



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

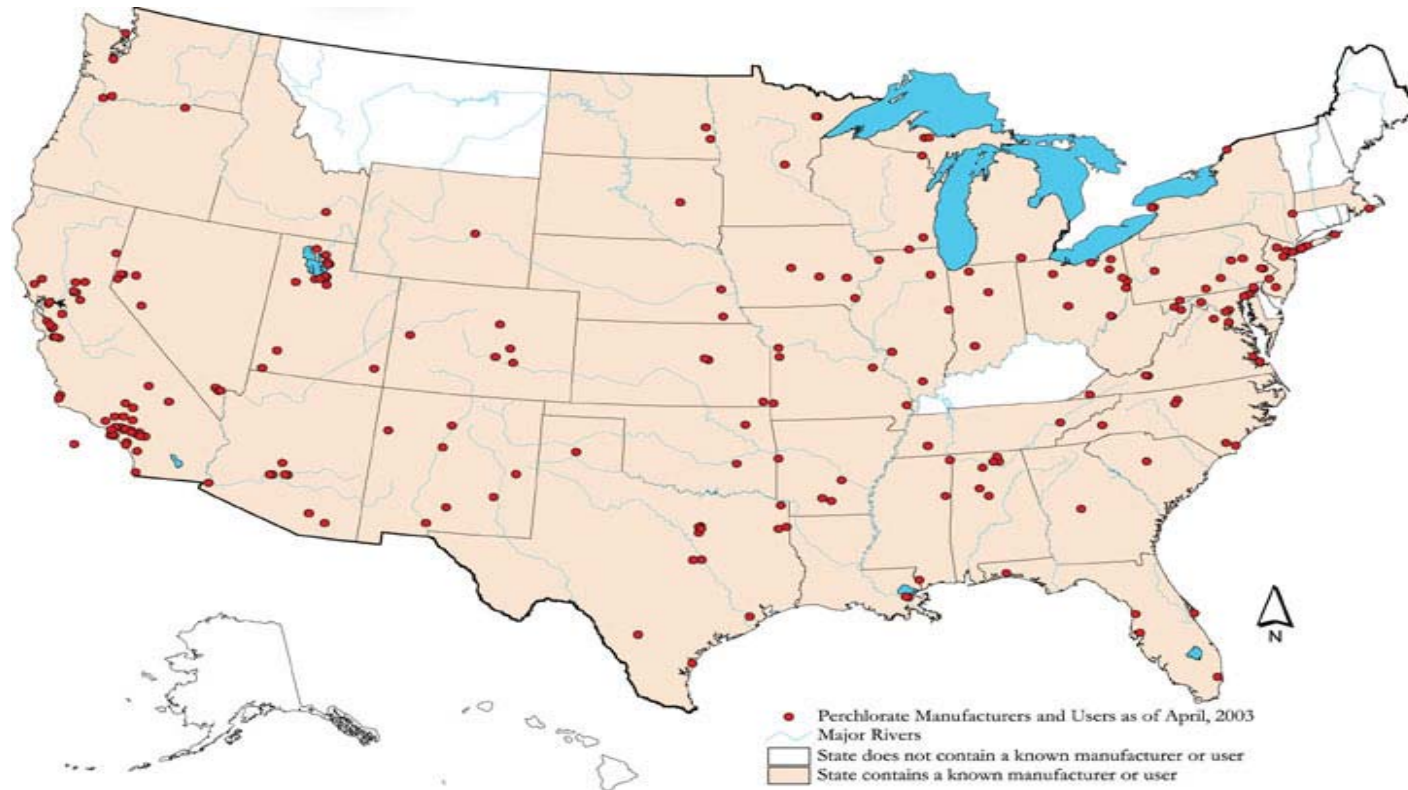
Perchlorate Background

- 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

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

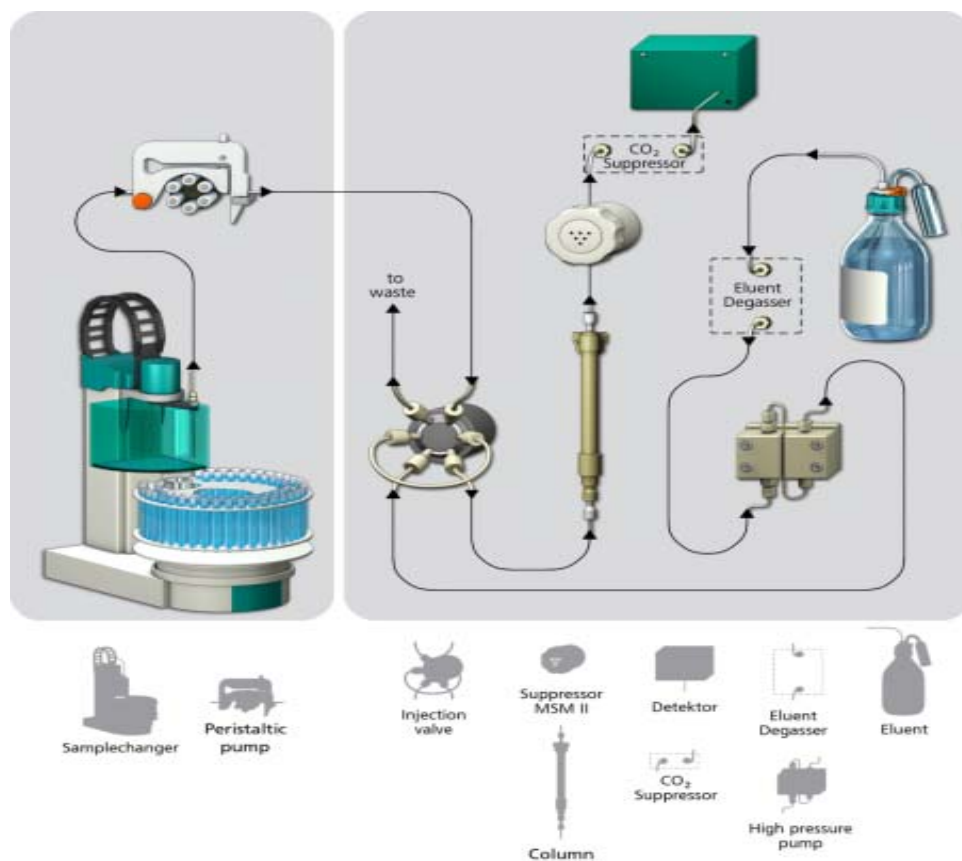
Perchlorate
by Suppressed Conductivity

USEPA method 314.0 (enhanced)

AW US6-0071

AW US6-0241

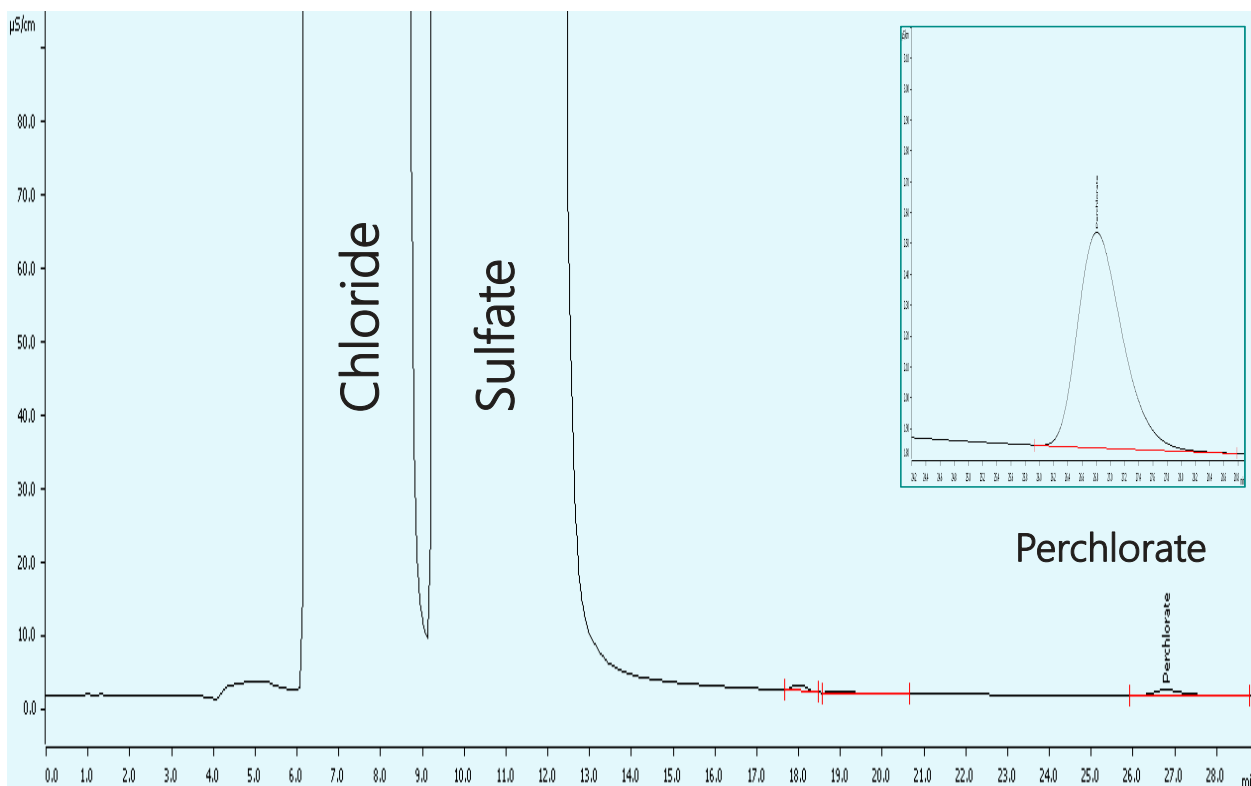
Using a Functionalized Monolithic Column or Anion Exchange Column



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

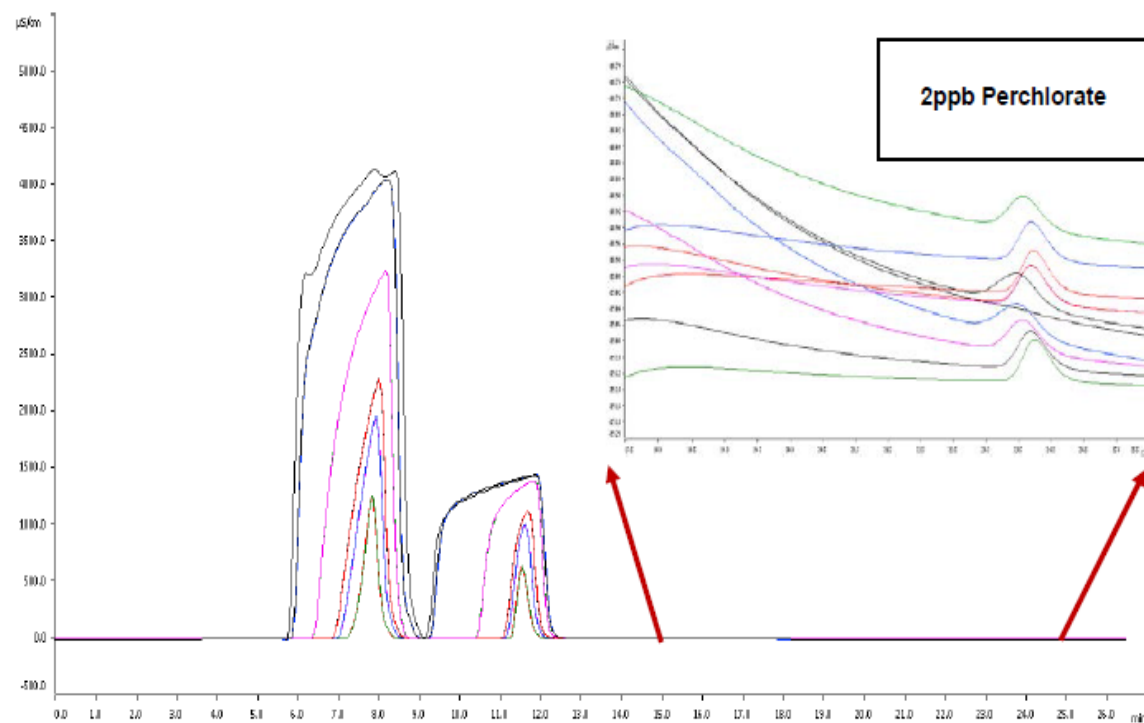


USEPA 314.0 MCT Study

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)

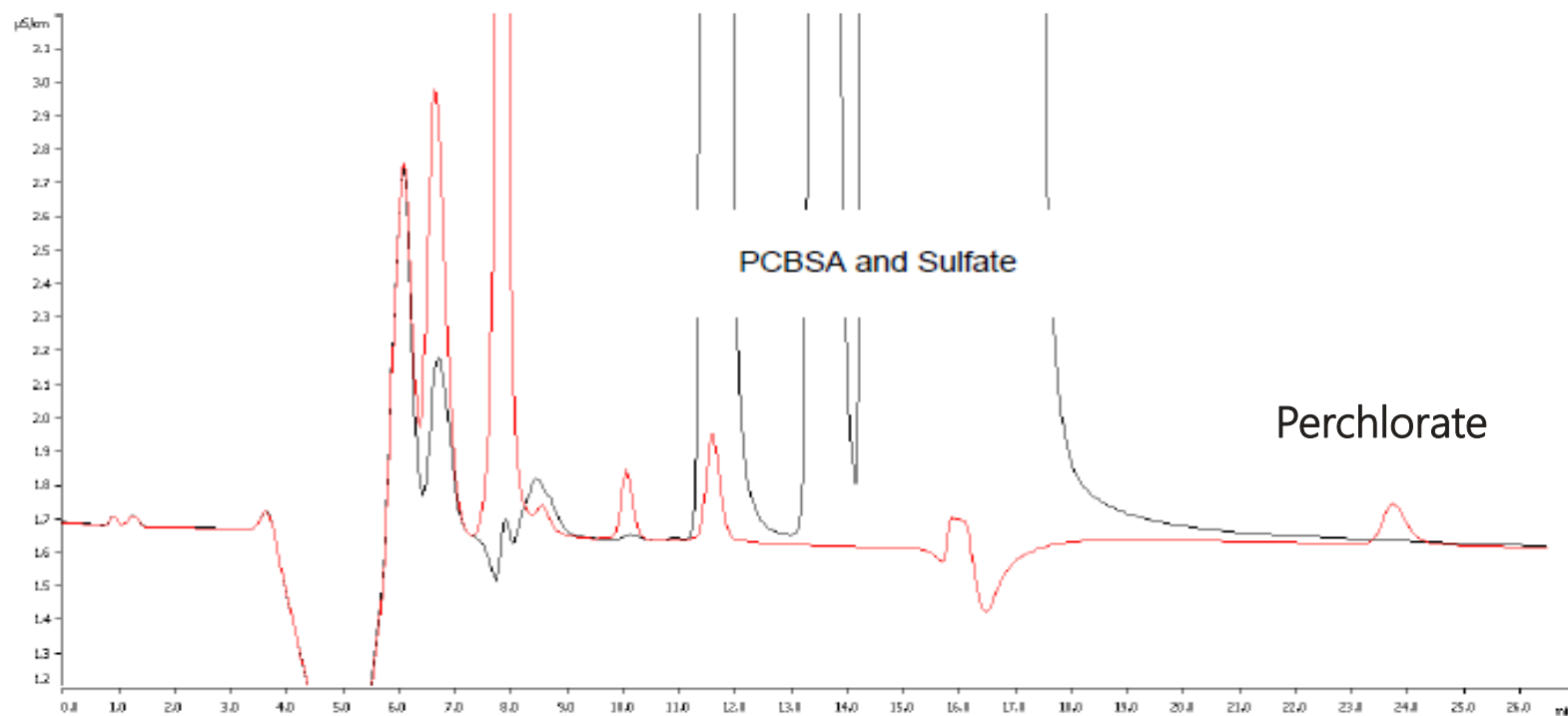


MCT Study Data (USEPA method 314.0, section 9)

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

Major 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 / 557.0



+

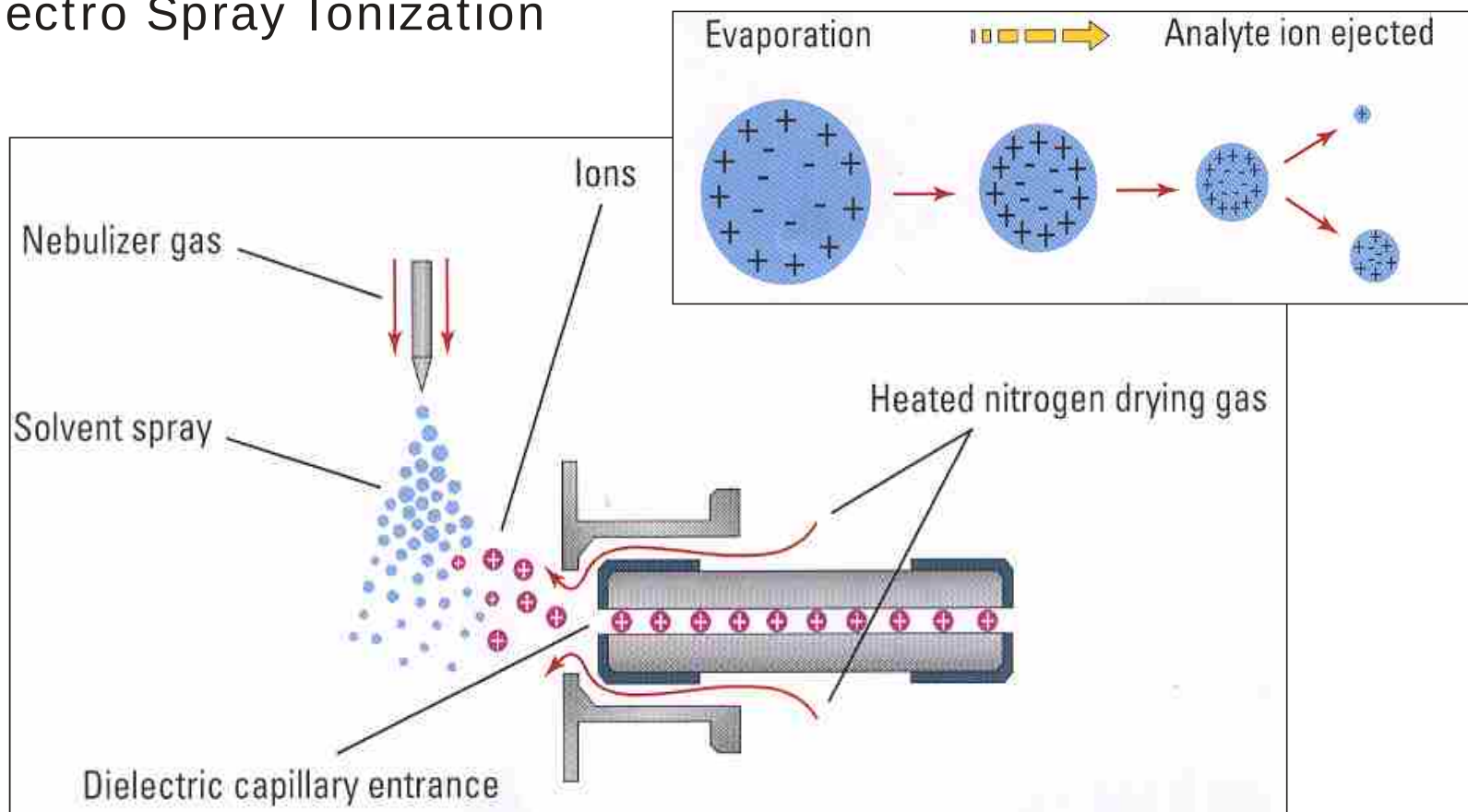


OR

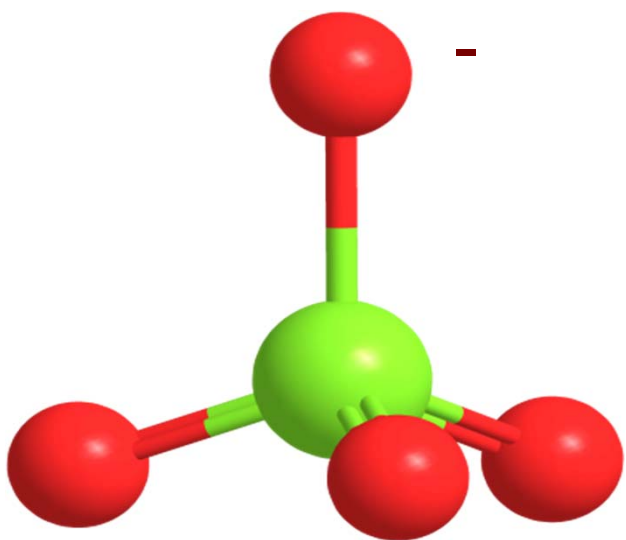


IC-MS

Electro Spray Ionization



Perchlorate Mass



Chlorine (Cl) = 35

+

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

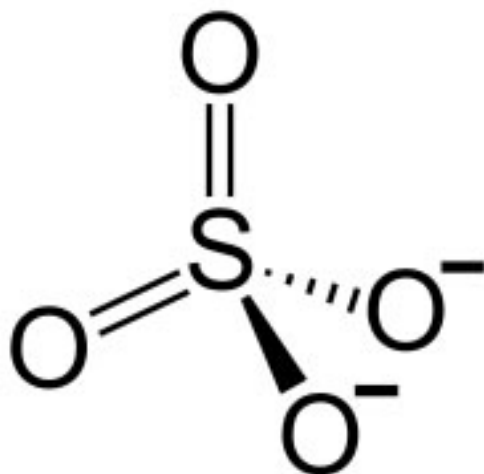
Perchlorate mass (Cl³⁵) =
35 + 64 = 99

→ 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

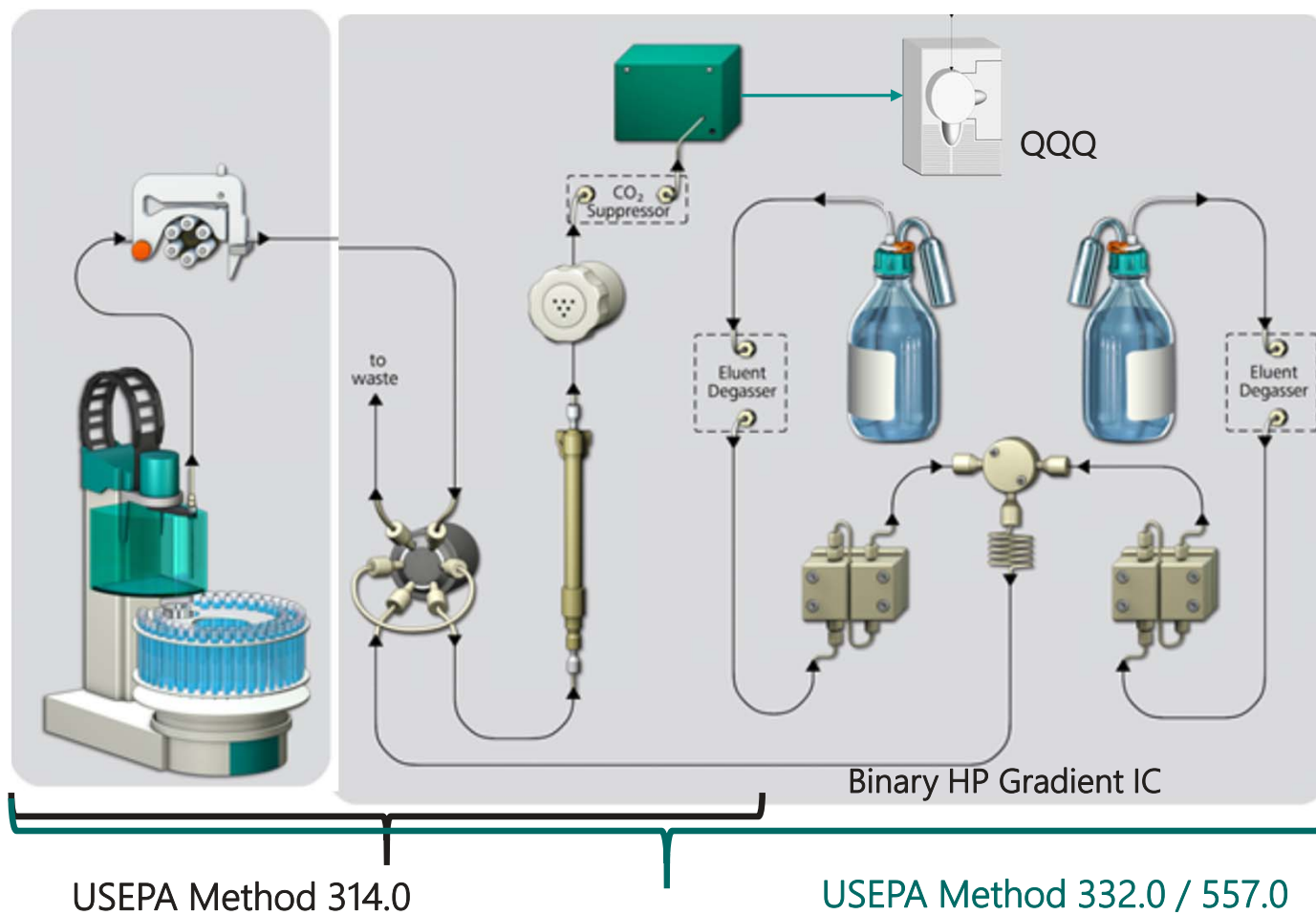
In Collaboration with
USEPA (ODW-OGW / OSW)



Metrohm Advanced IC – Agilent QQQ MSD



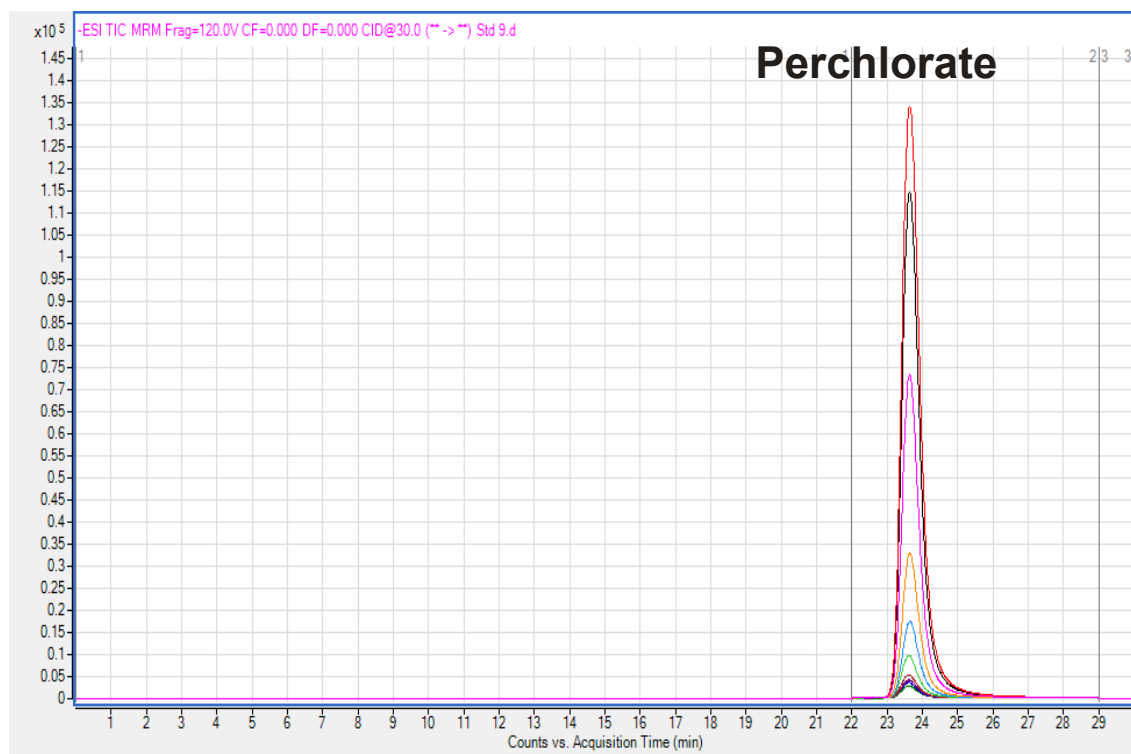
IC/MSMS Configuration



Chromatography

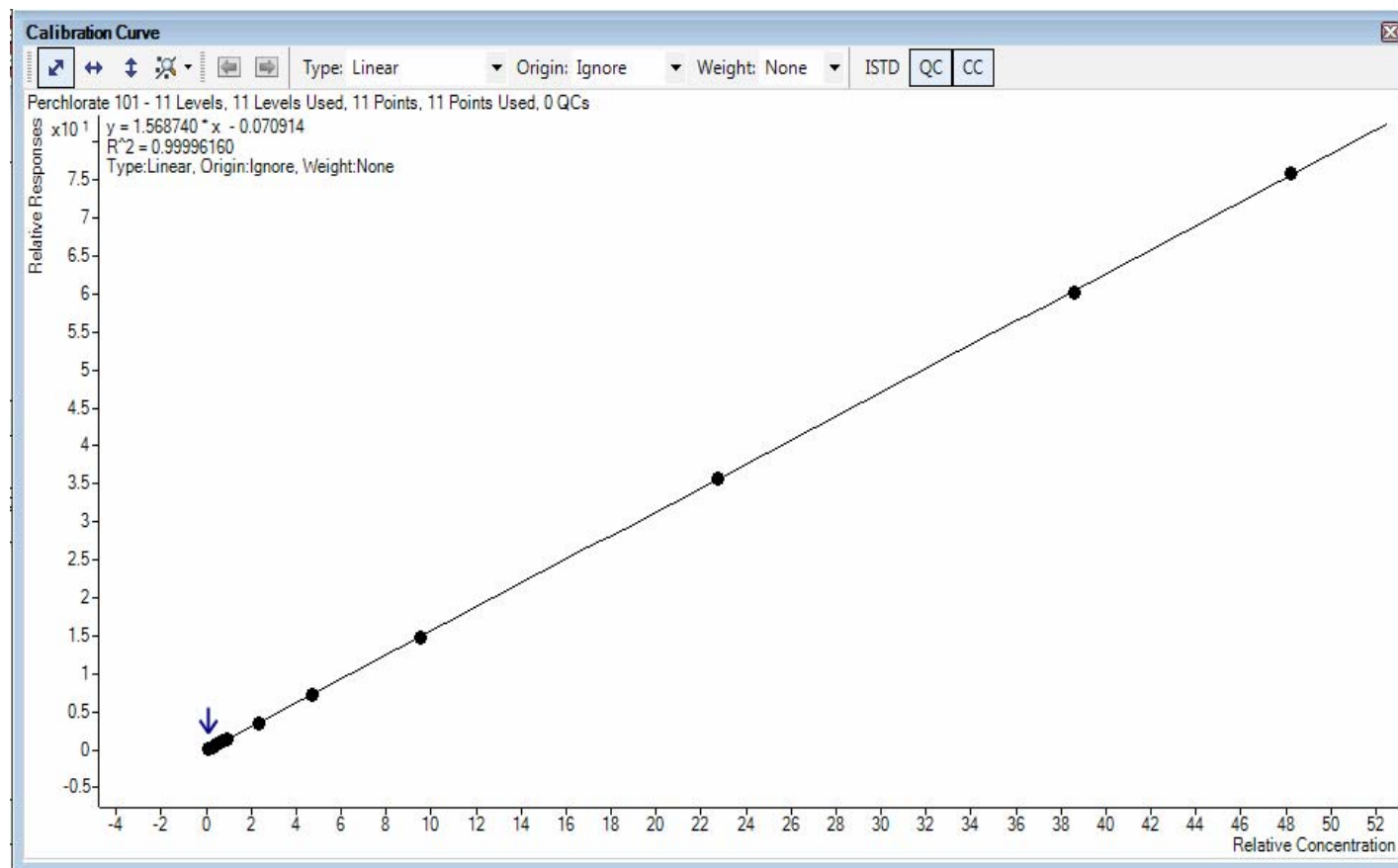
USEPA 332.0 – Perchlorate Calibration Overlay - ICMSMS

Eluent flow	0.7 mL/min
Eluent	10.6mM Na ₂ CO ₃ + 25% Acetonitrile
Column	Metrosep ASupp7-250
Column temperature	45°C
Sample volume	100 µL
Detector	Agilent QQQ



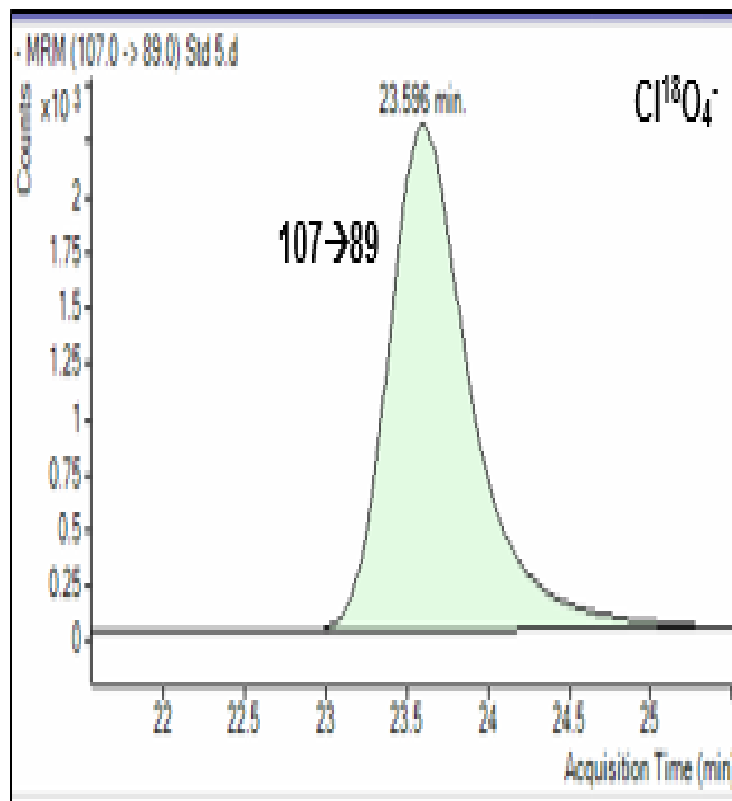
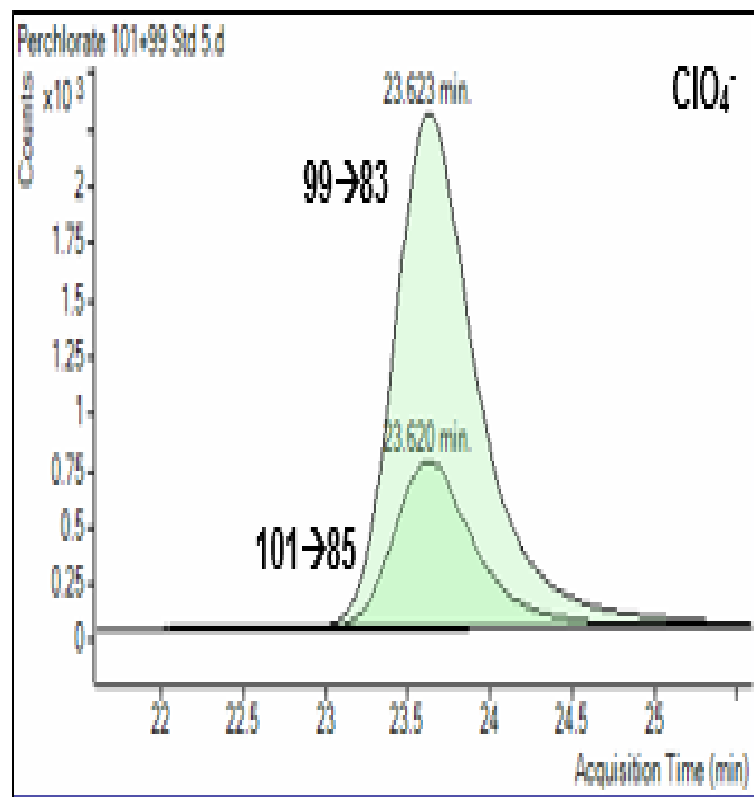
Perchlorate Calibration

AW IC US6-0240
AW IC US6-0244

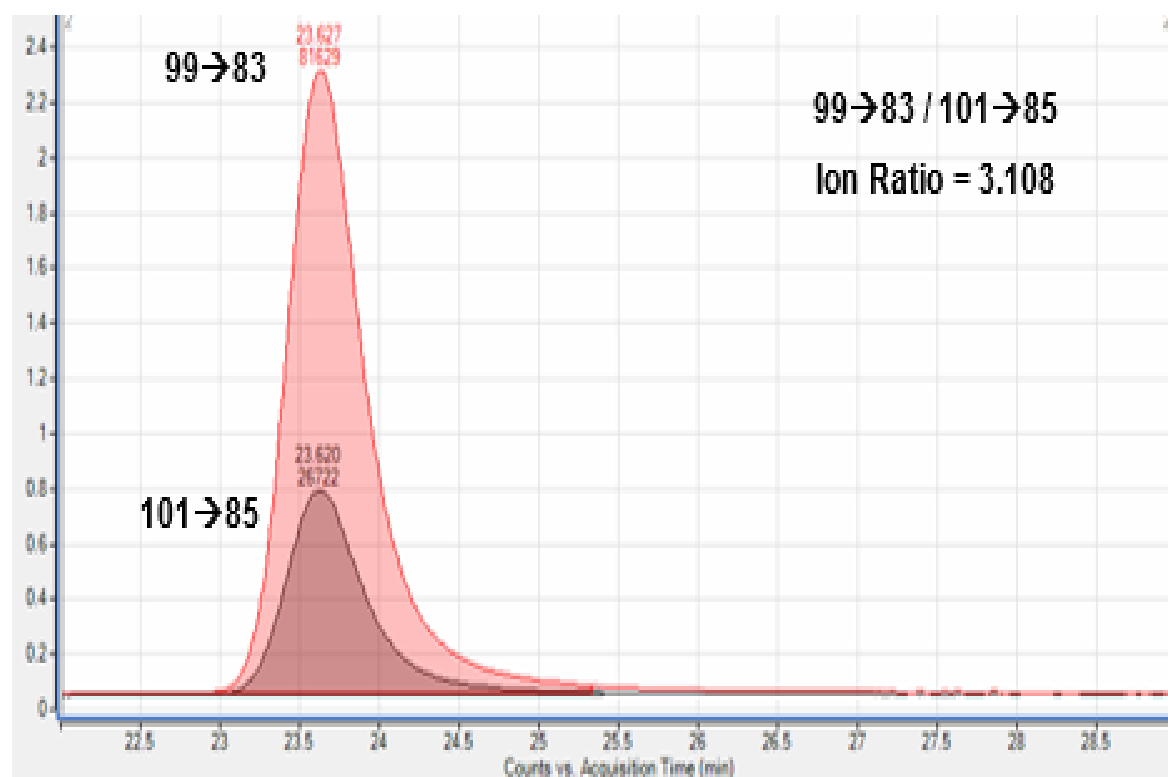


m/z 101
Range for
Calibration Standards
0.1ppb to 50ppb (ClO_4^{1-})

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

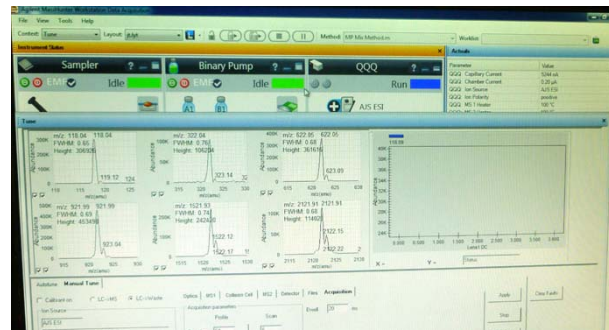
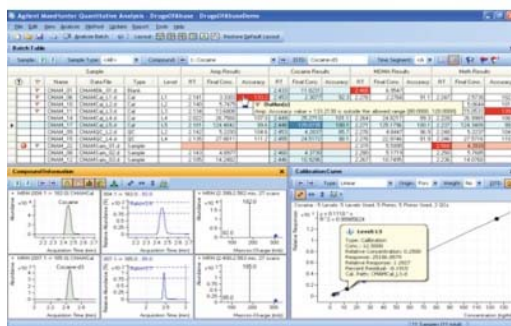
USEPA method acceptable value = 2.31 – 3.85

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	-
	Bromodichloroacetic 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 Na₂CO₃;
- 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

The screenshot displays the Agilent SourceOptimizer software interface. The main window has tabs for Acquisition, Source, Chromatogram, Instrument, and Diagnostics. The 'Source' tab is active, showing 'Source parameters' with input fields for Gas Temp (120 °C), Gas Flow (13 l/min), Nebulizer (45 psi), Sheath Gas Temp (390 °C), Sheath Gas Flow (12 l/min), and Chamber Current (0.36). Below these are sections for Positive and Negative ionization modes, with Capillary and Nozzle Voltage settings. A 'Project parameters' dialog box is overlaid on the right, showing the optimize method, project folder, and project name. It also contains an 'Instrument parameters' table with columns for Types, PreWait, Replicate, StepWait, StartValue, EndValue, and StepSize. The table lists parameters like Nozzle Voltage, Capillary, Gas Temp, Gas Flow, Sheath Gas Temp, Sheath Gas Flow, and Nebulizer. At the bottom of the dialog are buttons for 'Create Methods', 'Submit', and 'Close'.

Source parameters

Gas Temp: 120 °C

Gas Flow: 13 l/min

Nebulizer: 45 psi

Sheath Gas Temp: 390 °C

Sheath Gas Flow: 12 l/min

Chamber Current: 0.36

Positive Negative

Capillary: 3500 V 3000 V

Nozzle Voltage: 1500 V 1500 V

Project parameters

Optimize method: D:\MassHunter\Methods\SFC-MS-pesticide-1.m

Project Folder: D:\MassHunter\Data\SourceOpt

Project Name: Opt_1

Instrument parameters

	Types	PreWait (min)	Replicate	StepWait (min)	StartValue	EndValue	StepSize
☒	Nozzle Voltage	0	1	0	0	2500	250
☒	Capillary	0	1	0	2000	5000	250
☒	Gas Temp	30	1	20	160	340	20
☒	Gas Flow	30	1	0	4	13	1
☒	Sheath Gas Temp	30	1	20	200	400	20
☒	Sheath Gas Flow	30	1	0	8	12	1
☒	Nebulizer	0	1	0	20	50	5

Worklist parameters

Sample Name: PestStd_100ppb

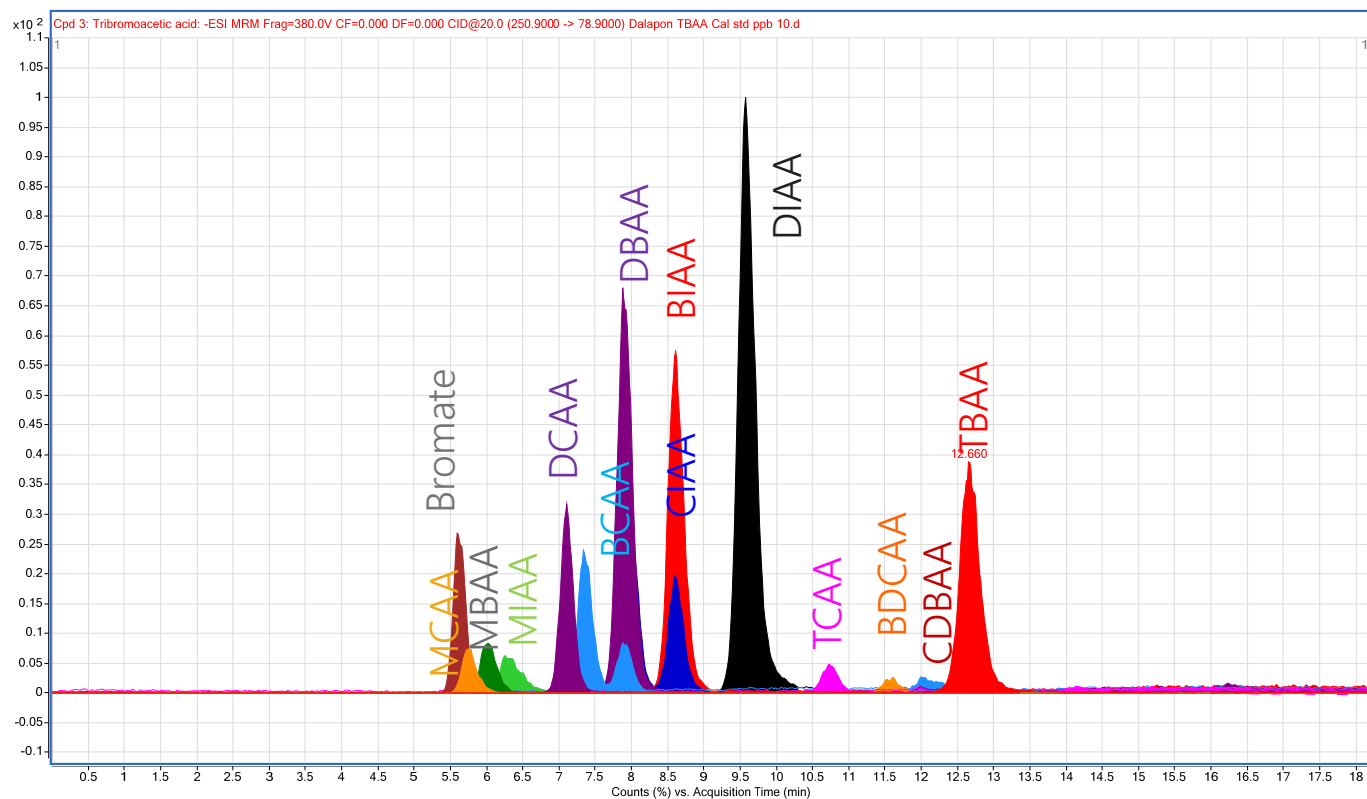
Sample Position: Val 61

Worklist position of data file used for calibration: 1

Create Methods Submit Close

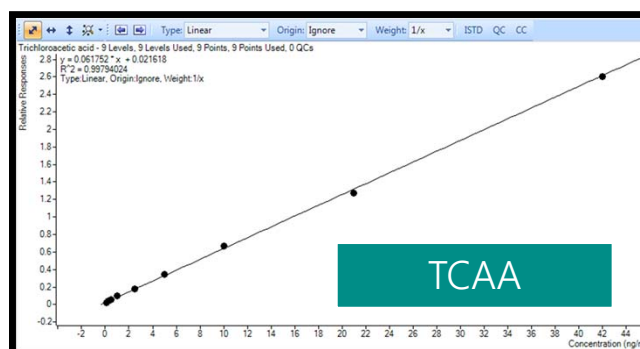
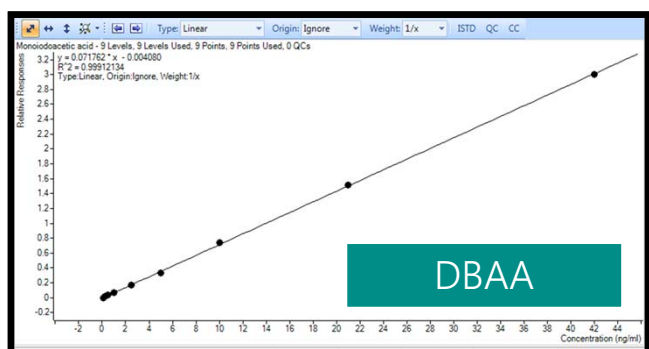
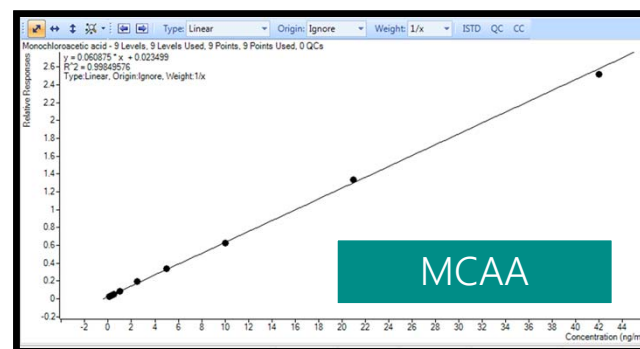
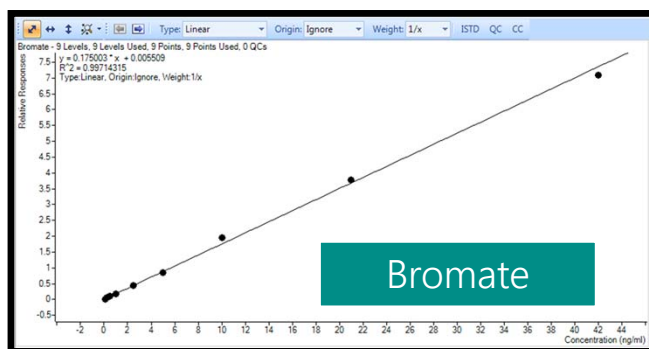
Chromatography

10 µg/L standard in Milli-Q water



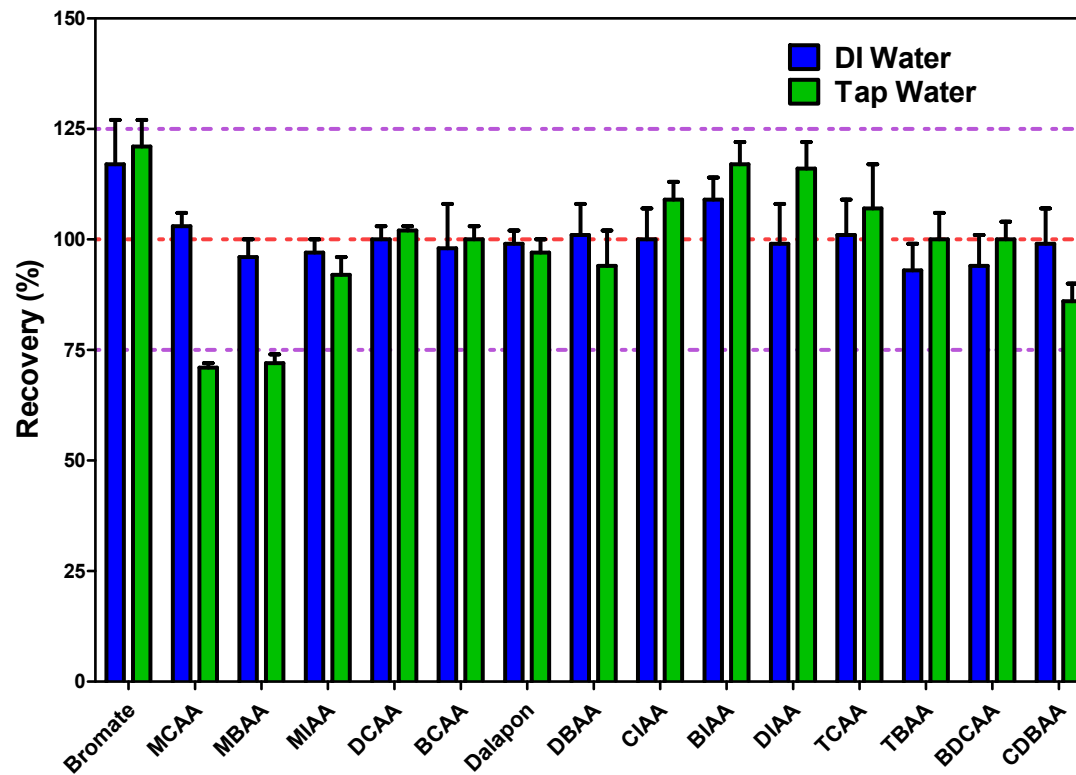
Linearity

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

Acknowledgements

- Ms. Shen Yi-Yang – Retired USEPA OSW
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- Dr. David Munch – Retired ODW/OGW
- Mr. Johnson Mathew – USEPA Region 6
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- Metrohm USA Applications Team
 - Mr. Jay Sheffer
- Agilent Technologies
 - Dr. Tarun Anumol
 - Mr. Craig Marvin

Q&A

Thank You