Trace-Level Analysis Of Perchlorate by IC/MS

Presented by

Johnson Mathew – US EPA Region-6

Dr. Joe Hedrick – Agilent Technologies

Jay Gandhi – Metrohm-Peak Inc

metrohm-peak ion chromatography

Agilent Technologies

Need for Trace Level Perchlorate Analysis

- Trace level Perchlorate analysis has driven conventional methods (EPA 314.0) to the edge
- In high matrix interferences (TDS = 3000ppm), it is difficult to accurately measure Perchlorate by conductivity detection below 1 ppb
- A collaborative study between these three organizations has developed a method which will show…..

metrohm-peak ion chromatography

Agilent Technologies

Goals And Solutions For IC/MS Analysis Of Perchlorate

- Simple and rugged
  - External standard method (within EPA 314)
  - Single stage MS (quadrupole)
  - 4mm column, (Flow rate < 1mls/min)

- Accurate and precise to 1 **part per billion (ppb)**
  - MDL < 100 parts per trillion (ppt)
  - Must be able to meet QC for prolonged unattended operation

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

The Bottom Line

- **Precision, Sensitivity and Accuracy**
  - RSD <4% at 1ppb for both m/z 99 and 101
  - MDL~70 parts per trillion (ppt)
  - >90% Recovery for Spikes at 0.5 and 1 ppb in heavy matrix and real samples
- **Reliability for High Through-Put Laboratories**
  - Meets standard QC procedures over 24 hour period

Instrument Set - Up

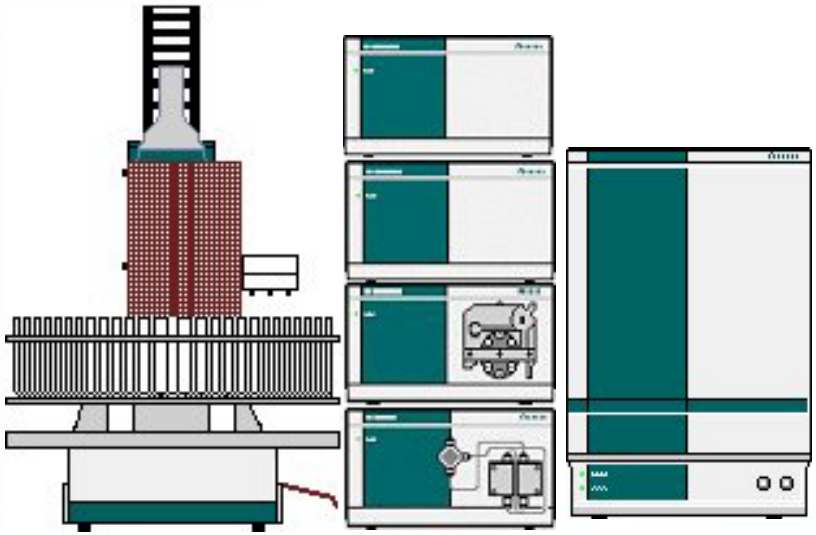
- **Metrohm Advanced IC**
  - 100 uL loop injection
  - Column: MetroSep ASUPP-5 (4mm x 100mm)
  - Eluant: 30mM NaOH + 30% Methanol
  - Flow rate: 0.8 ml/min with NO SPLITTING.
- **Agilent 1100LC/MSD ESI**
  - Negative mode "auto-tune"
  - V_{cap} = 1400V, Drying Gas = 9L/min@320 C.
  - Nebulizer Pressure=20 psig.
  - Fragmentor = 140 V.

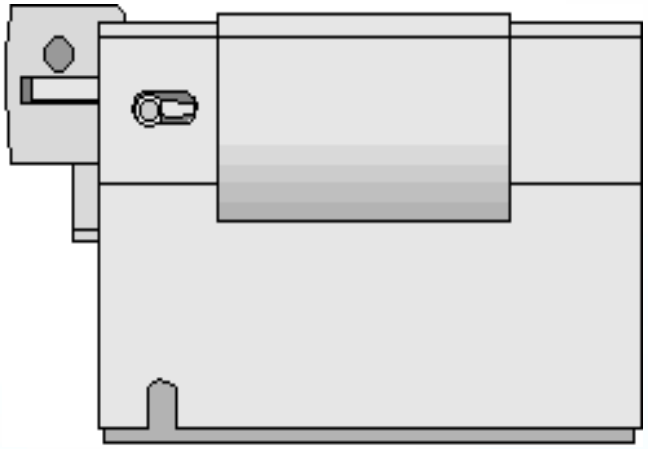
metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Metrohm Advanced Modular IC – Agilent 1100 MSD





metrohm-peak
ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Picture of Instrument Set-up

metrohm-peak
ion chromatography

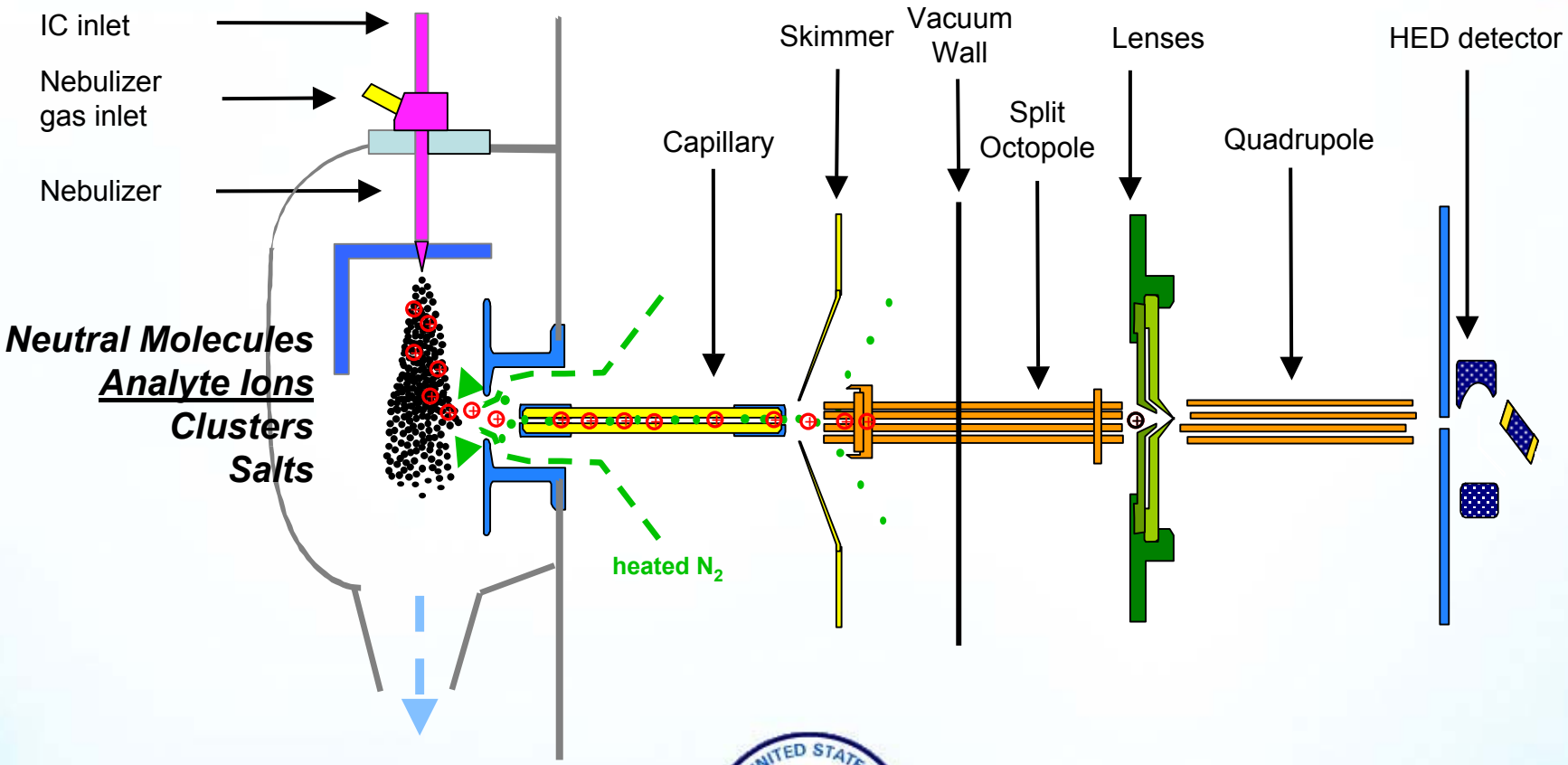
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Experimental Conditions
Metrohm Advanced IC

- **Metrohm Modular IC**
  - Metrohm 818 Dual Piston Pump
  - Metrohm 820 IC Separation Center
  - Metrohm 819 IC Detector
  - Metrohm 833 Suppressor Module
  - Metrohm 788 Ultra Filtration Auto Sampler
  - Metrohm 830 Interface with ICNet Software
  - MetroSep ASUPP 5-100 Column + RP Guard

Agilent 1100 LC/MSD SL AP Electrospray



metrohm-peak ion chromatography

Agilent Technologies

The Samples

- UHP water matrix (18meg Ω)
- Simulated Matrix
  - Low Matrix = 200ppm each of Cl^{-1}, CO_3^{2-}, SO_4^{2-}
  - Mid Matrix = 500ppm each of Cl^{-1}, CO_3^{2-}, SO_4^{2-}
  - High Matrix = 1000ppm each of Cl^{-1}, CO_3^{2-}, SO_4^{2-}
- "Real World Samples" submitted by customers

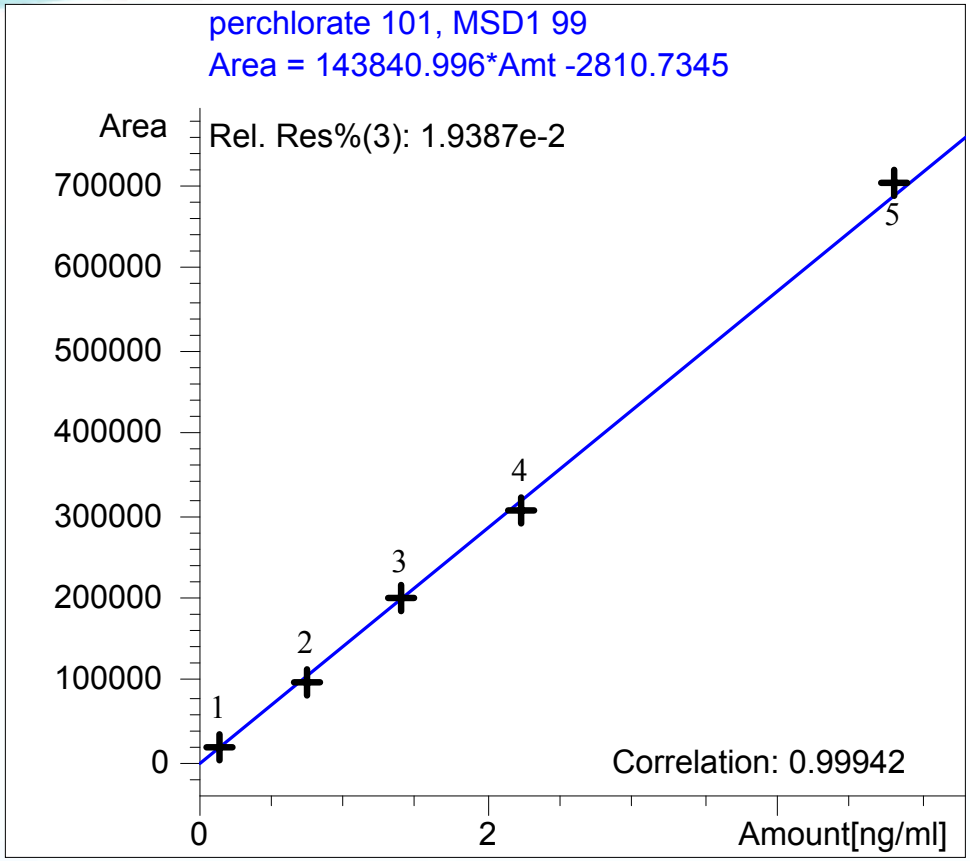
Calibration Data for MSD

metrohm-peak
ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Calibration Data (m/z 99)

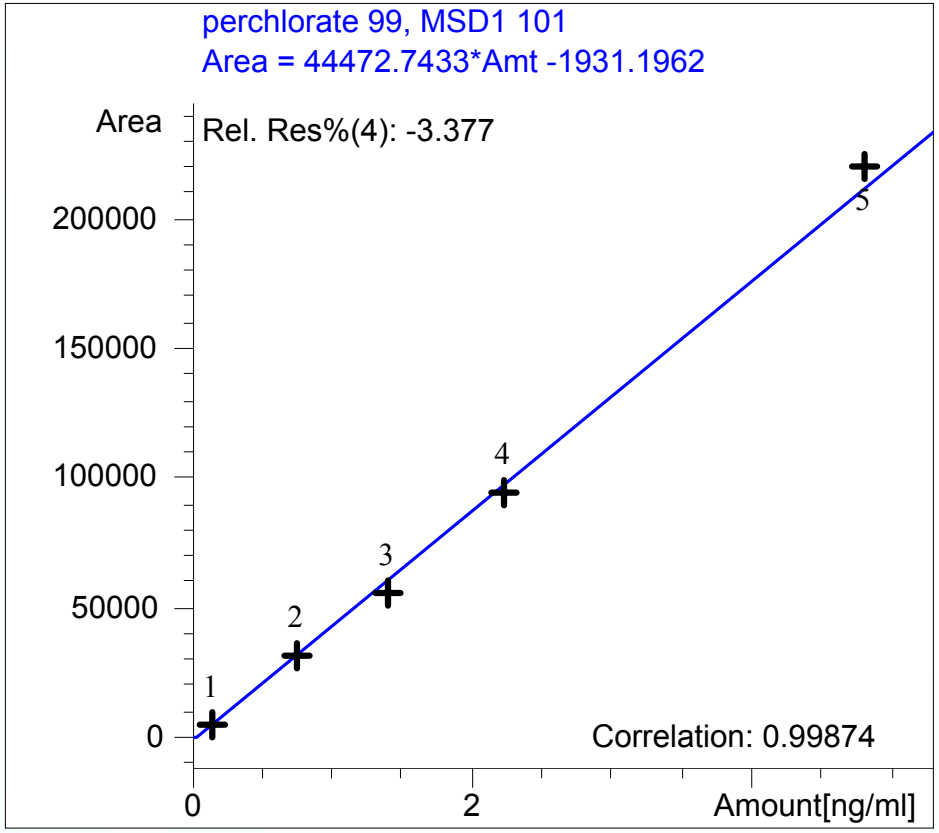


Range for Calibration Standards 0.1ppb to 10ppb (ClO_4^{1-})

metrohm-peak ion chromatography

Agilent Technologies

Calibration Data (m/z 101)



Range for Calibration Standards 0.1ppb to 10ppb (ClO_4^{1-})

metrohm-peak ion chromatography

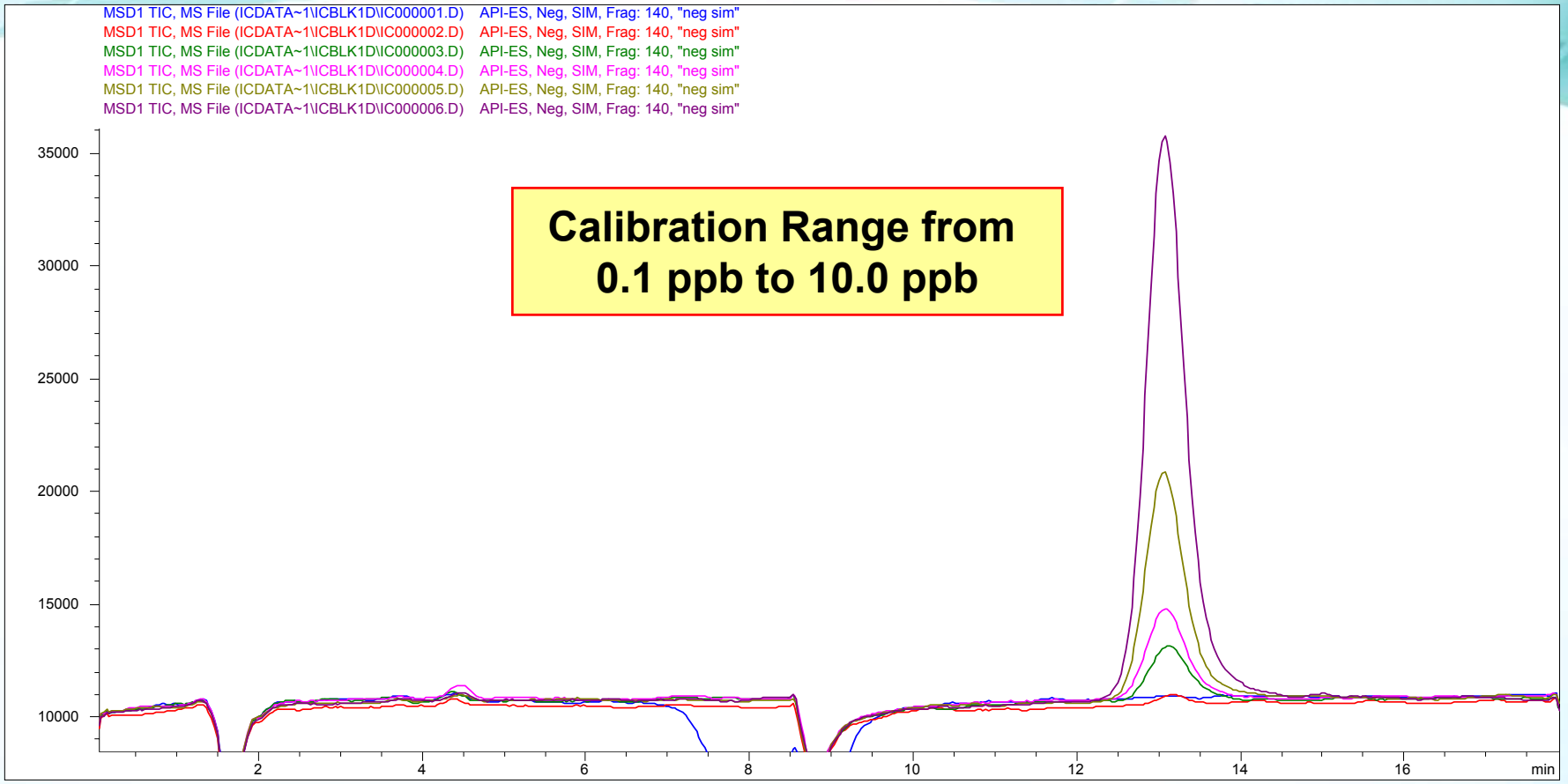
Agilent Technologies

Chromatography

metrohm-peak
ion chromatography

Agilent Technologies

Total Ion Chromatograms (TIC) Calib. Standards and Blank



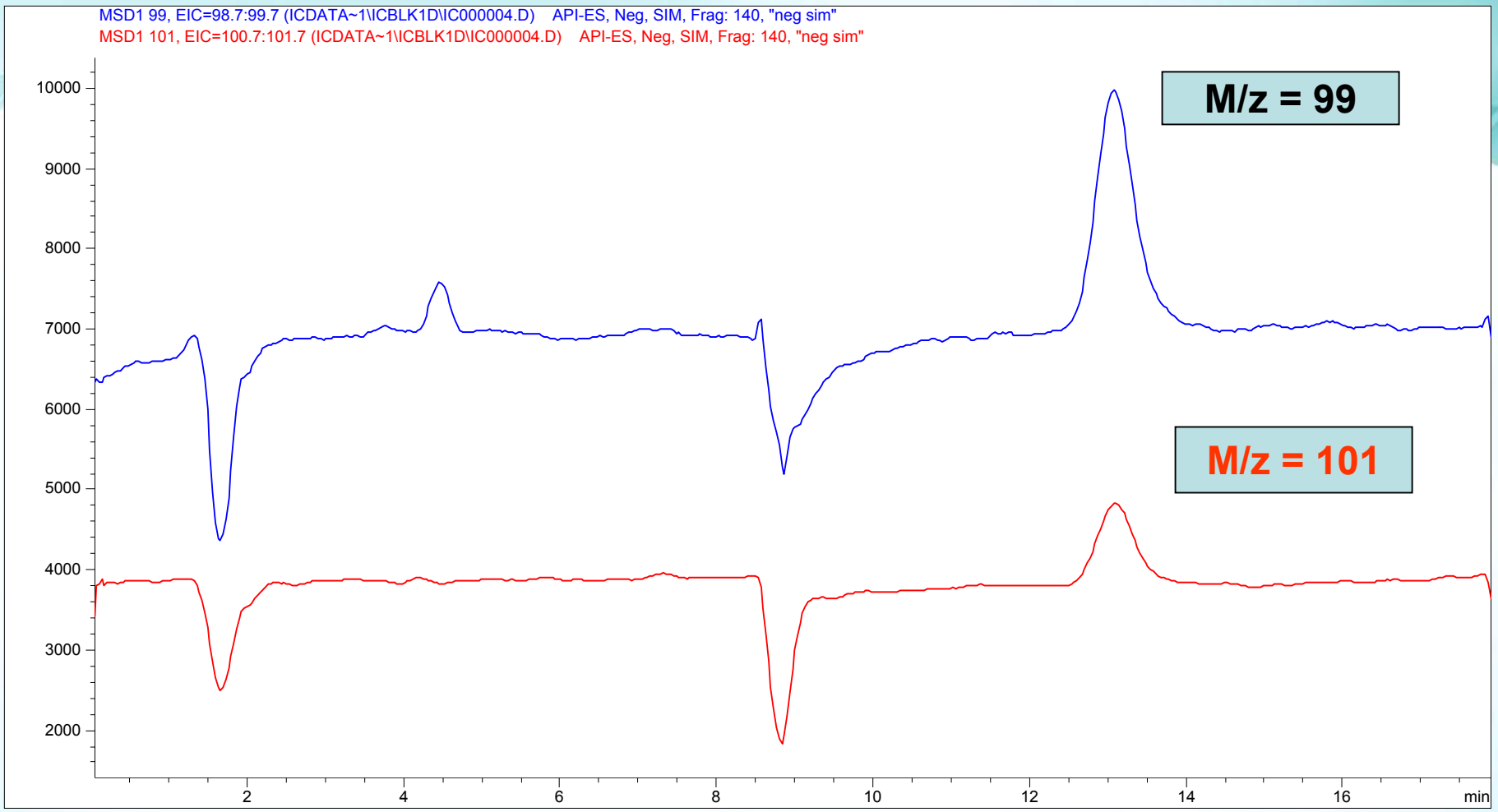
Calibration Range from 0.1 ppb to 10.0 ppb

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

0.79 ppb Standard

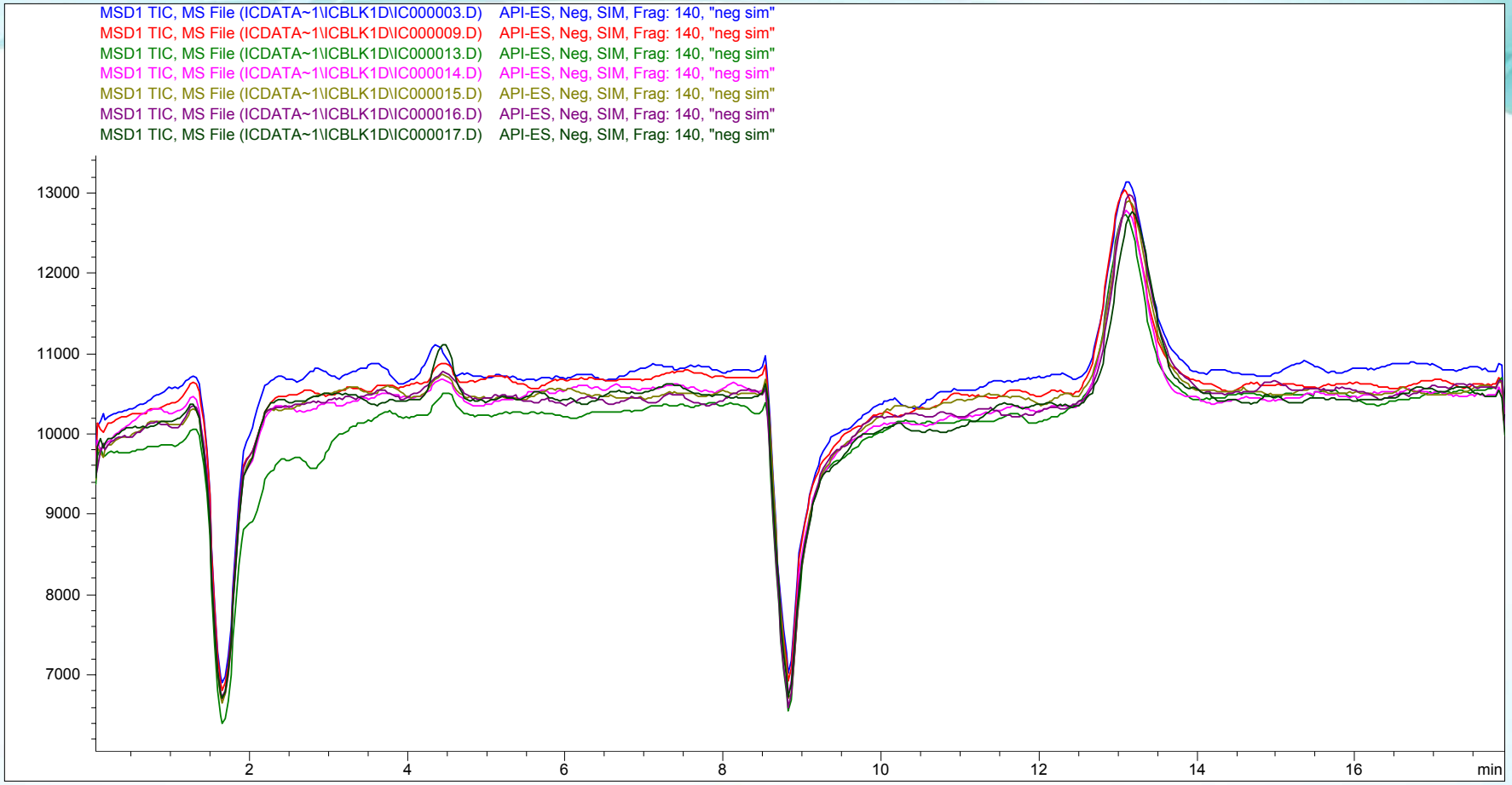


metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Replicates - TIC 0.5 ppb Standards



metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Extracted Ion Chromatograms for 0.5 ppb standard

metrohm-peak ion chromatography

Agilent Technologies

Results of UHP Water Fortified with Perchlorate

0.5 ppb replicates

SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
0.5 PPB	0.480	0.487	101.46%	0.519	108.13%
0.5 PPB	0.480	0.477	99.38%	0.471	98.13%
0.5 PPB	0.480	0.460	95.83%	0.490	102.08%
0.5 PPB	0.480	0.477	99.38%	0.492	102.50%
0.5 PPB	0.480	0.520	108.33%	0.505	105.21%
0.5 PPB	0.480	0.494	102.92%	0.509	106.04%
Average	0.480	0.486	101.22%	0.498	103.68%
Std. Dev		0.020	0.042	0.017	0.035
RSD		4.18%	4.18%	3.41%	3.41%

1.0 ppb replicates

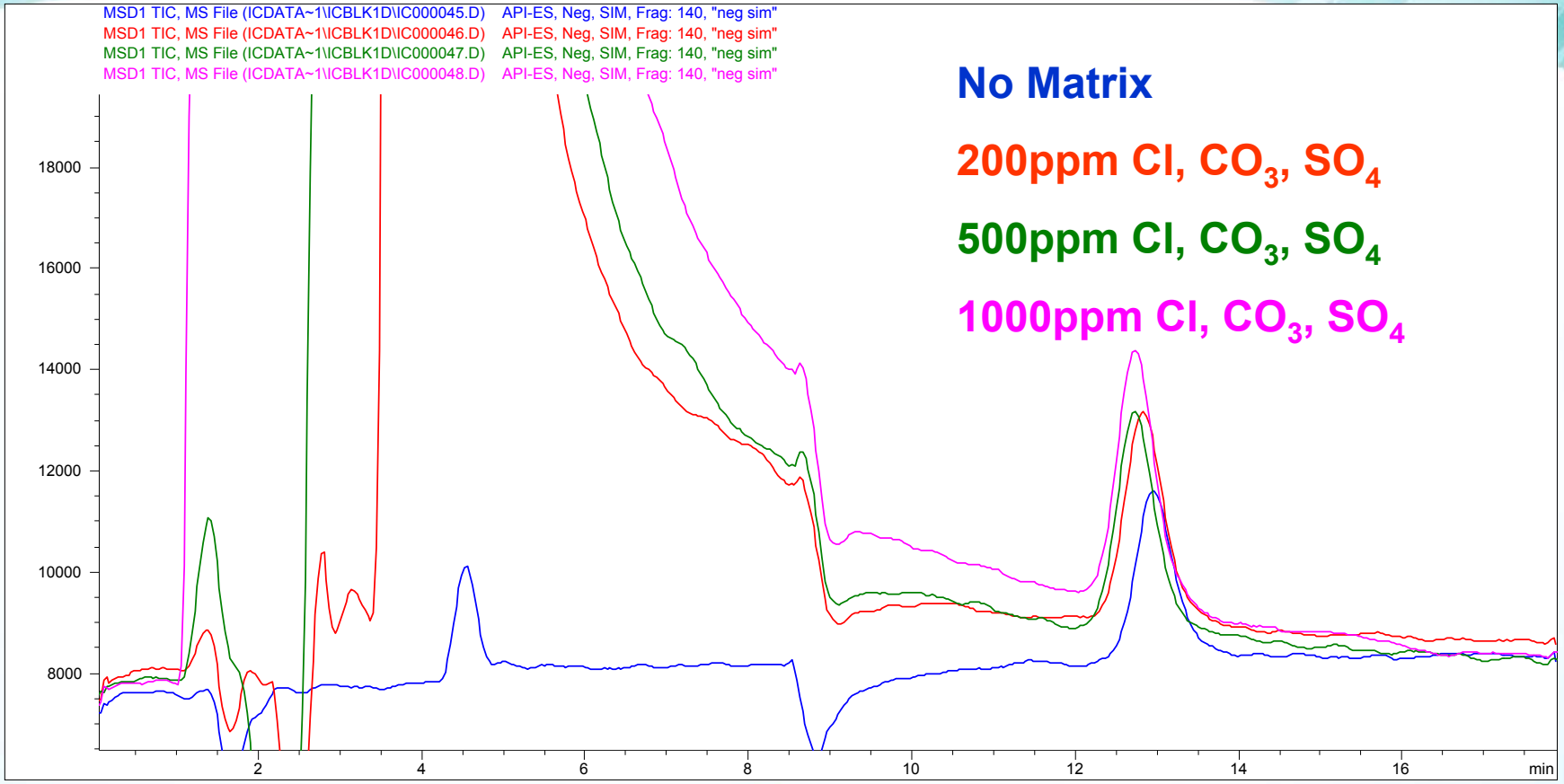
SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
1.0 PPB	0.780	0.756	96.92%	0.768	98.46%
1.0 PPB	0.780	0.810	103.85%	0.830	106.41%
1.0 PPB	0.780	0.776	99.49%	0.772	98.97%
1.0 PPB	0.780	0.799	102.44%	0.754	96.67%
1.0 PPB	0.780	0.788	101.03%	0.768	98.46%
1.0 PPB	0.780	0.792	101.54%	0.807	103.46%
Average	0.780	0.787	100.88%	0.783	100.41%
Std. Dev		0.019	0.024	0.029	0.037
RSD		2.40%	2.40%	3.70%	3.70%

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Synthetic Matrix Spikes Overlaid with 1ppb Standard



metrohm-peak ion chromatography

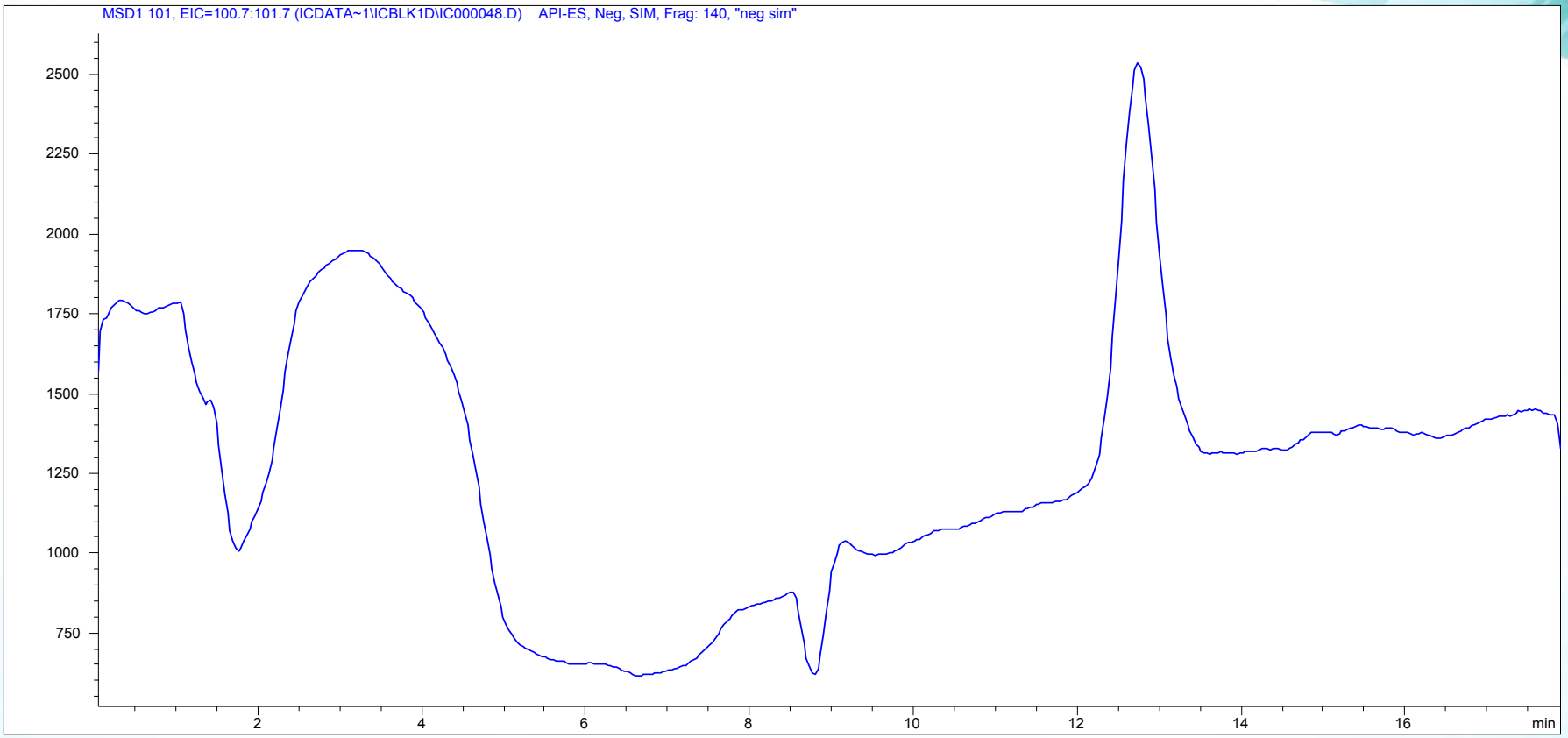
Agilent Technologies

Single Ion Chromatograms of High Matrix Spike

metrohm-peak ion chromatography

Agilent Technologies

1000ppm each of Cl^-, CO_3^{2-}, SO_4^{2-} in Matrix + 1ppb Perchlorate (m/z 101)



metrohm-peak ion chromatography

Agilent Technologies

Results of Matrix Fortified with Perchlorate

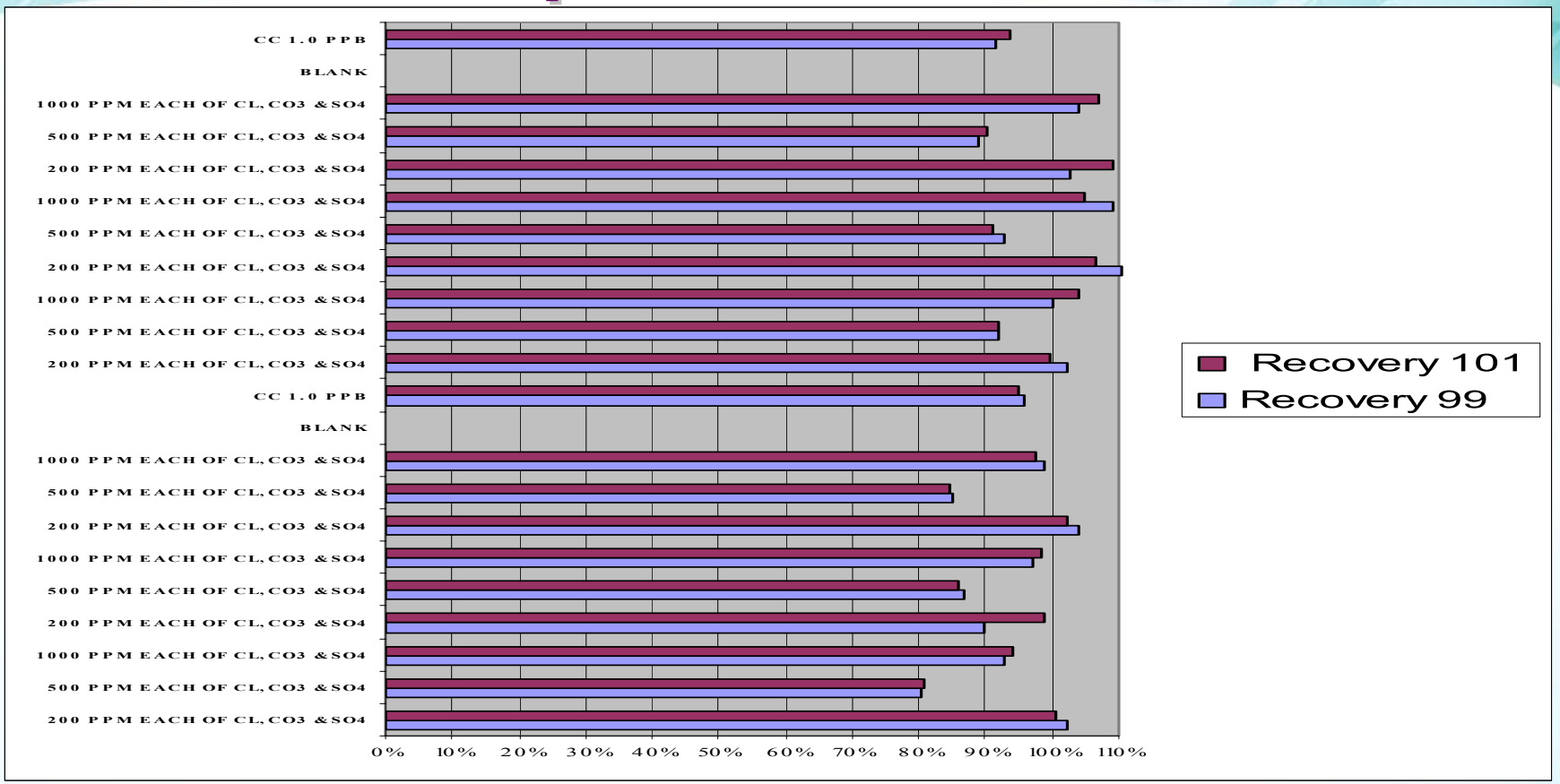
SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
200 PPM EACH OF CL,CO3 & SO4	0.780	0.799	102.44%	0.784	100.51%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.804	80.40%	0.808	80.80%
1000 PPM EACH OF CL,CO3 & SO4	1.000	0.930	93.00%	0.940	94.00%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.700	89.74%	0.770	98.72%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.870	87.00%	0.860	86.00%
1000 PPM EACH OF CL,CO3 & SO4	1.000	0.973	97.30%	0.986	98.60%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.810	103.85%	0.796	102.05%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.851	85.10%	0.846	84.60%
1000 PPM EACH OF CL,CO3 & SO4	1.000	0.990	99.00%	0.977	97.70%
BLANK	0.000	0.000		0.000	
CC 1.0 PPB	0.780	0.747	95.77%	0.742	95.13%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.799	102.44%	0.777	99.62%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.920	92.00%	0.921	92.10%
1000 PPM EACH OF CL,CO3 & SO4	1.000	1.000	100.00%	1.040	104.00%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.860	110.26%	0.830	106.41%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.930	93.00%	0.913	91.30%
1000 PPM EACH OF CL,CO3 & SO4	1.000	1.090	109.00%	1.050	105.00%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.800	102.56%	0.850	108.97%
500 PPM EACH OF CL,CO3 & SO4	1.000	0.890	89.00%	0.904	90.40%
1000 PPM EACH OF CL,CO3 & SO4	1.000	1.040	104.00%	1.070	107.00%
Average			96.67%		97.10%
Std.Dev			0.082		0.080
RSD %			8.48%		8.22%

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Recovery for Matrix Set
20 samples over 7 hours



metrohm-peak
ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

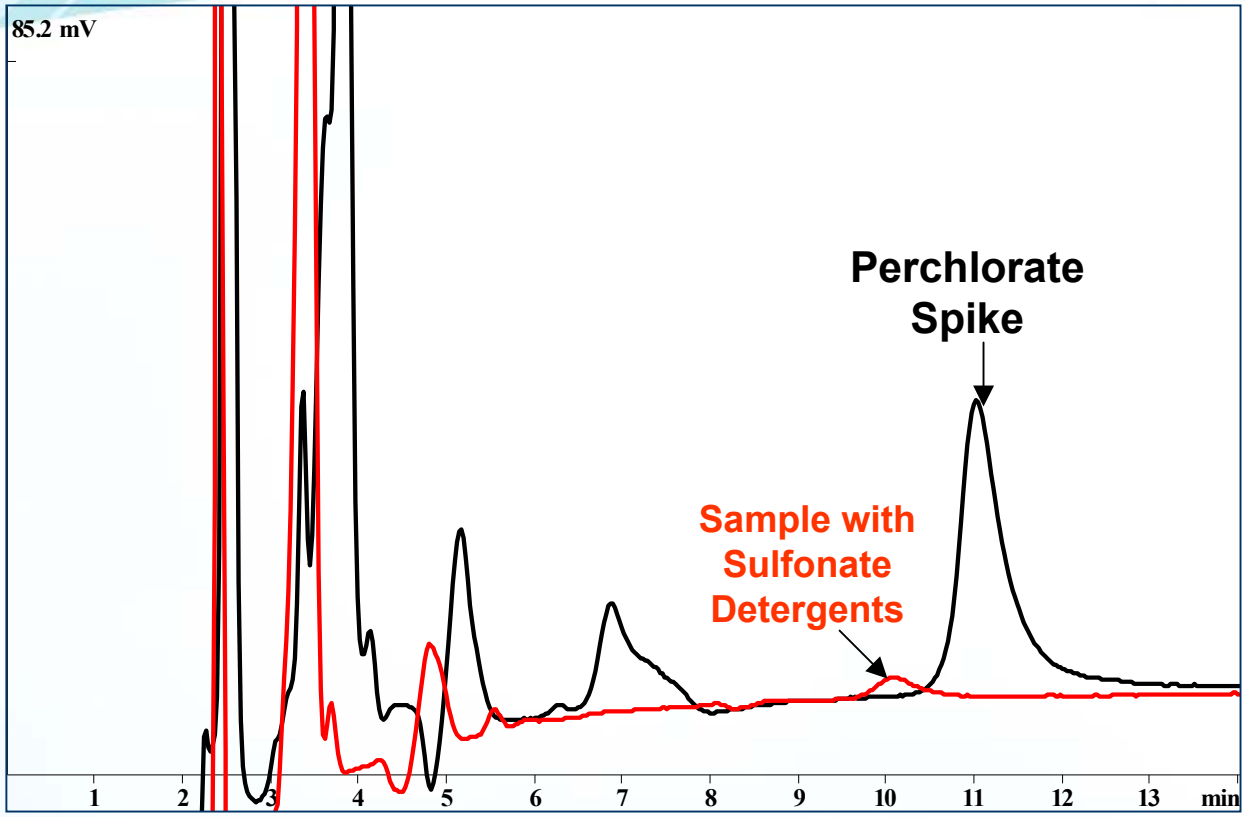
Agilent Technologies

“Real World Samples”

metrohm-peak
ion chromatography

Agilent Technologies

Sample and Sample Spike (with Sulfonate Detergents)



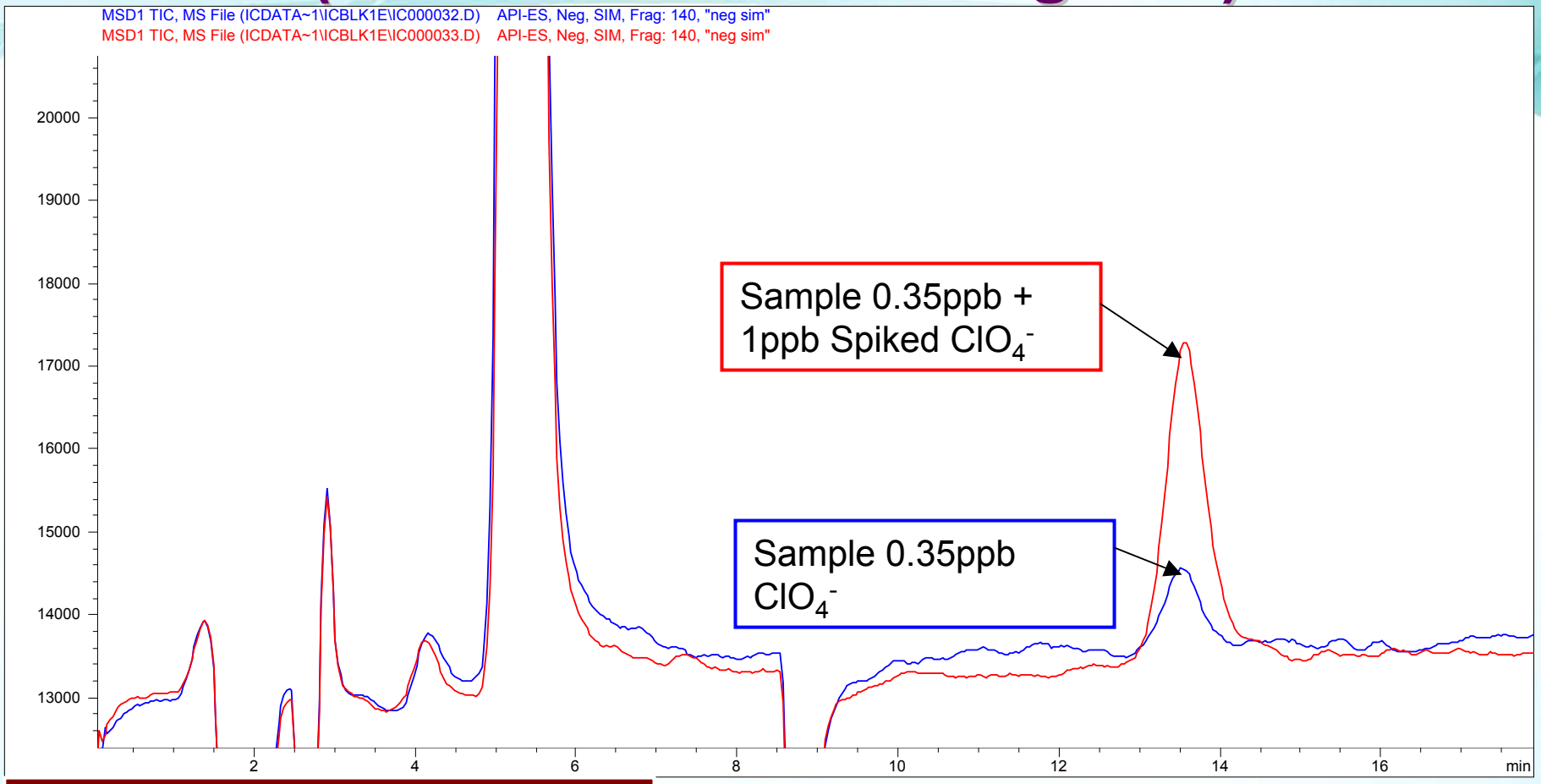
Sulfonate Compounds Elute in the same Region as ClO_4^{1-} Causing interference For Conductivity Detector

IC with Conductivity Detector

metrohm-peak ion chromatography

Agilent Technologies

Sample and Sample Spike (with Sulfonate Detergents)



IC with Mass Spectrometer

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

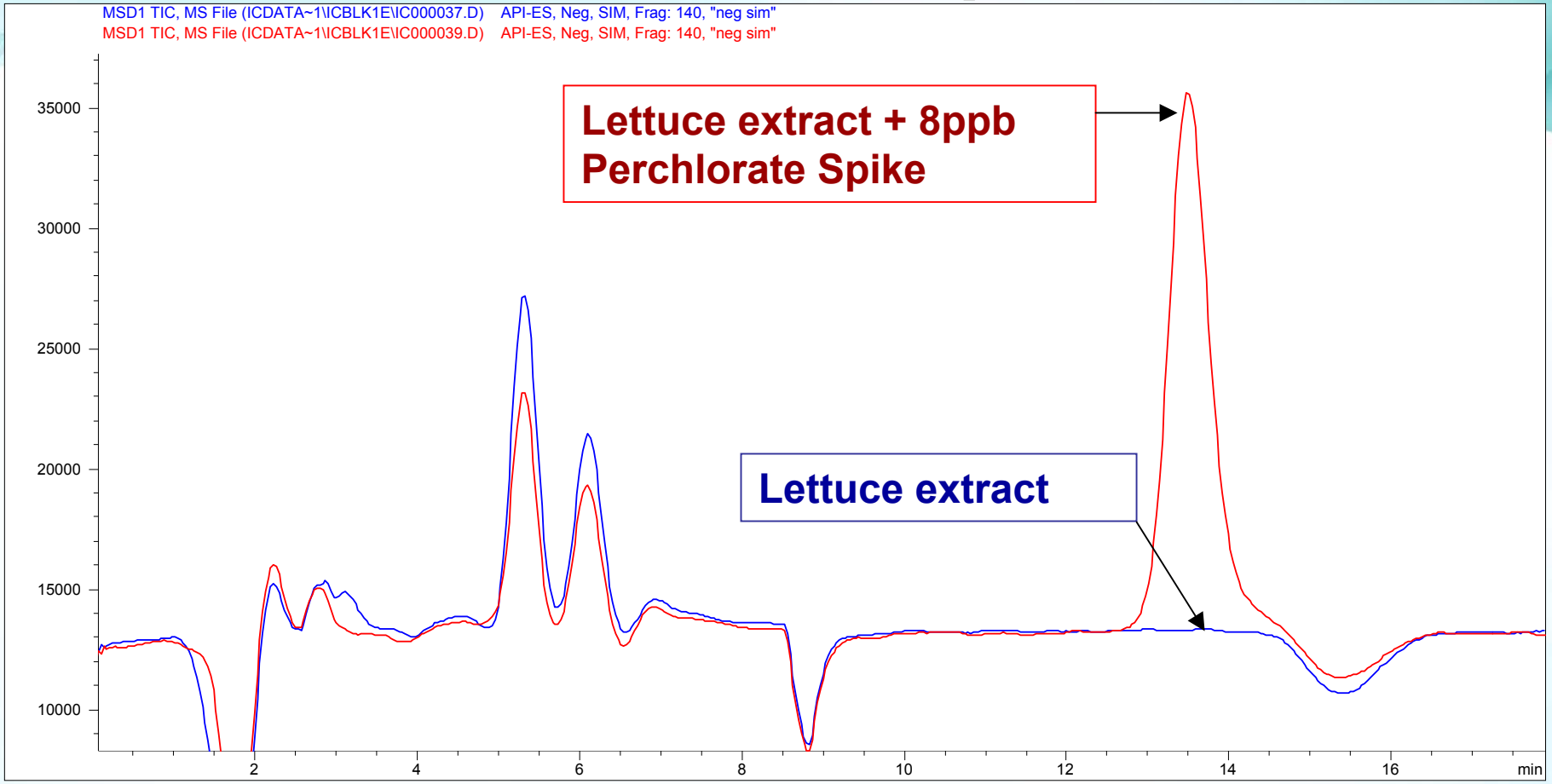
Green Leafy Vegetables ….

metrohm-peak
ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Lettuce and Spike

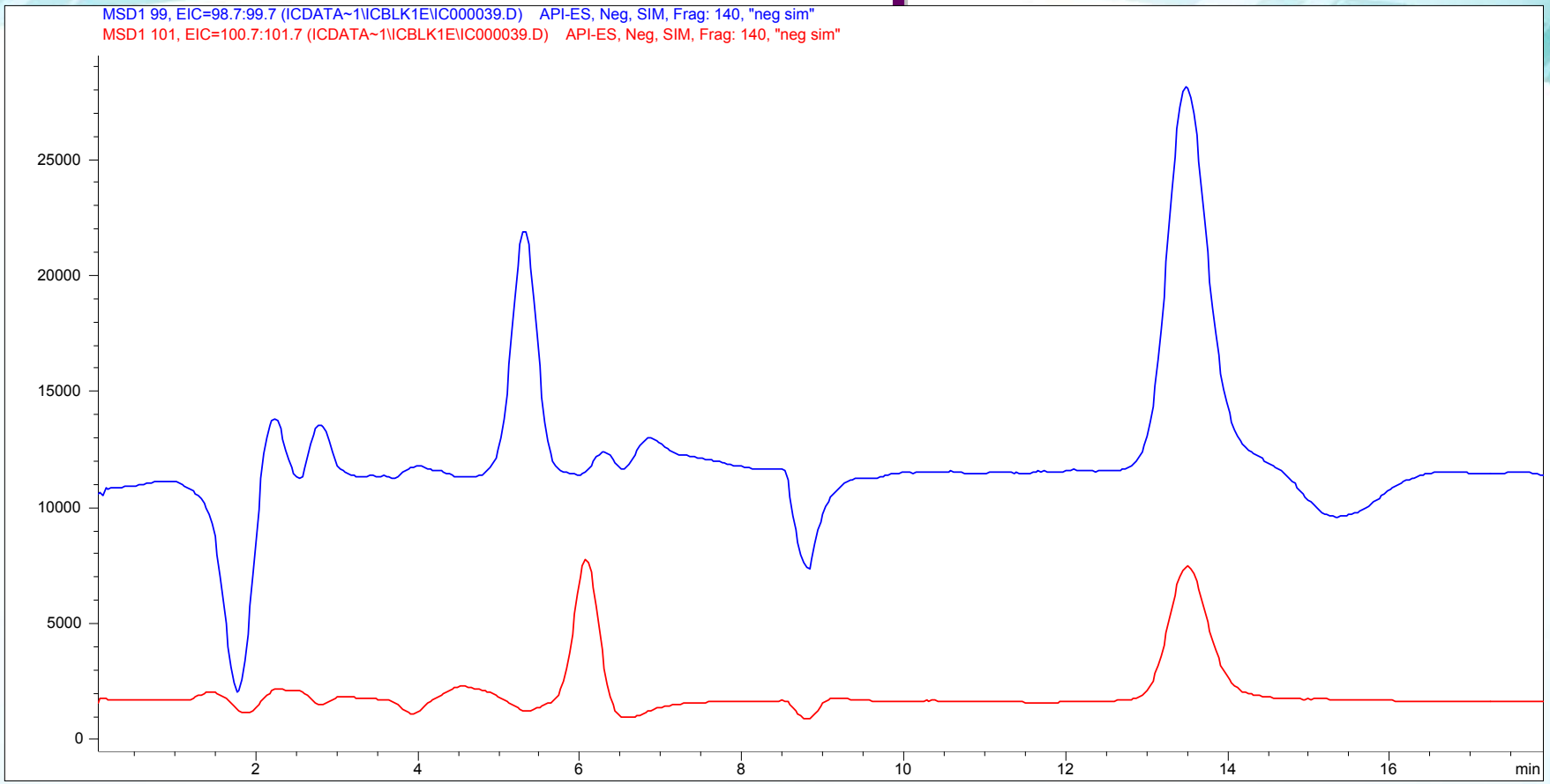


metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Single Ion Chromatograms of Lettuce Spike



metrohm-peak ion chromatography

Agilent Technologies

Results of "Real World Samples"

Sample Submitted by Metrohm-Peak Customer						
	Perchlorate Data					
Sample ID	Actual ppb	m/z99, ppb	m/z 101, ppb	m/z99, recovery	m/z101, recovery	Notes
Sample-1	0.50	0.44	0.51	88.00%	102.0%	0.5ppb in Distilled Water
Sample-2	1.00	0.91	1.01	91.00%	100.7%	1.0ppb in Distilled Water
Sample-3	1.00	0.95	1.00	95.16%	99.7%	1.0ppb in Tap Water
Sample-4	0.42	0.41	0.43	97.33%	102.1%	ground water w/0.42ppb
Sample-5	???	0.00	0.00			Unknown value, but sample is loaded with Sulfonate surfactants
Sample-6	0.35	0.30	0.33	86.93%	95.0%	ground water w/0.35ppb
Sample-6A	1.35	1.18	1.36	87.41%	100.6%	Sx-6 + 1ppb spike
Sample-7	0.00	0.00	0.00	100.00%	100.0%	ground water w/ no Percholrate
Sample-8	0.00	0.00	0.00			Lettuce extract
Sample-9	7.92	7.35	7.41	92.86%	93.6%	Lettuce extract spike

metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

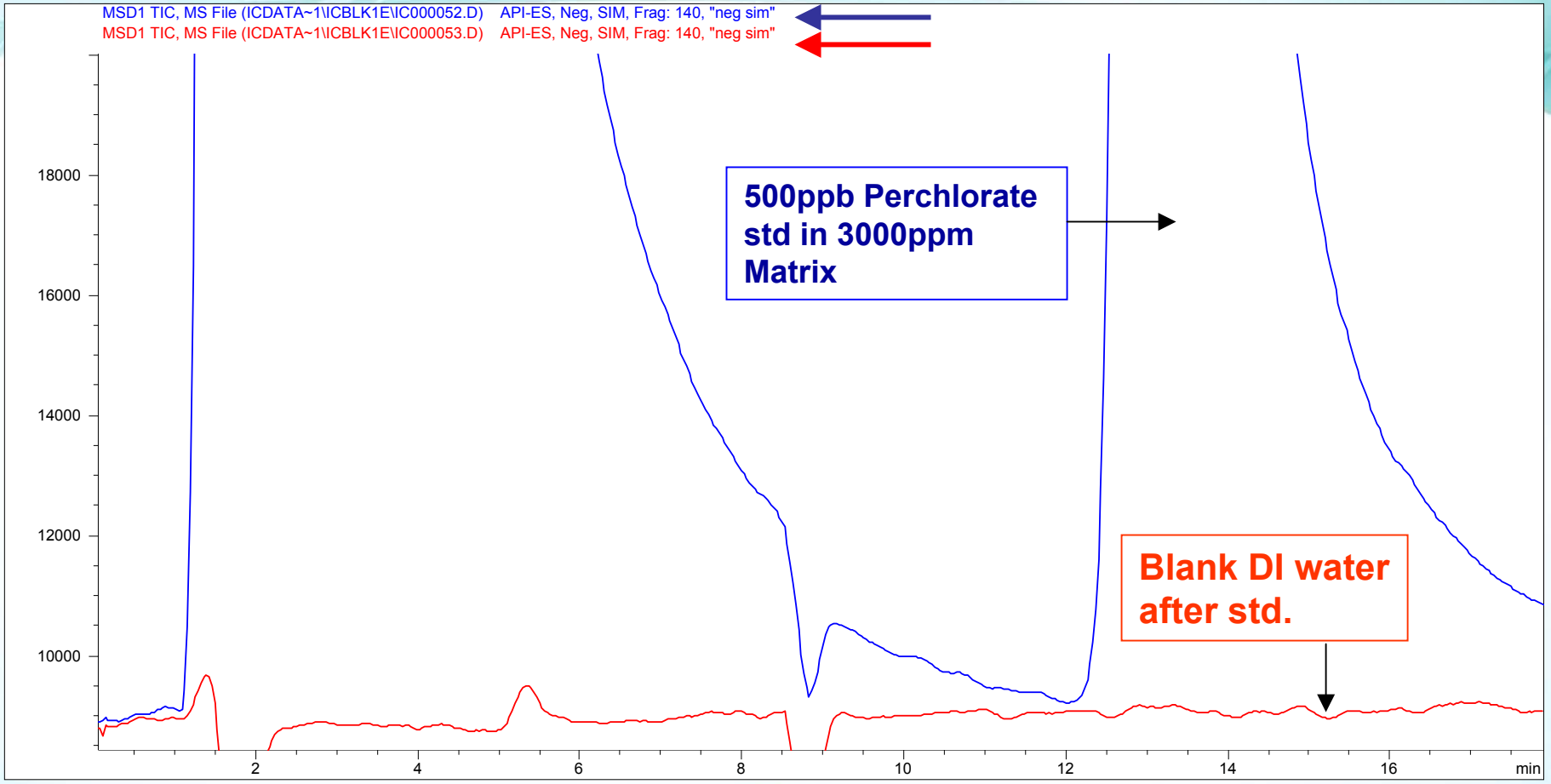
Agilent Technologies

Carry Over ….

metrohm-peak
ion chromatography

Agilent Technologies

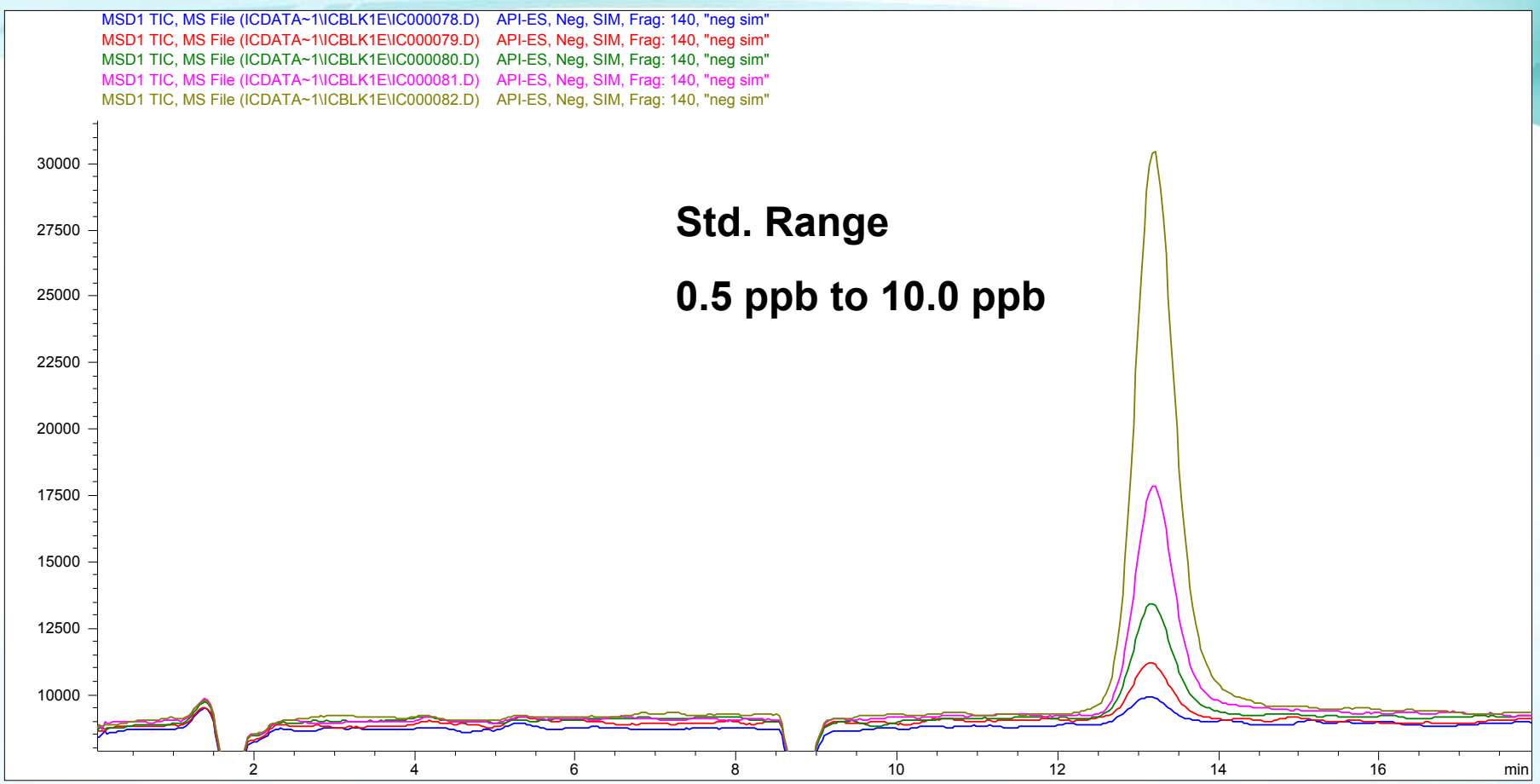
500 ppb and sequential blank



metrohm-peak ion chromatography

Agilent Technologies

Calibration Block after 76 injections

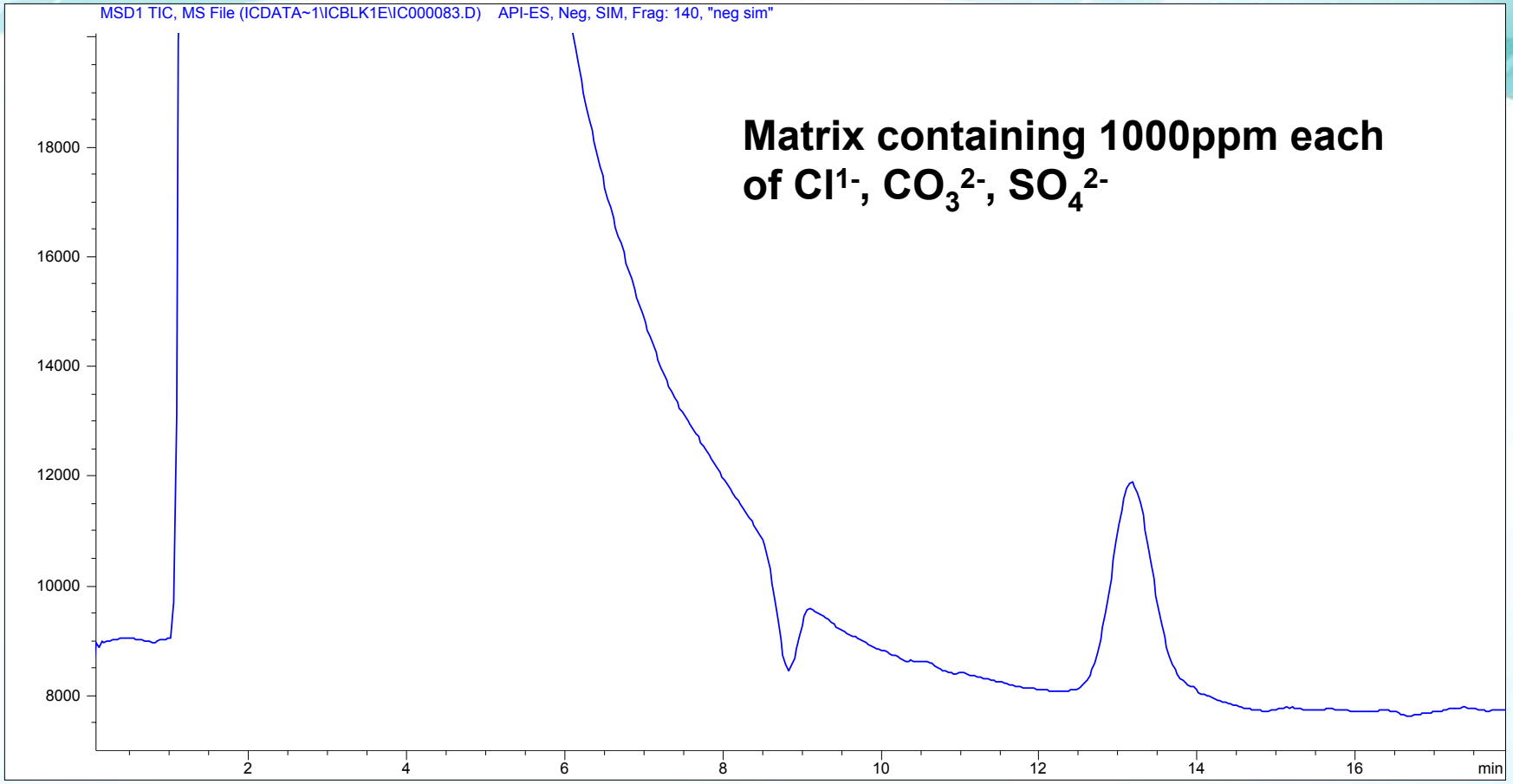


metrohm-peak ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

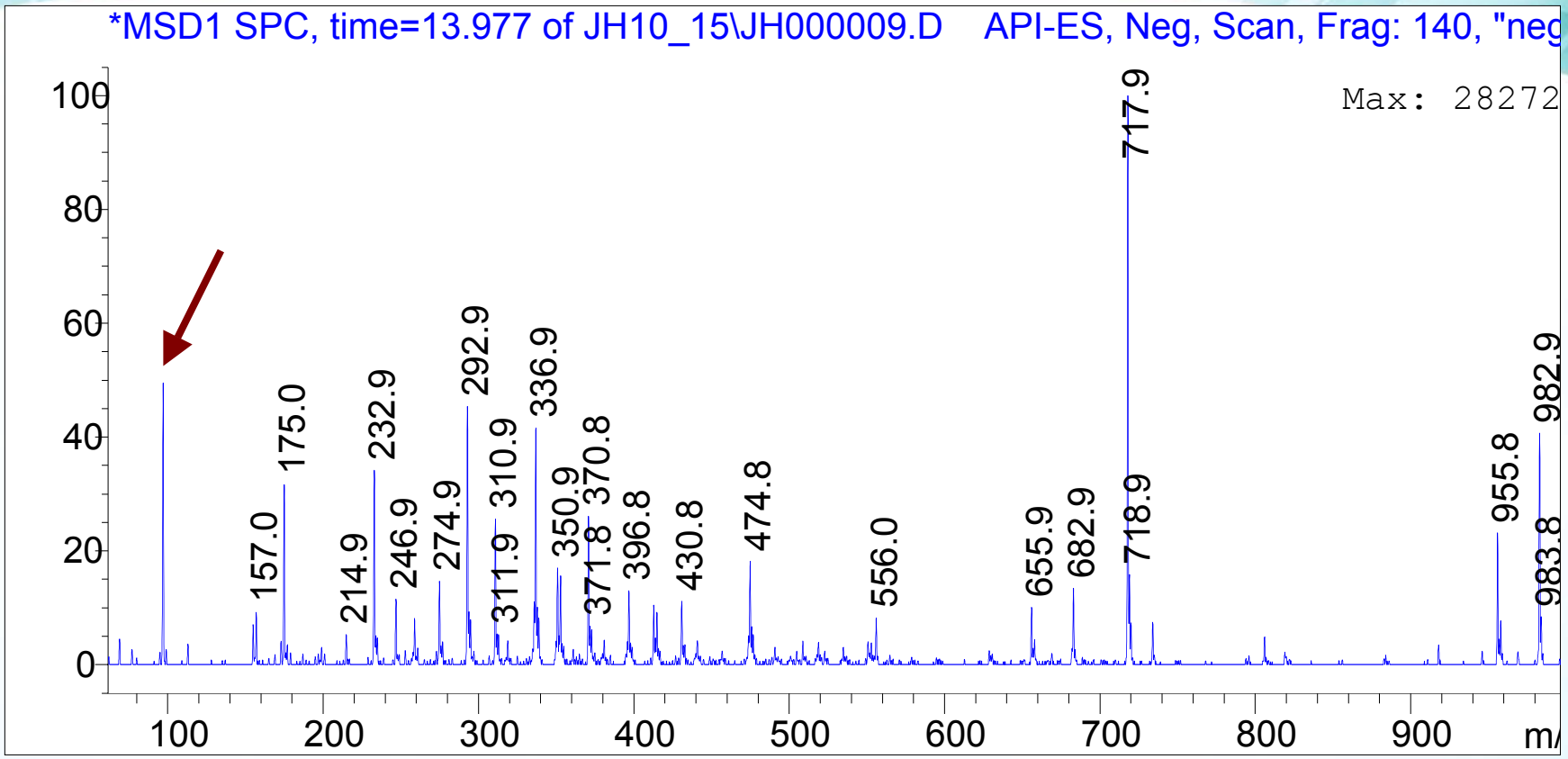
1 ppb Perchlorate in 3000ppm Total Dissolved Salt (TDS) after 125 injections



metrohm-peak ion chromatography

Agilent Technologies

Full Scan of Sample with Sulfonates



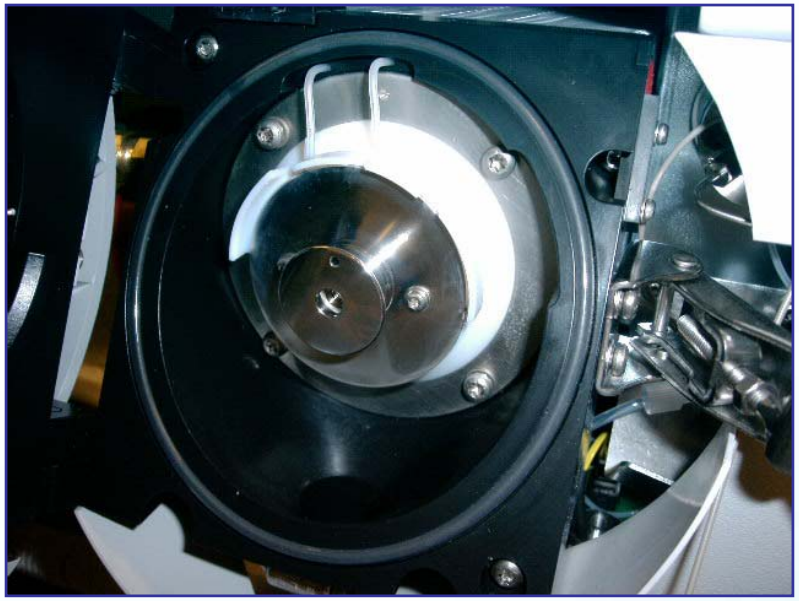
metrohm-peak ion chromatography

Agilent Technologies

Metrohm Modular IC-Agilent MS(1100 MSD)

- 4 mm column, 100uL loop and normal flows minimize matrix overload of chromatography
  - No need for Sample preparation to eliminate high ionic matrix
  - No matrix suppression of Perchlorate in the ESI source witnessed

MSD Interface after 150 injections



metrohm-peak
ion chromatography

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Agilent Technologies

Acknowledgements

- **Rick McMillin**, Deputy Branch Chief - USEPA Region 6
- **Melvin Ritter**, Team Leader - USEPA Region 6
- **Diane Gregg**, Team Leader - USEPA Region 6
- **Dr. Carl Zhang**, University of Houston, Clear Lake Campus

metrohm-peak ion chromatography

Agilent Technologies