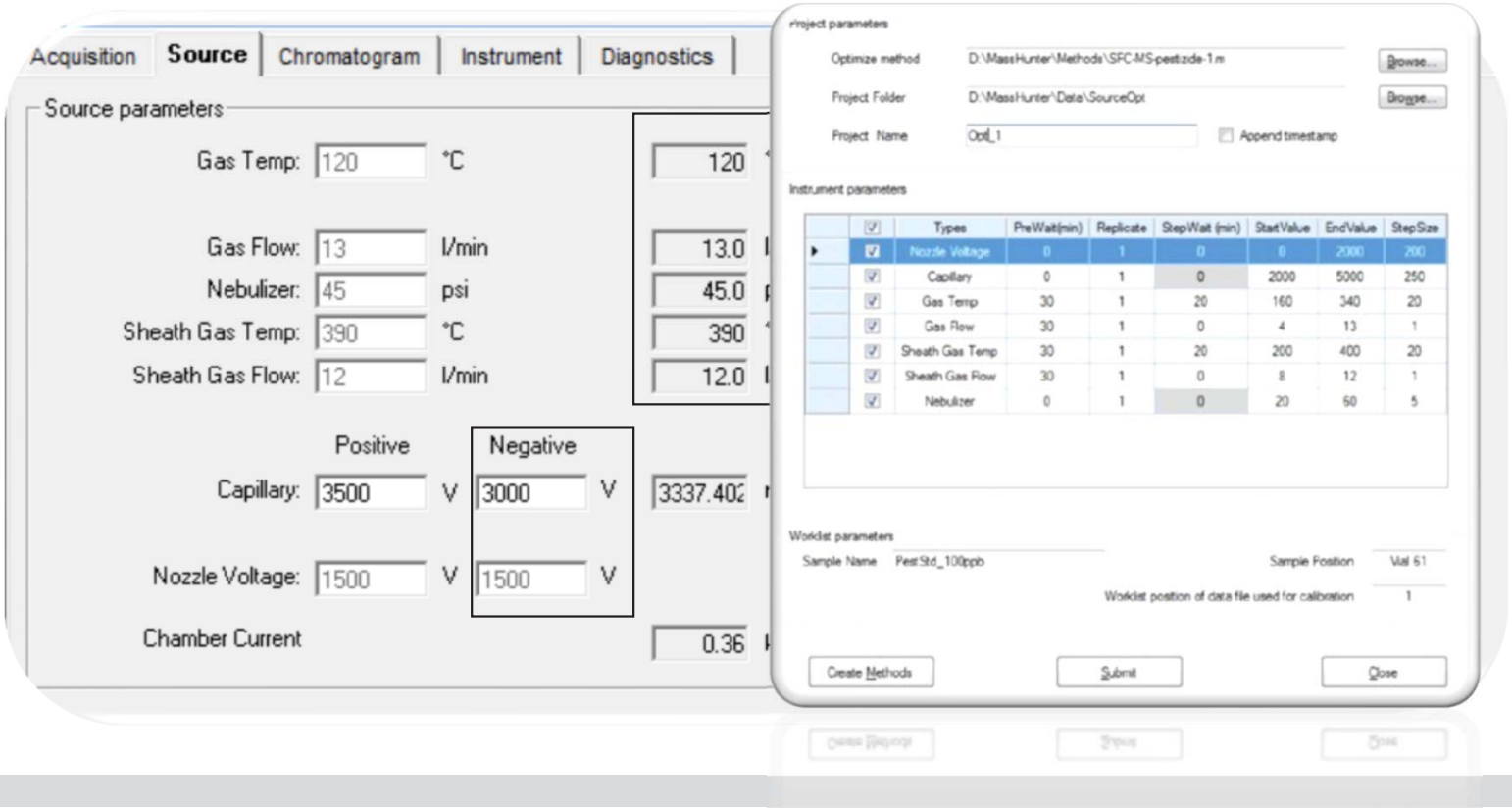
IC Conditions

- Column: Metrosep A Supp 7 (250mm x 4.0mm)
- Column Temperature: 45°C
- 100uL Loop injection using variable volume inject
- Eluent A: [85/15: HPLC Water/ACN] + 50 mM KOH + 7 mM Na_2CO_3;
- Eluent B: HPLC Water

Time (min)	Gradient (%A)
0.0	20
2.0	20
12	95
16	95
17	20
18.5	20

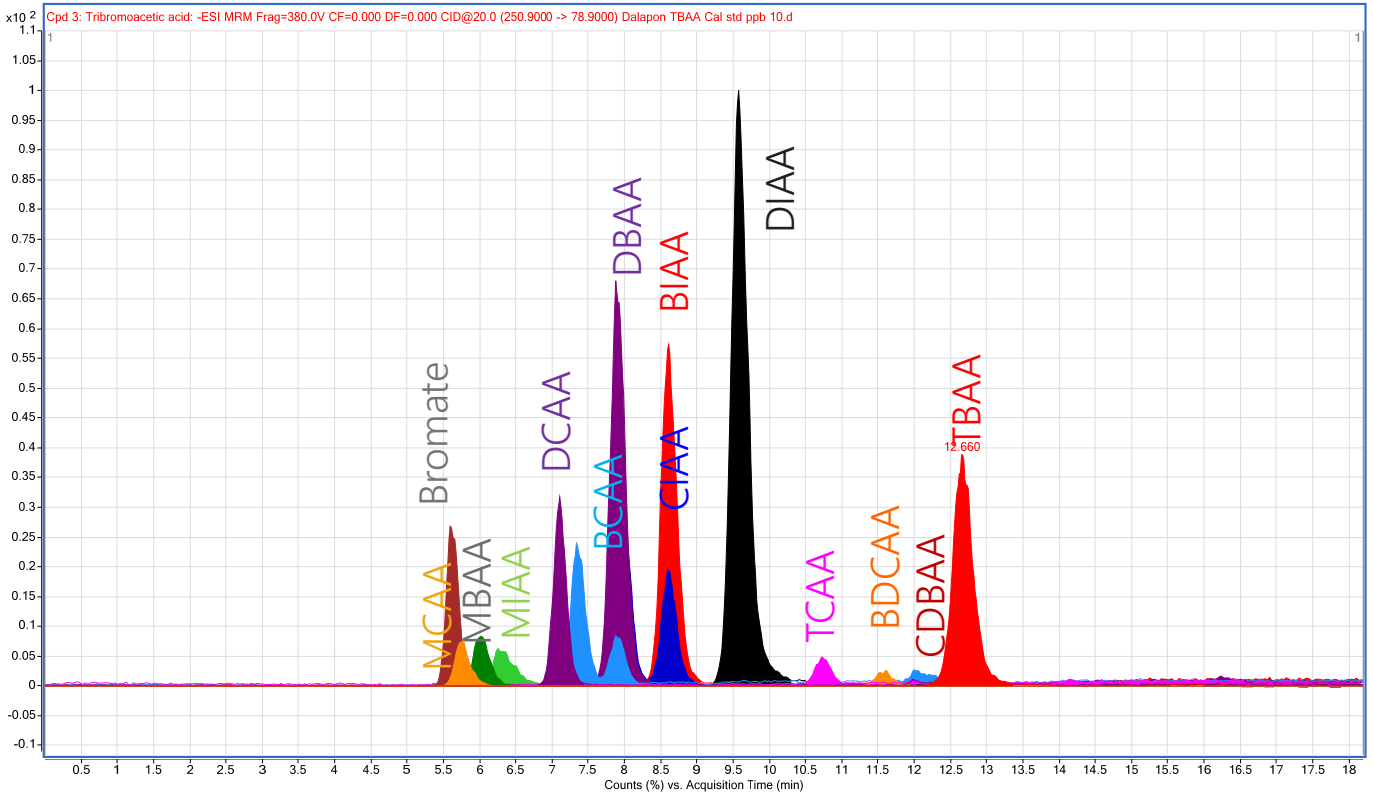
Mass Spectrometer - 6490 Agilent QQQ MS

- All parameters optimized using Agilent SourceOptimizer Software



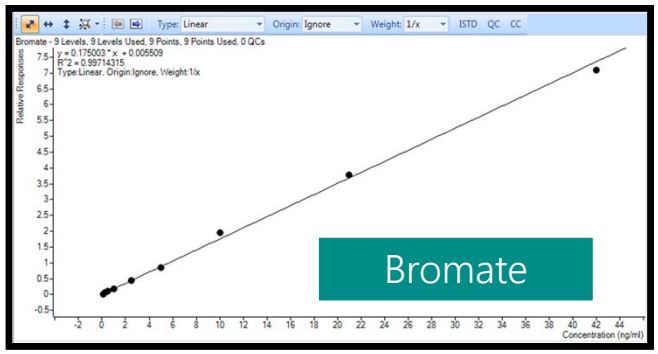
Chromatography

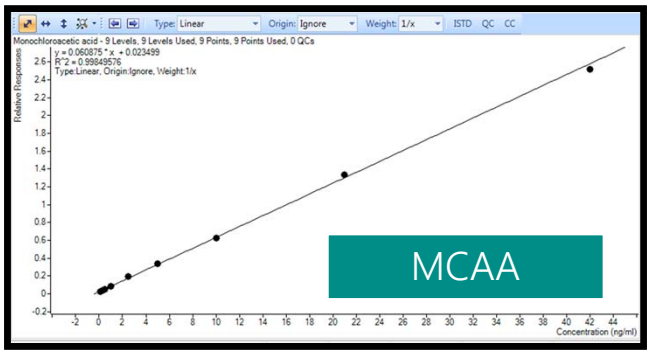
10 µg/L standard in Milli-Q water

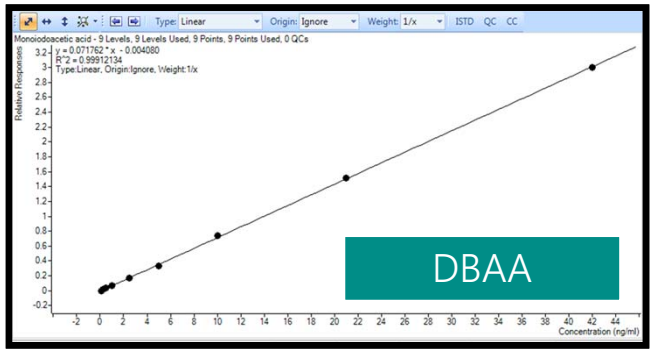


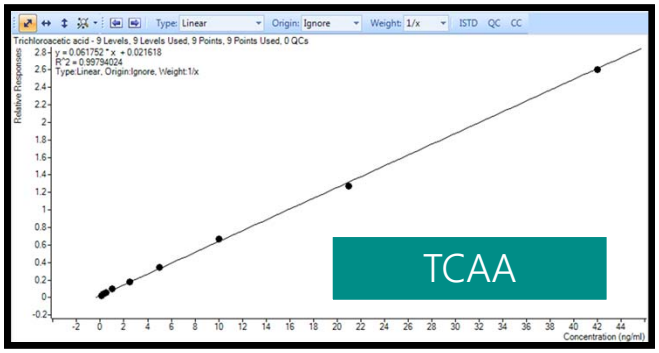
Linearity

Calibration curves from MRL – 40 µg/L



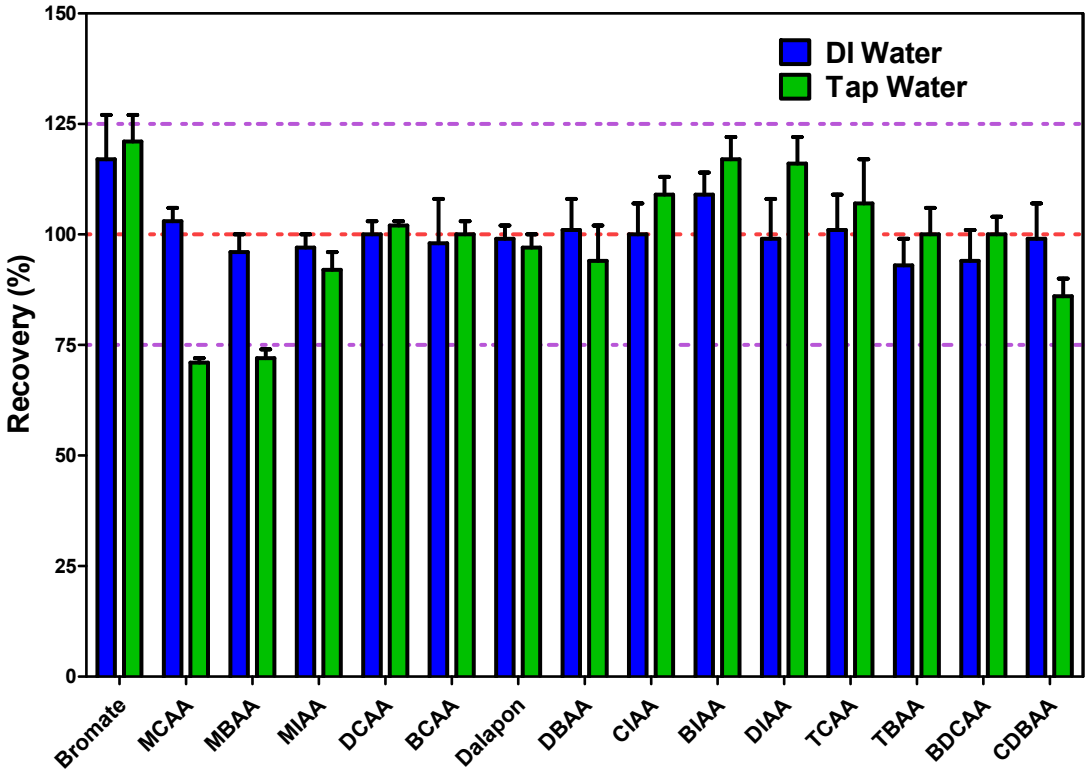






Real World Samples

DI & Tap water matrix spike recoveries



Summary

- Metrohm Developed (in collaboration with UofAz and USEPA)
  - 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)
- Direct Inject, improved method for Halo Acetic Acid, Bromate and Dalapon with minimal sample preparation and rapid analysis time (<20 min) were achieved
- In our work for HAAs, we have NOT observed any degradation of MCAA as illustrated in USEPA method

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Acknowledgements

- Ms. Shen Yi-Yang – Retired USEPA OSW
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  - Mr. Jay Sheffer
- Agilent Technologies
  - Dr. Tarun Anumol
  - Mr. Craig Marvin

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Q&A

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