

# An IC/MS Production Method for the Analysis of Perchlorate

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# 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.....



# Goals And Solutions For IC/MS Analysis Of Perchlorate

- **Simple and rugged**
  - **External standard method (within EPA 314)**
  - **Single stage MS (quadrupole)**
  - **4mm column**
  
- **Accurate and precise to 1ppb**
  - **MDL < 100 parts per trillion (ppt)**
  - **Must be able to meet QC for prolonged unattended operation**

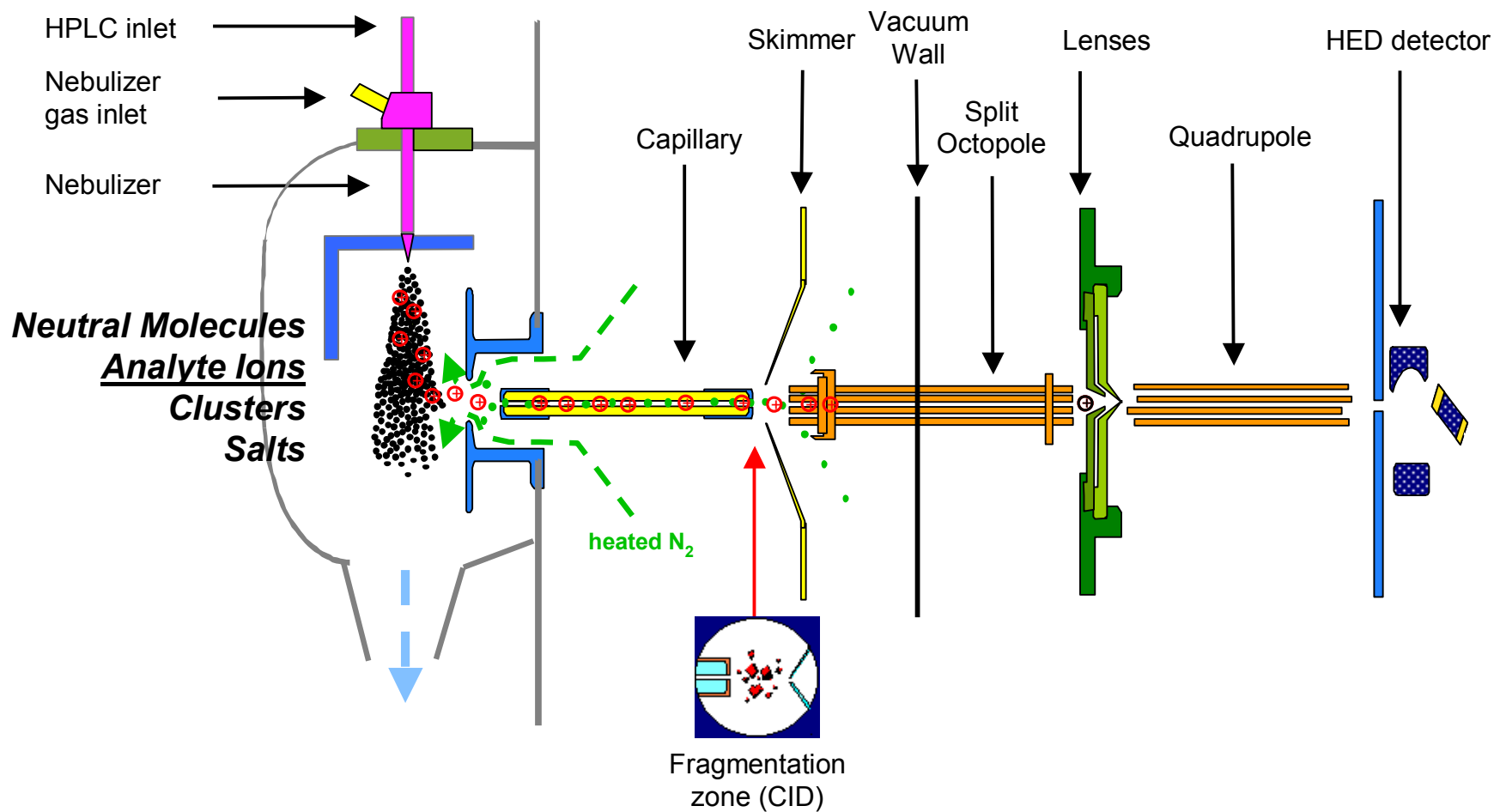
# The Bottom Line

- 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”
  - $V_{\text{cap}} = 1400\text{V}$ , Drying Gas = 9L/min @ 320 C.
  - Nebulizer Pressure=20 psig.
  - Fragmentor = 140 V.

# Agilent 1100 LC/MSD SL AP Electrospray

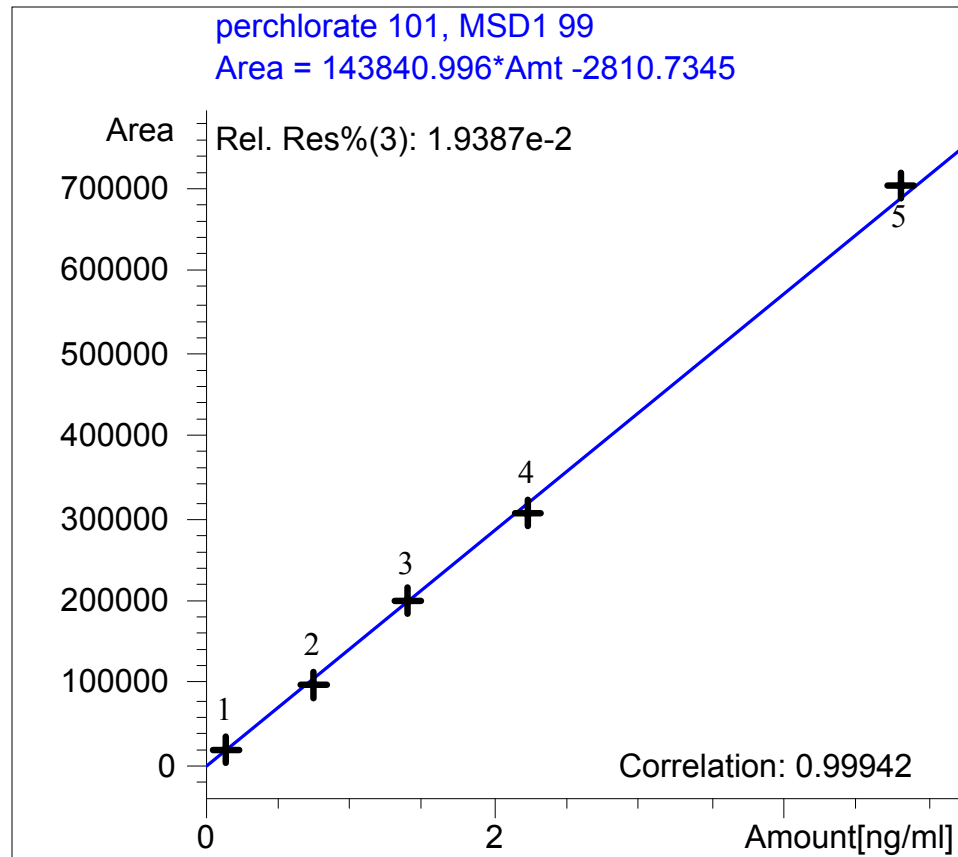


# Picture of Instrument Set-up



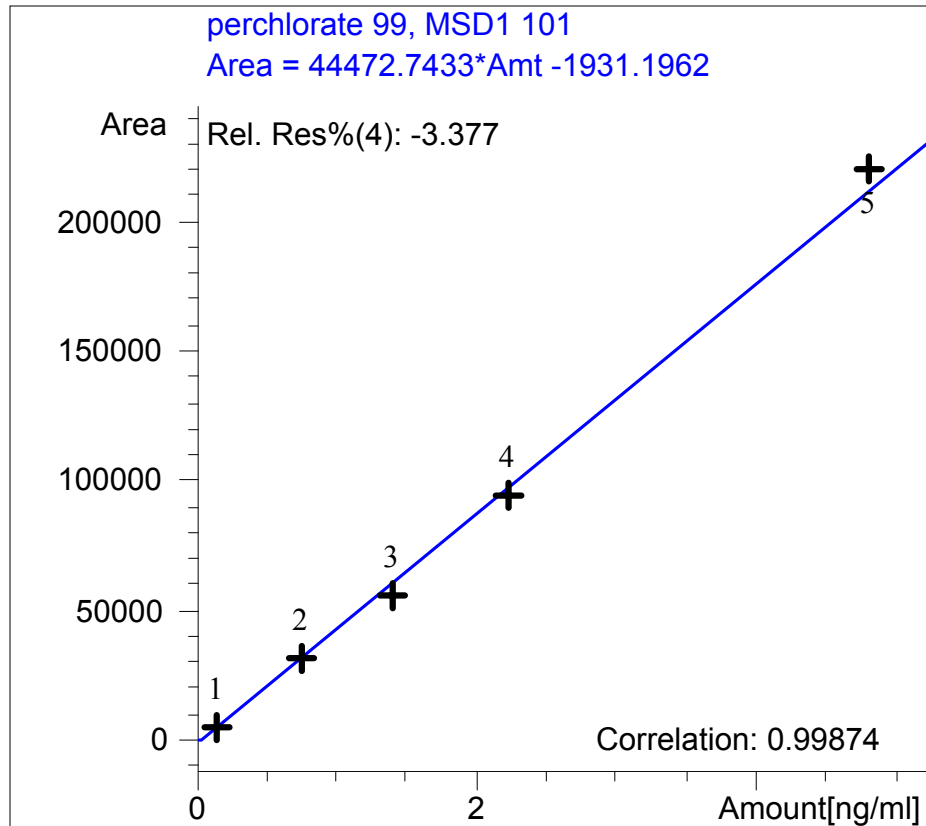


# Calibration Data (m/z 99)



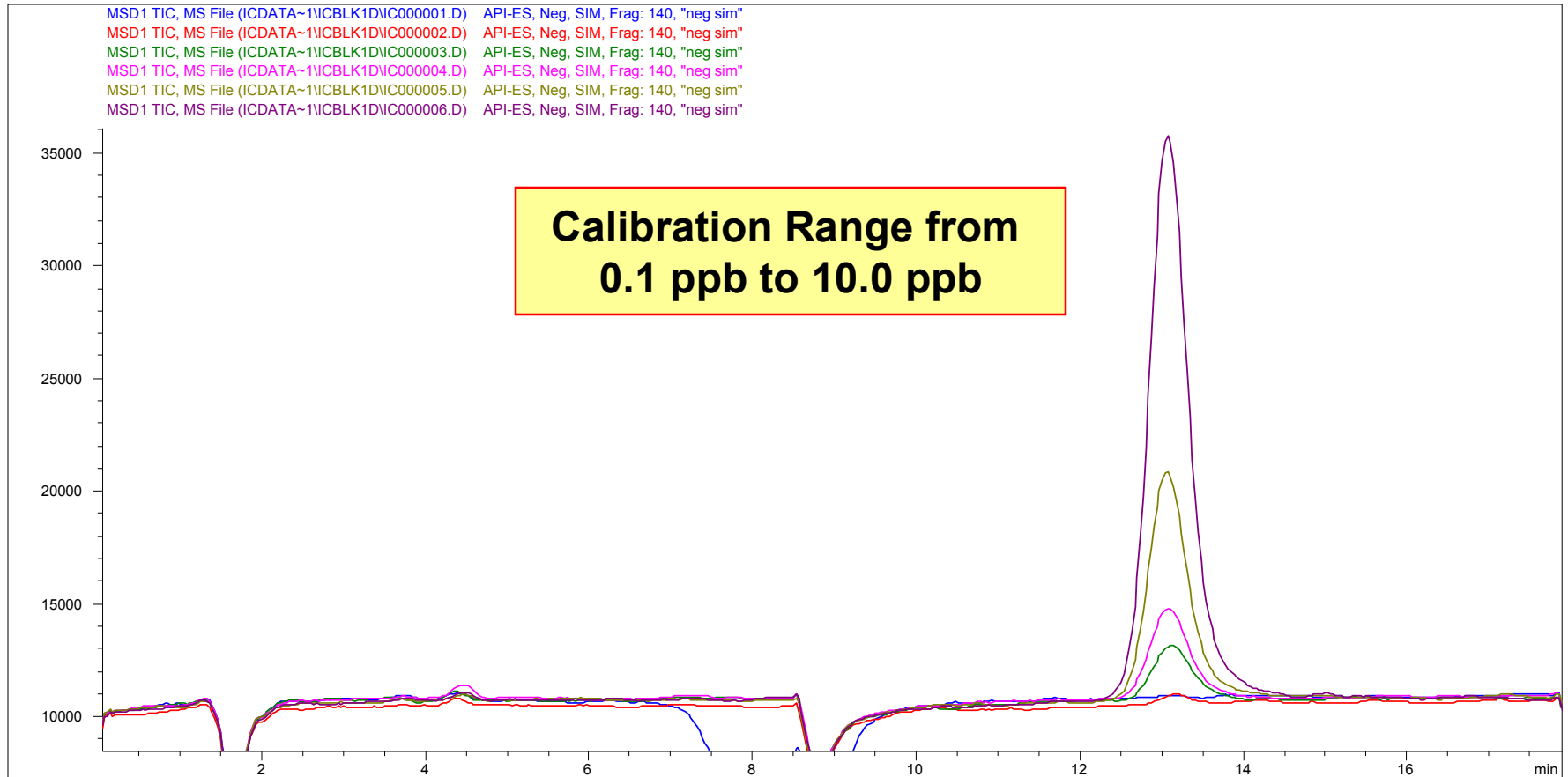
**Range for  
Calibration Standards  
0.1ppb to 10ppb ( $\text{ClO}_4^{1-}$ )**

# Calibration Data (m/z 101)

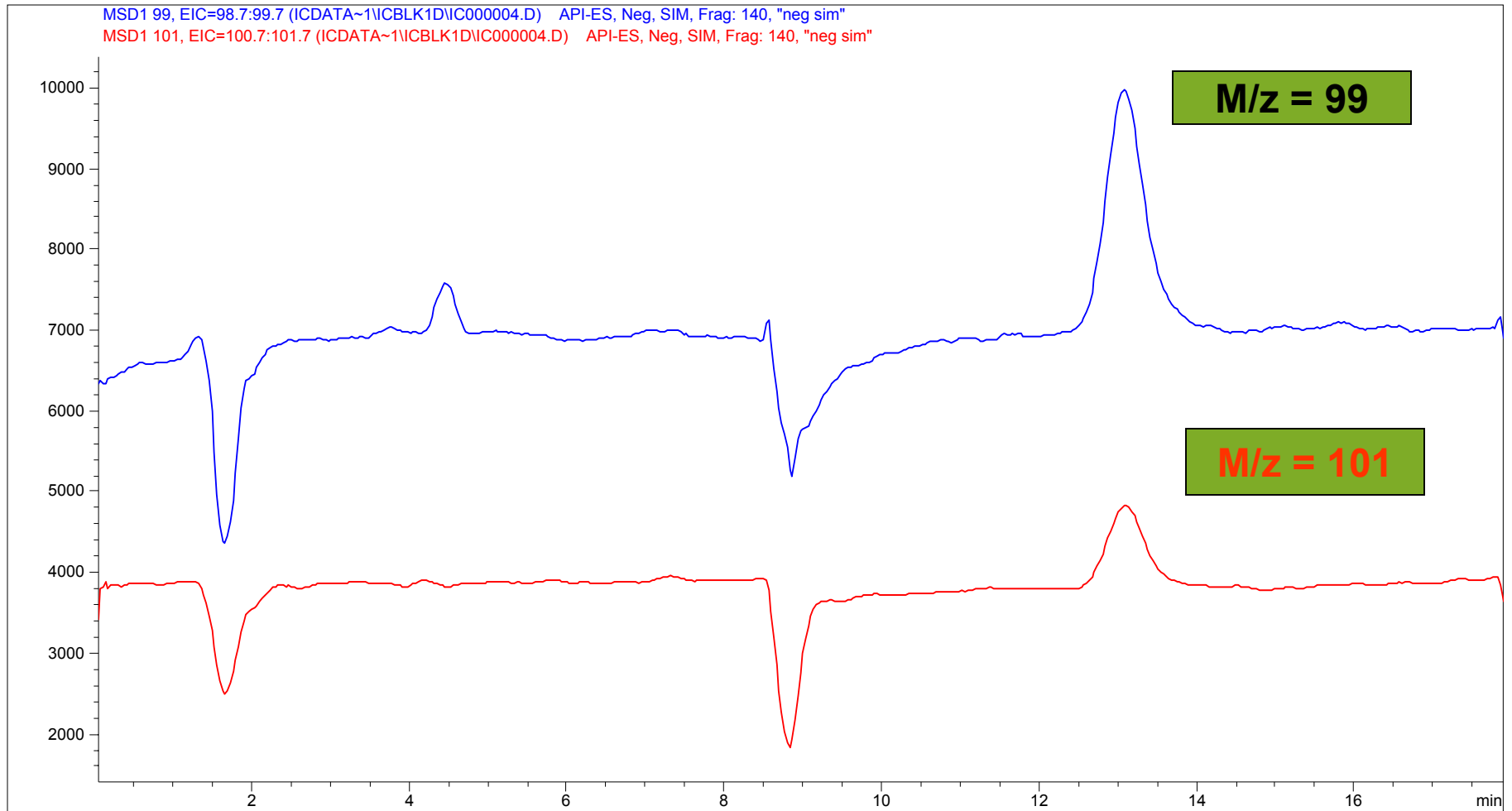


**Range for  
Calibration Standards  
0.1ppb to 10ppb ( $\text{ClO}_4^{1-}$ )**

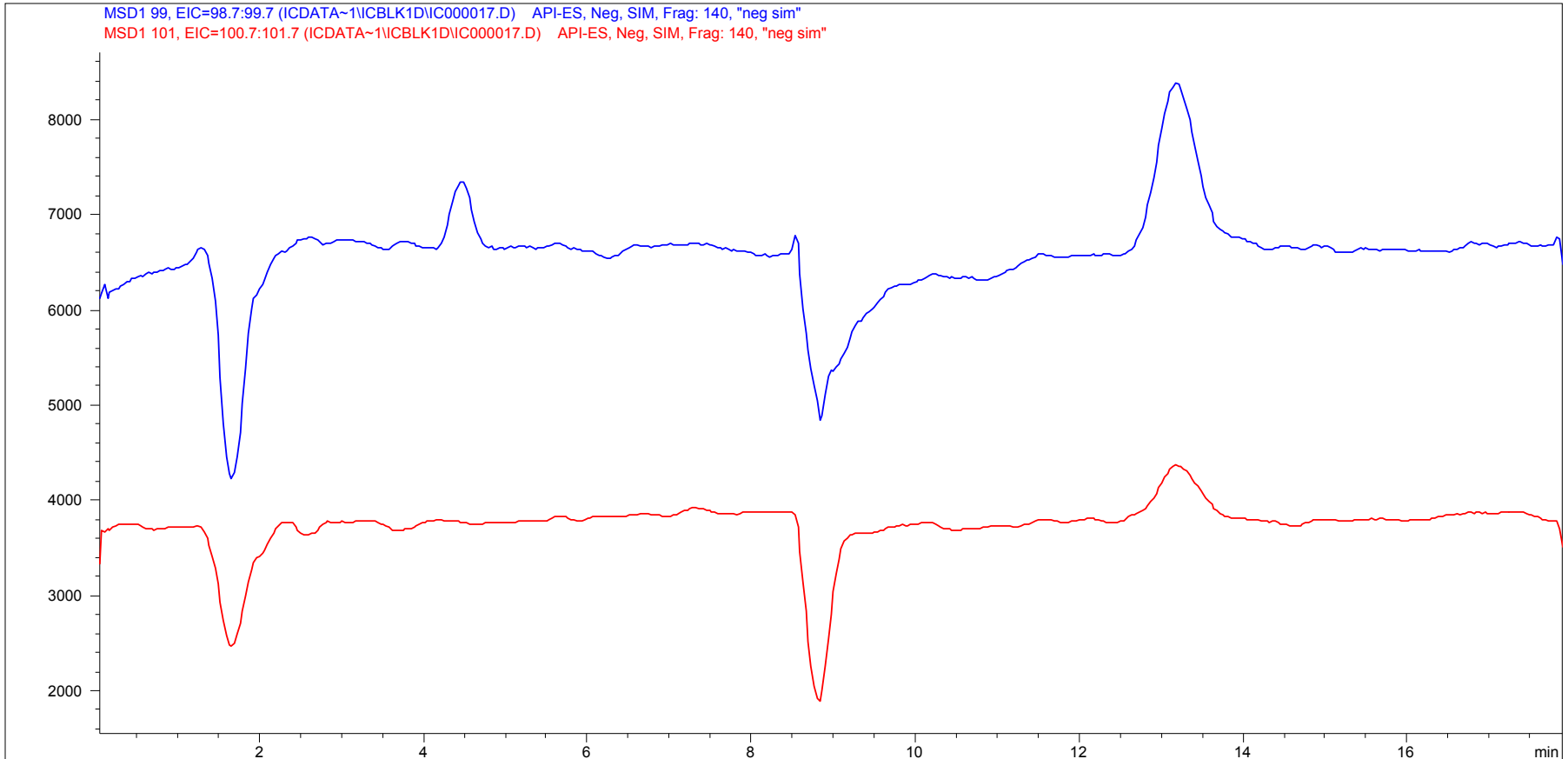
# Total Ion Chromatograms (TIC) Calib. Standards and Blank



# 0.79 ppb Standard



# Extracted Ion Chromatograms for 0.5 ppb standard



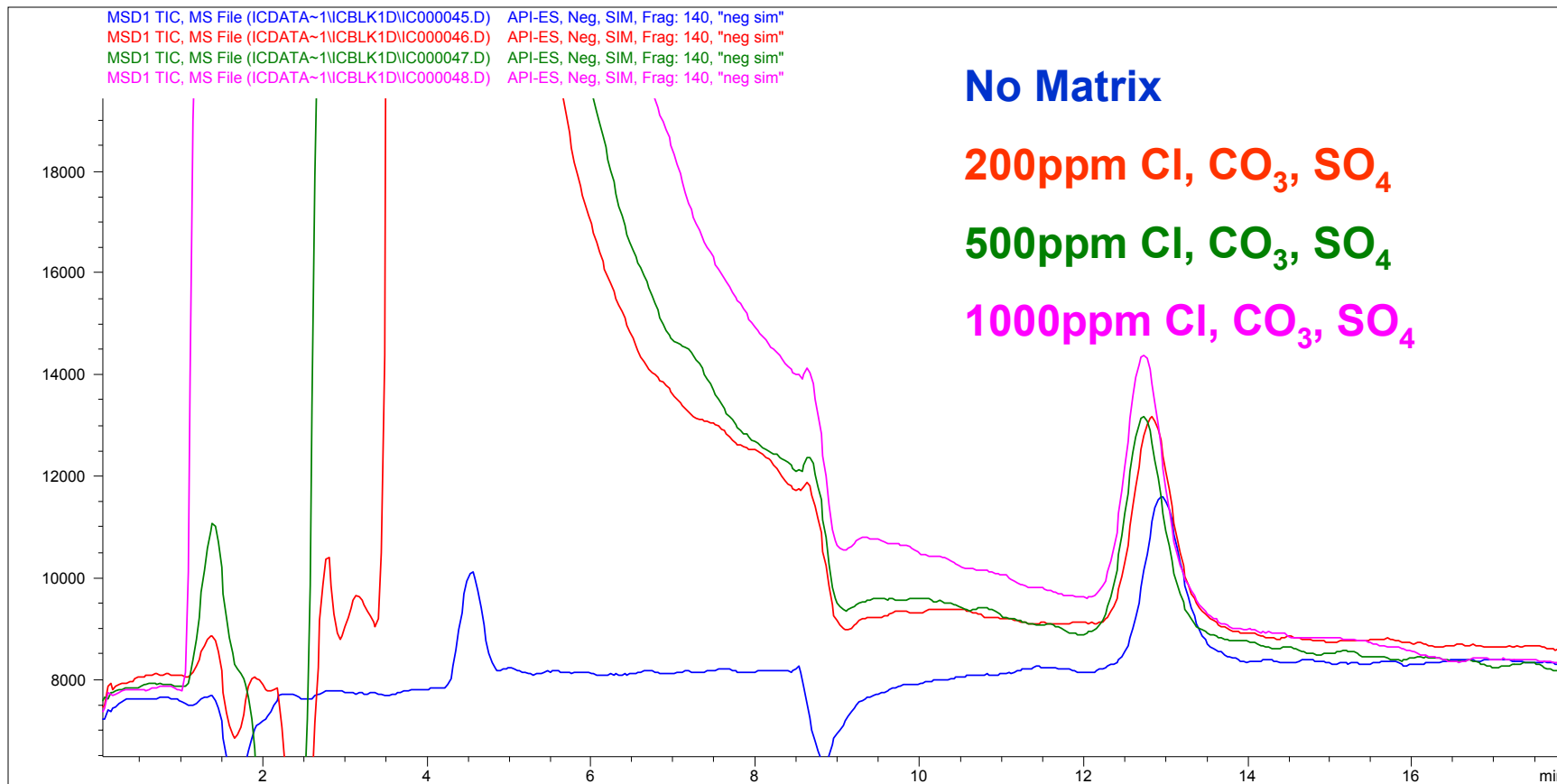
# Results of UHP Water Fortified with Perchlorate

**0.5 ppb replicates**

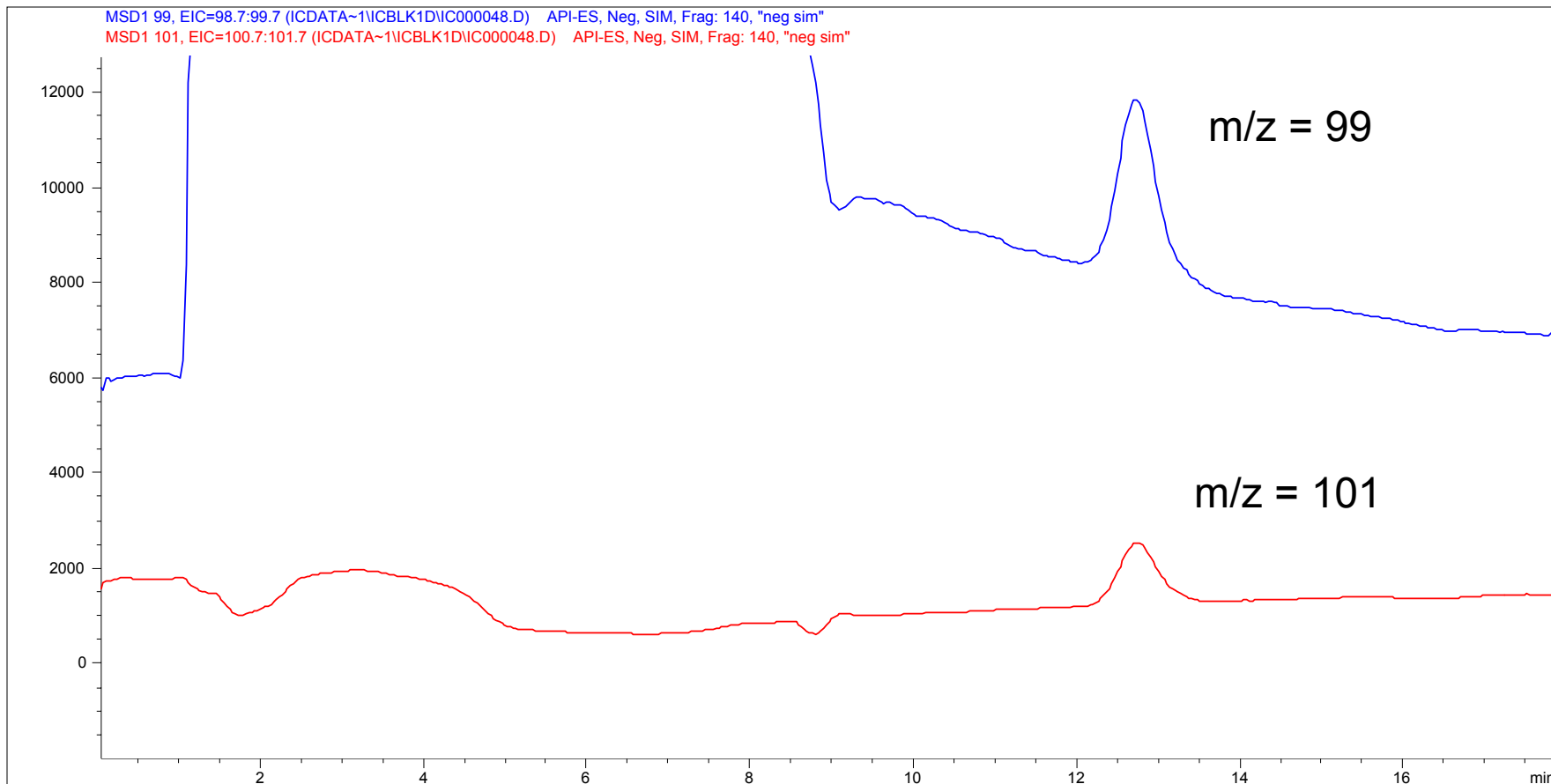
SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
0.5 PPB	0.480	0.487	101.46%	0.519	108.13%
0.5 PPB	0.480	0.477	99.38%	0.471	98.13%
0.5 PPB	0.480	0.460	95.83%	0.490	102.08%
0.5 PPB	0.480	0.477	99.38%	0.492	102.50%
0.5 PPB	0.480	0.520	108.33%	0.505	105.21%
0.5 PPB	0.480	0.494	102.92%	0.509	106.04%
<b>Average</b>	<b>0.480</b>	<b>0.486</b>	<b>101.22%</b>	<b>0.498</b>	<b>103.68%</b>
<b>Std. Dev</b>		<b>0.020</b>	<b>0.042</b>	<b>0.017</b>	<b>0.035</b>
<b>RSD</b>		<b>4.18%</b>	<b>4.18%</b>	<b>3.41%</b>	<b>3.41%</b>
SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
10 PPB	0.780	0.756	96.92%	0.768	98.46%
10 PPB	0.780	0.810	103.85%	0.830	106.41%
10 PPB	0.780	0.776	99.49%	0.772	98.97%
10 PPB	0.780	0.799	102.44%	0.754	96.67%
10 PPB	0.780	0.788	101.03%	0.768	98.46%
10 PPB	0.780	0.792	101.54%	0.807	103.46%
<b>Average</b>	<b>0.780</b>	<b>0.787</b>	<b>100.88%</b>	<b>0.783</b>	<b>100.41%</b>
<b>Std. Dev</b>		<b>0.019</b>	<b>0.024</b>	<b>0.029</b>	<b>0.037</b>
<b>RSD</b>		<b>2.40%</b>	<b>2.40%</b>	<b>3.70%</b>	<b>3.70%</b>

**1.0 ppb replicates**

# Synthetic Matrix Spikes Overlaid with 1ppb Standard



# Single Ion Chromatograms of High Matrix Spike



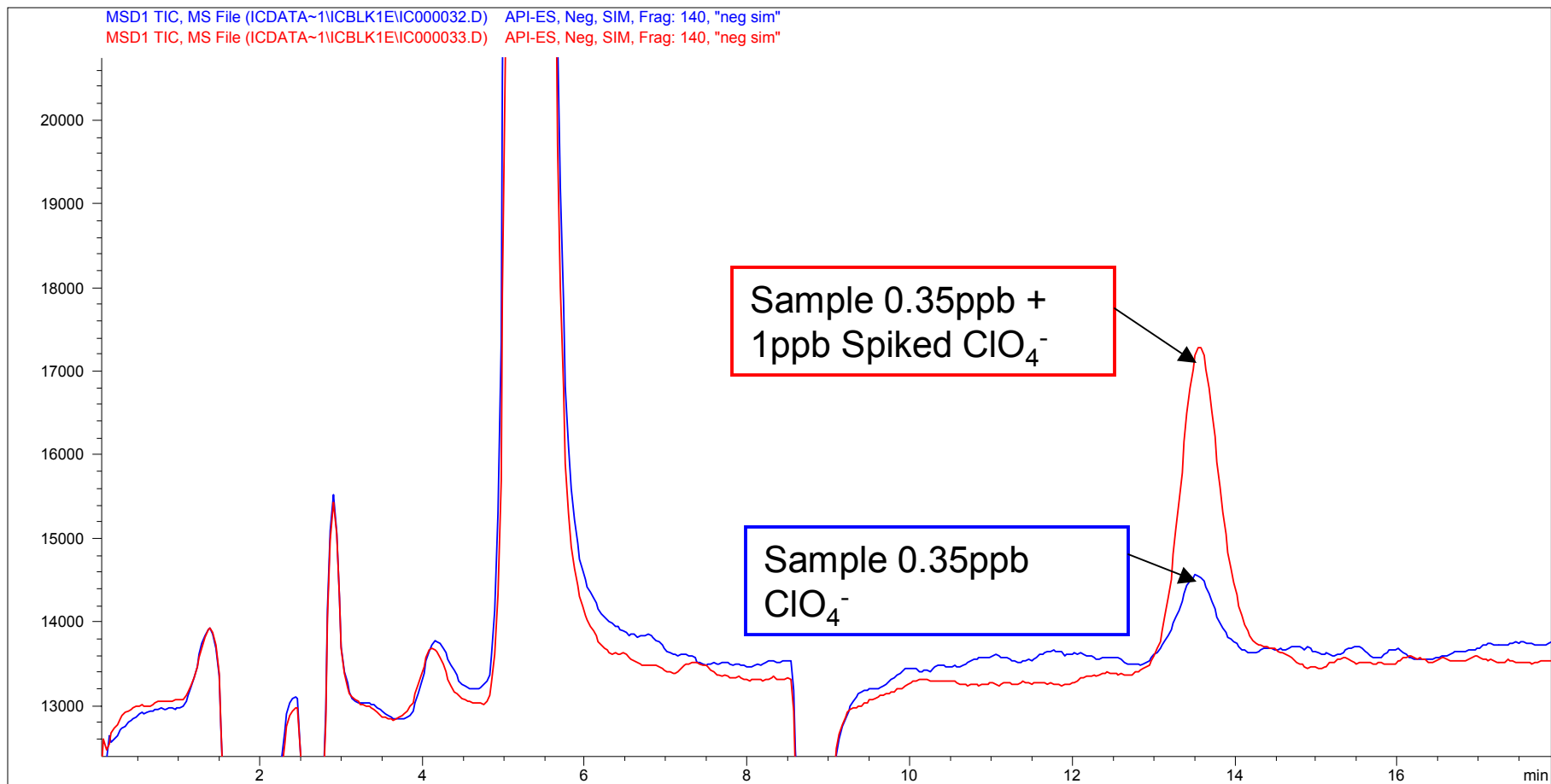


# Results of Matrix Fortified with Perchlorate

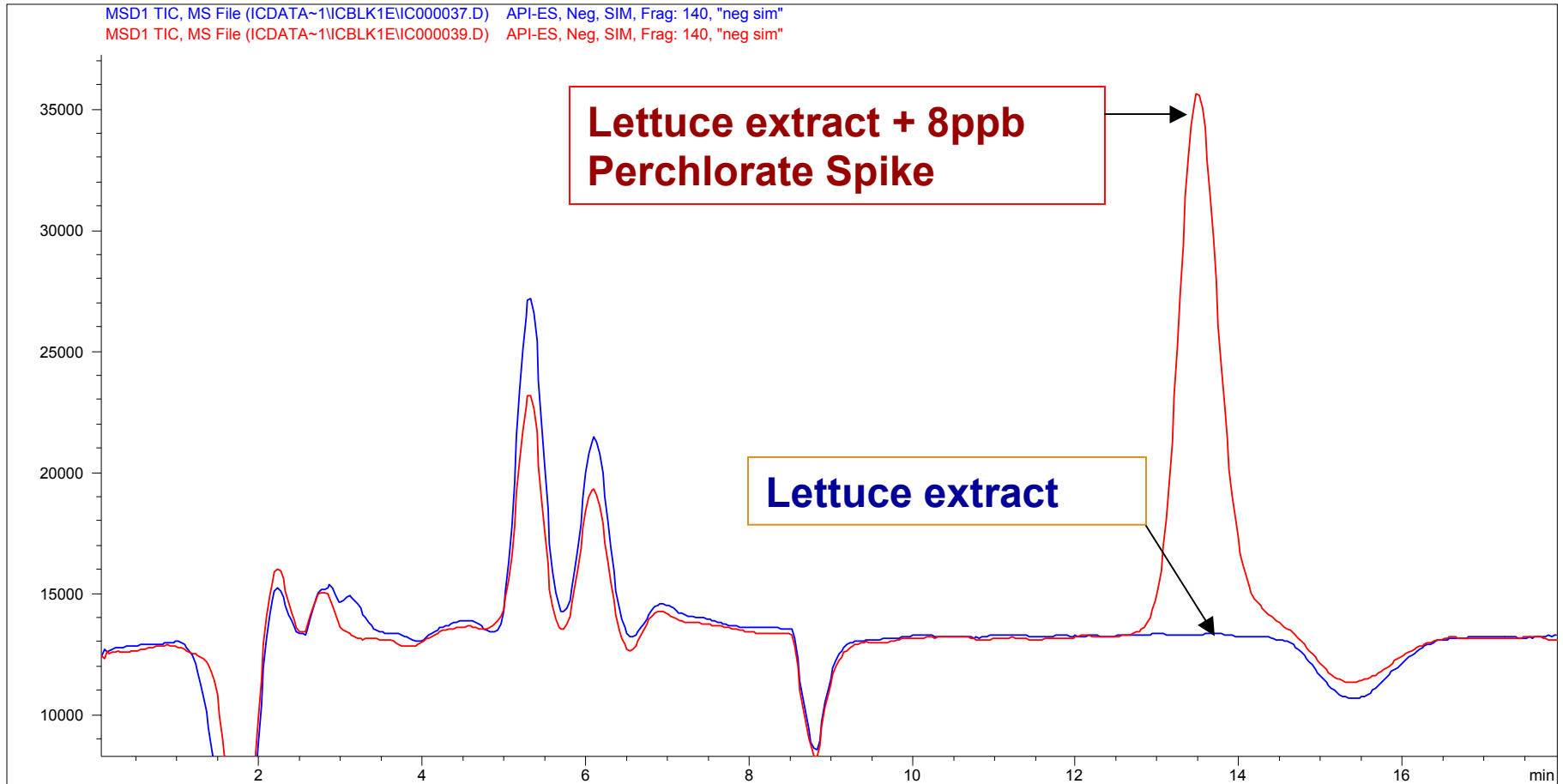
SAMPLE ID	TRUE CONCENTRATION	PPB (M/Z = 99)	% Recovery (m/z99)	PPB (M/Z = 101)	% Recovery (m/z101)
200 PPM EACH OF CL,CO3 & SO4	0.780	0.799	102.44%	0.784	100.51%
500 PPM EACH OF CL,CO3 & SO4	1000	0.804	80.40%	0.808	80.80%
1000 PPM EACH OF CL,CO3 & SO4	1000	0.930	93.00%	0.940	94.00%
200 PPM EACH OF CL,CO3 & SO4	0.780	0.700	89.74%	0.770	98.72%
500 PPM EACH OF CL,CO3 & SO4	1000	0.870	87.00%	0.860	86.00%
1000 PPM EACH OF CL,CO3 & SO4	1000	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	1000	0.851	85.10%	0.846	84.60%
1000 PPM EACH OF CL,CO3 & SO4	1000	0.990	99.00%	0.977	97.70%
BLANK	0.000	0.000		0.000	
CC 10 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	1000	0.920	92.00%	0.921	92.10%
1000 PPM EACH OF CL,CO3 & SO4	1000	1000	100.00%	1040	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	1000	0.930	93.00%	0.913	91.30%
1000 PPM EACH OF CL,CO3 & SO4	1000	1090	109.00%	1050	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	1000	0.890	89.00%	0.904	90.40%
1000 PPM EACH OF CL,CO3 & SO4	1000	1040	104.00%	1070	107.00%
Average			96.67%		97.10%
Std.Dev			0.082		0.080
RSD %			8.48%		8.22%



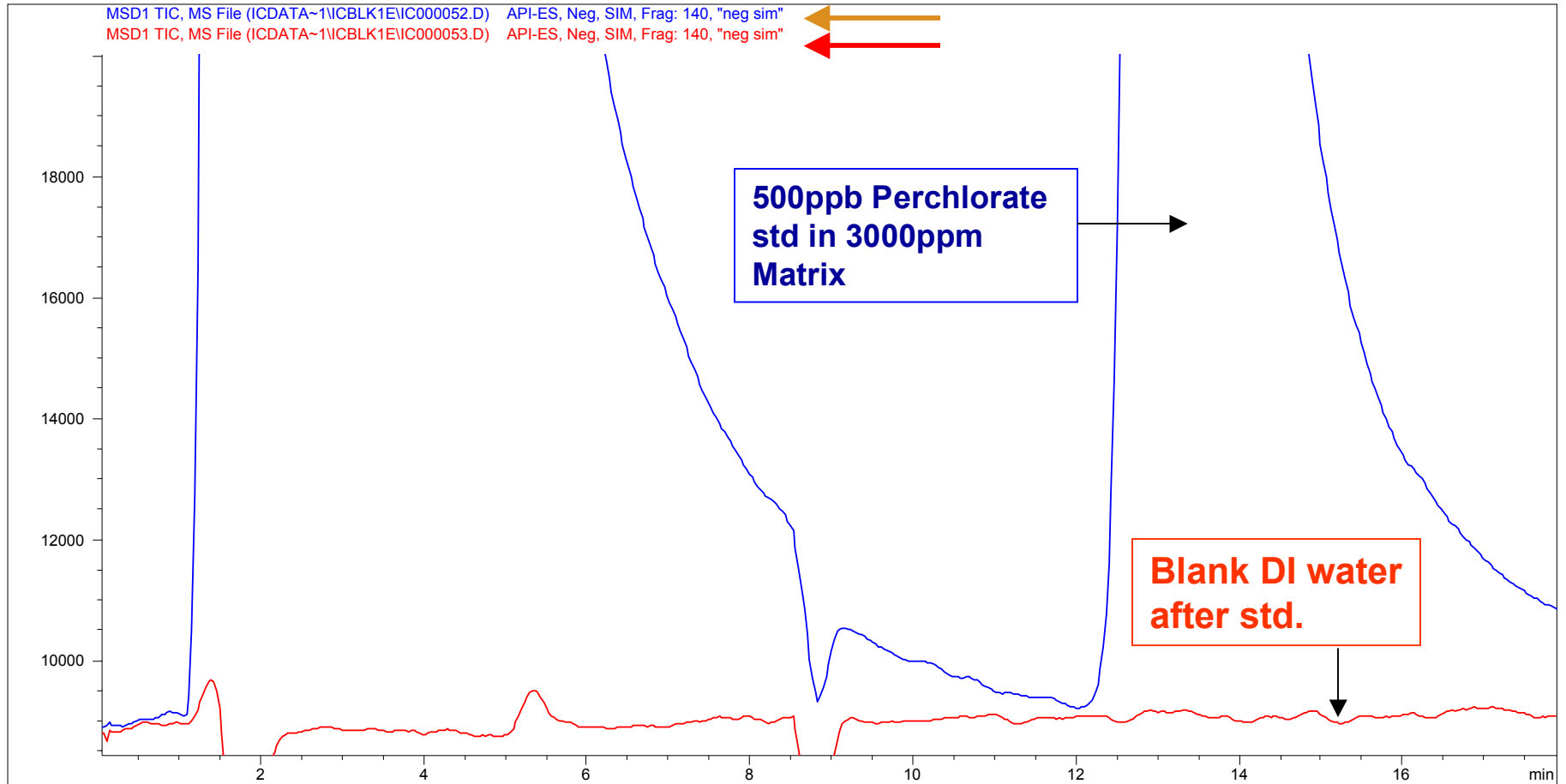
# Sample and Sample Spike (with Sulfonate Detergents)



# Lettuce and Spike

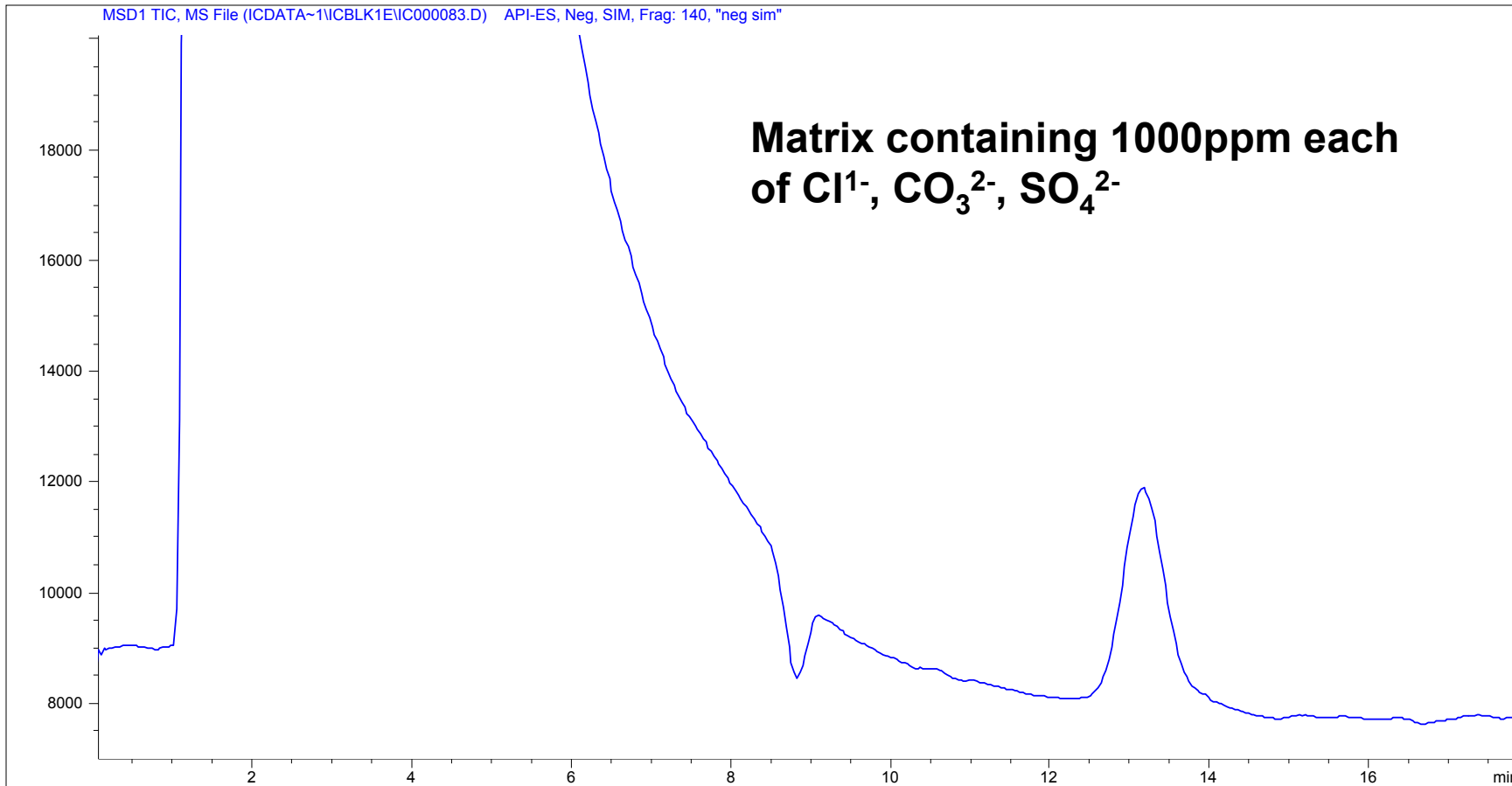


# 500 ppb and sequential blank

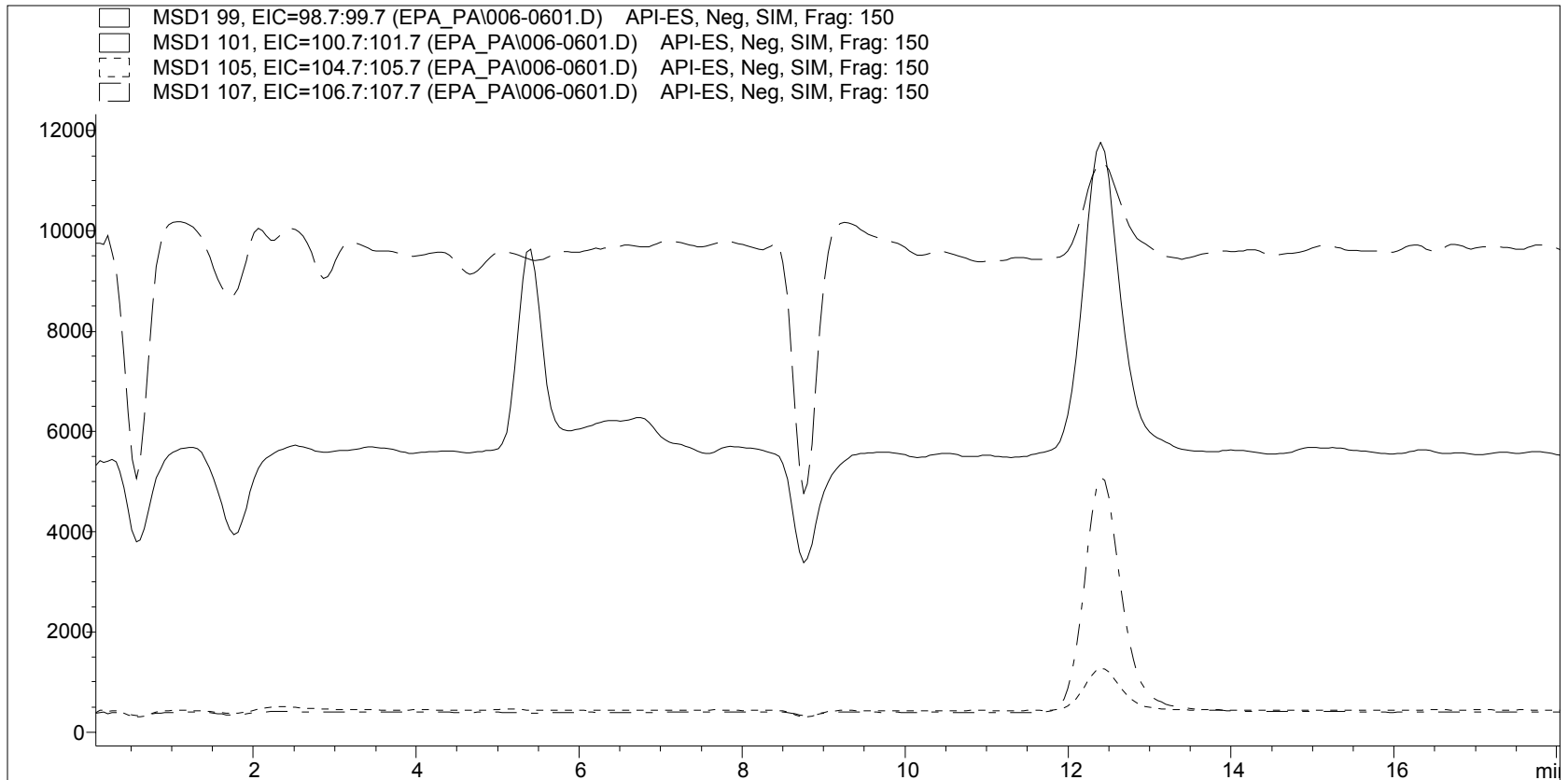


# 1 ppb Perchlorate in 3000ppm Total Dissolved Salt (TDS) after 125 injections

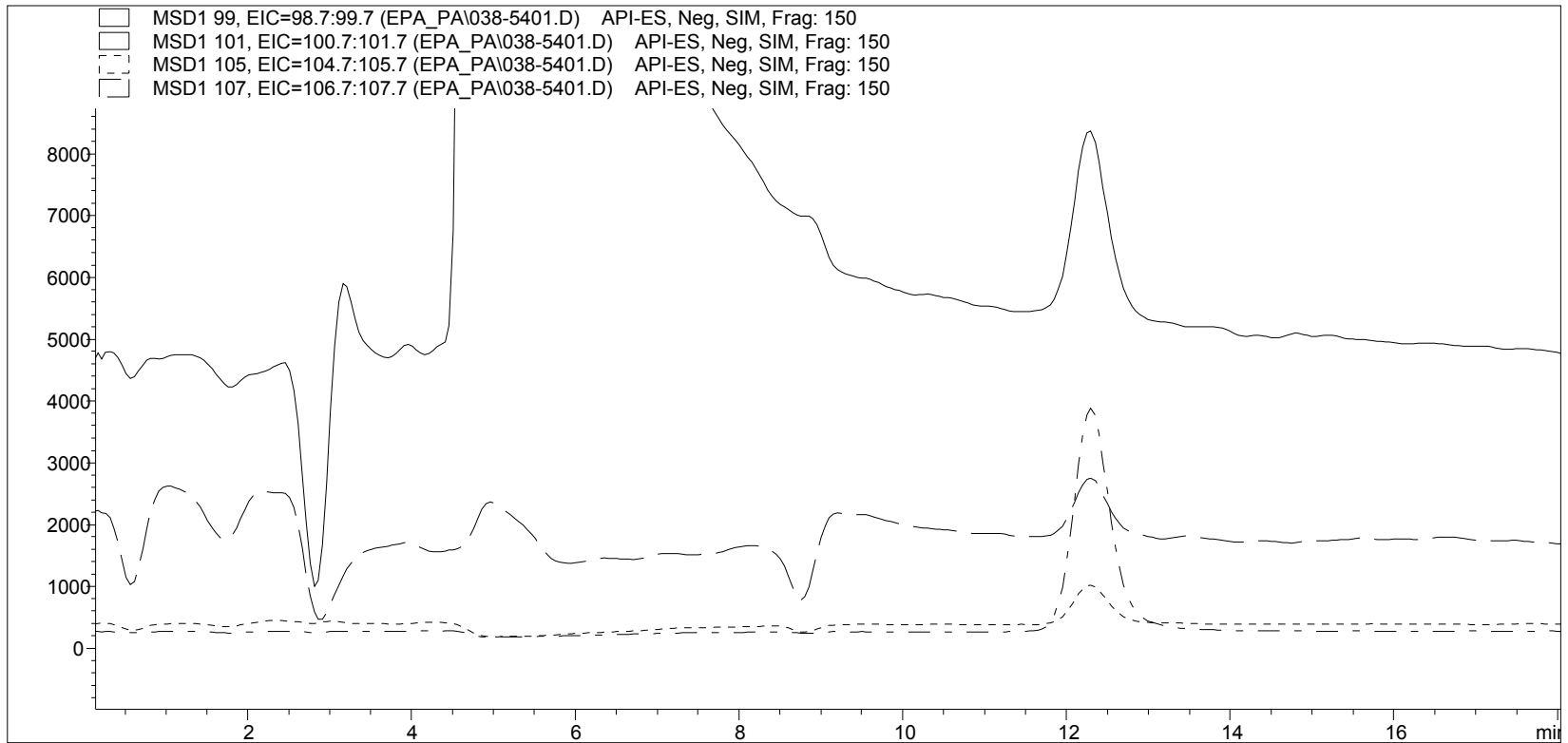
## 95% Recovery



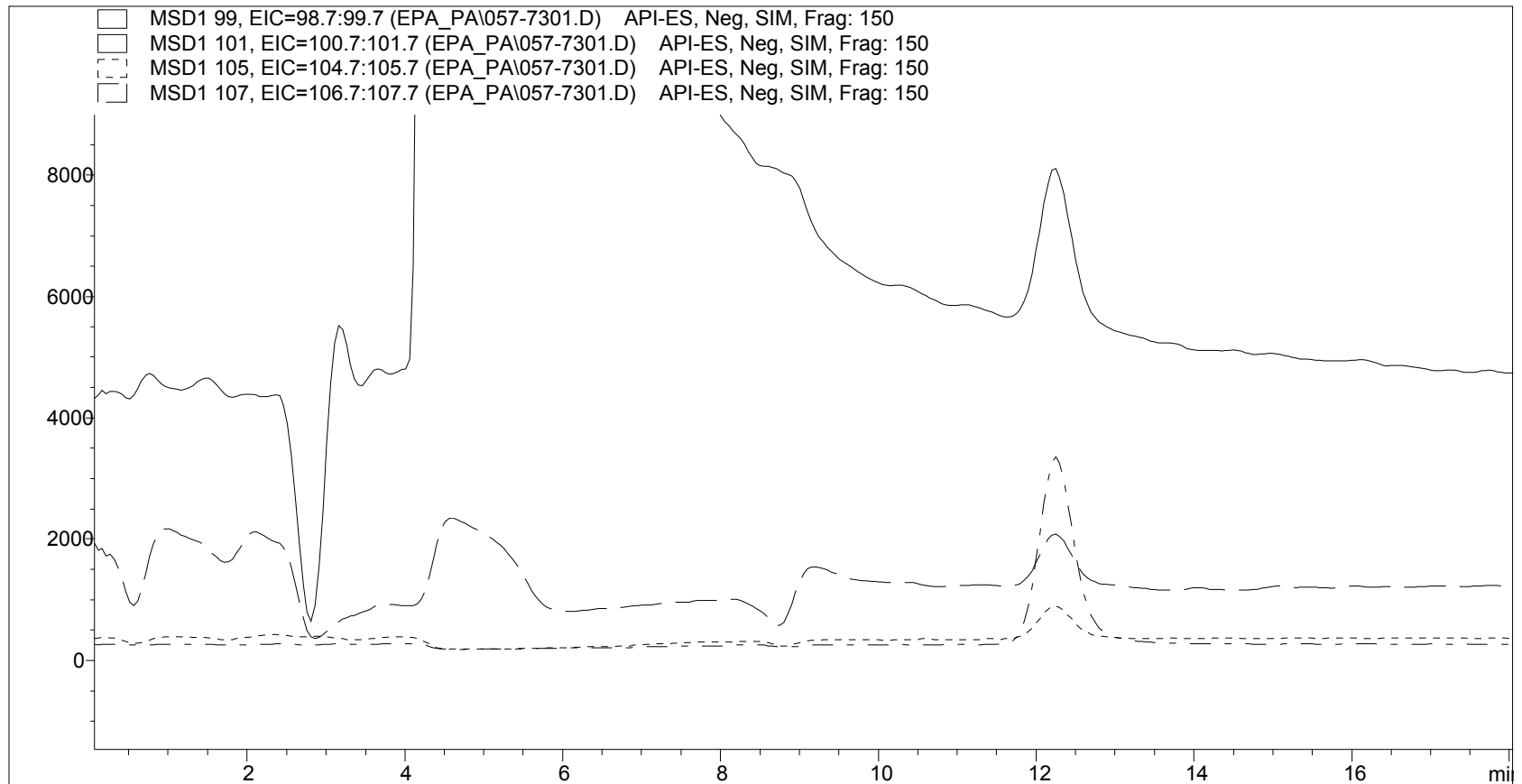
# 1 ppb Perchlorate Standard w/IS



# Houston 1ppb spike

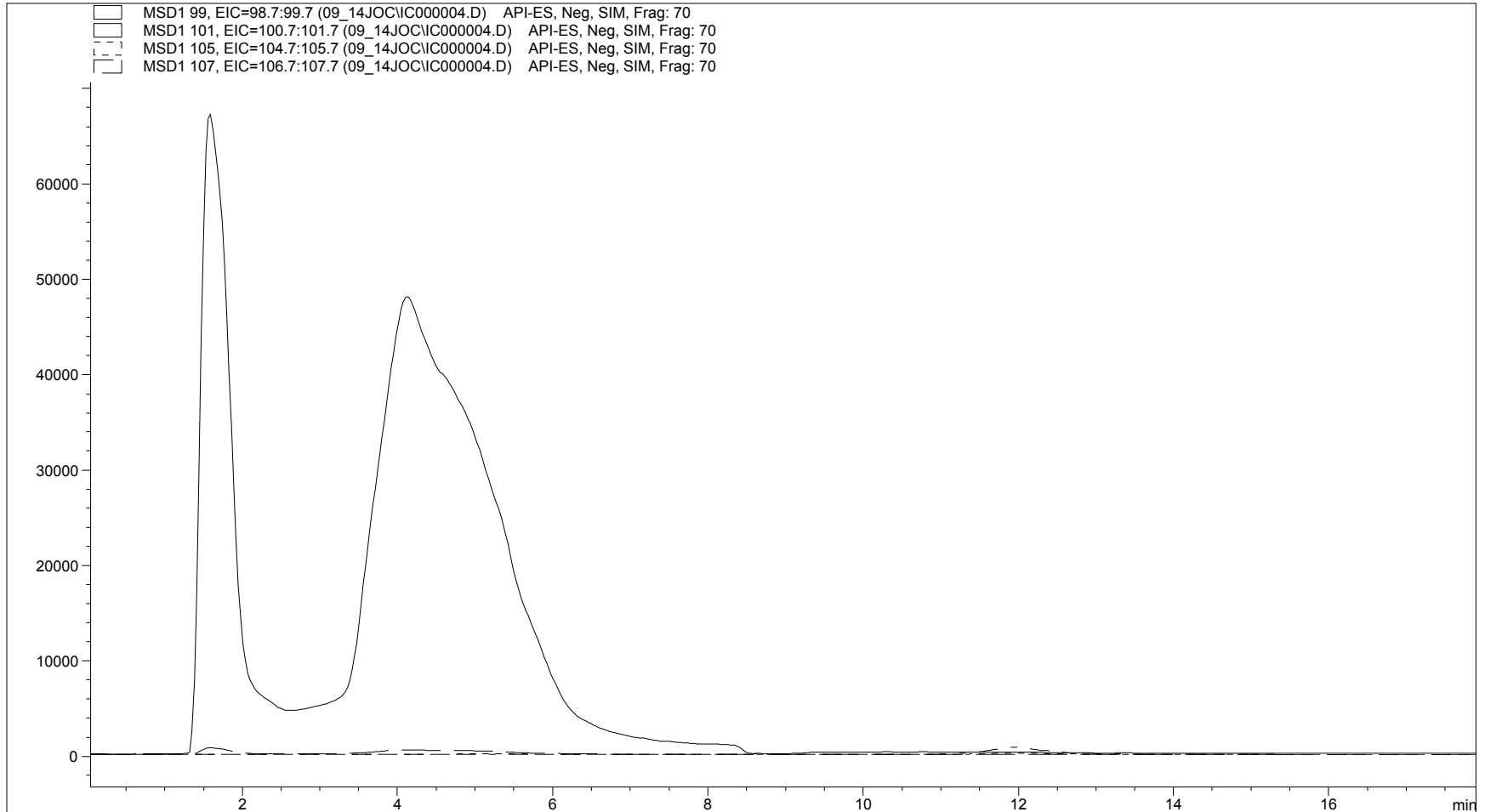


# College Station 0.5 ppb spike

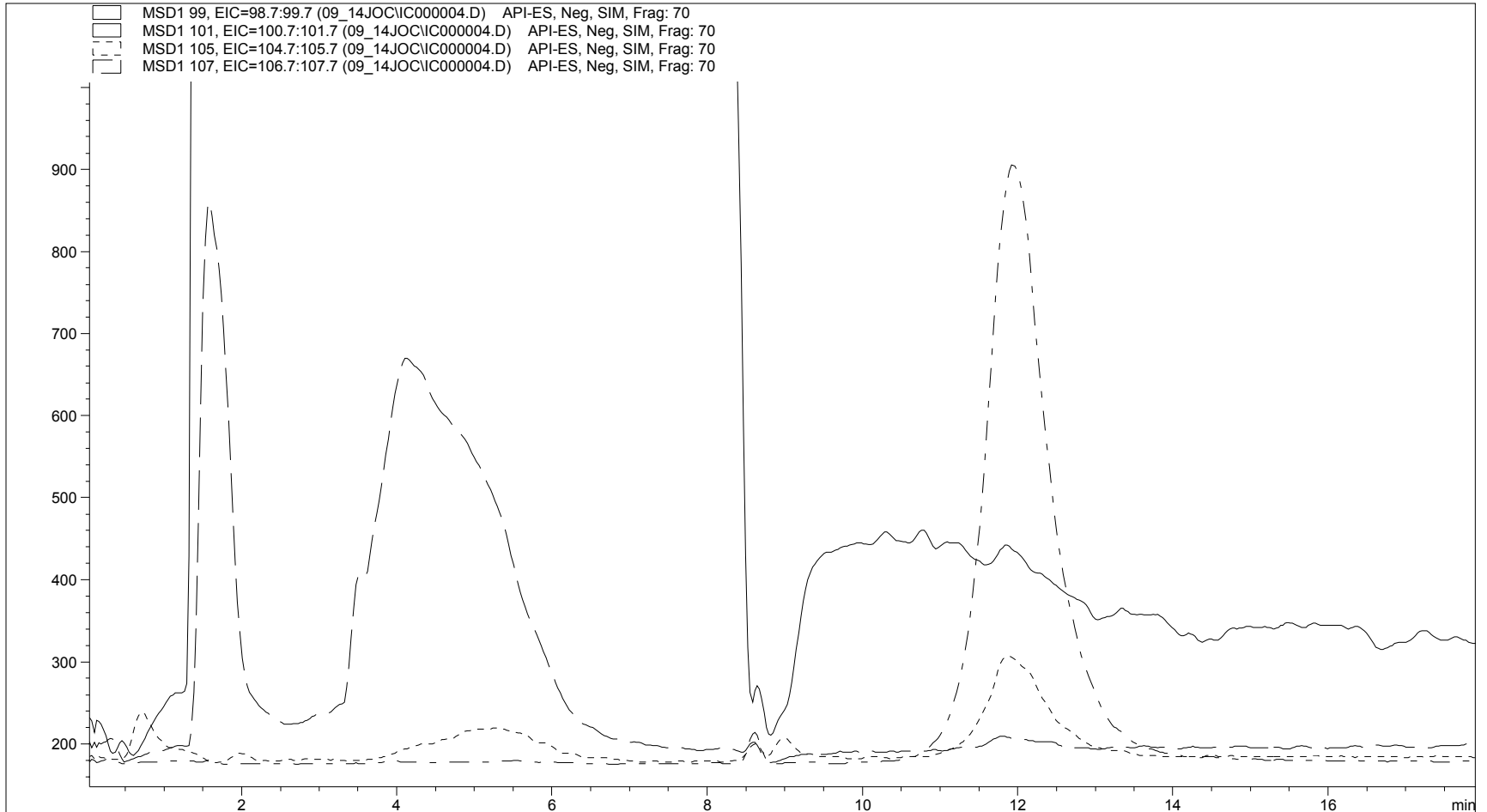




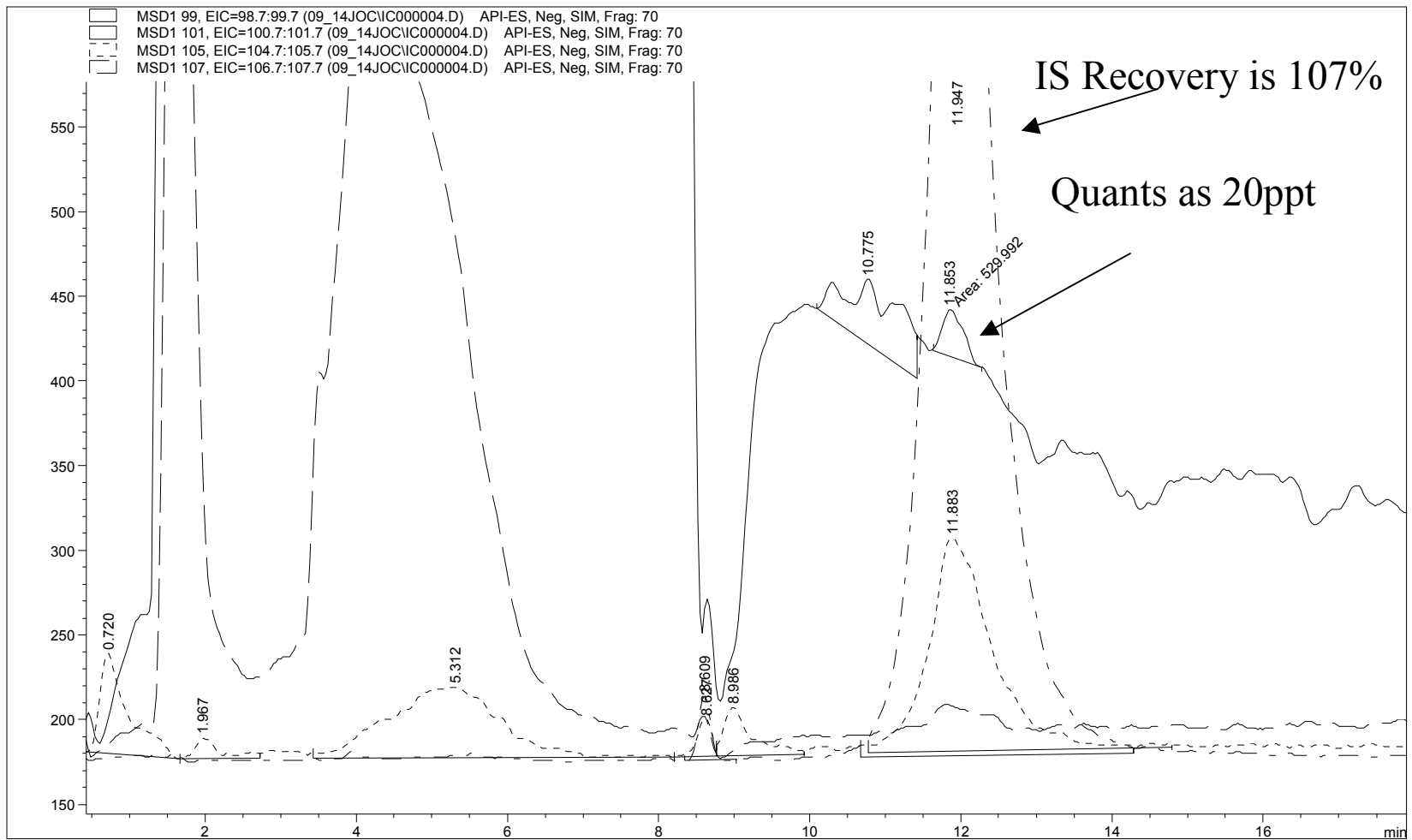
# SF Bay Water with 1ppb IS



# SF Bay Water with 1ppb IS



# San Francisco Bay Water with 1ppb IS



# Current Work

- **Current MeOH/NaOH mobile phase column combo is “bullet proof”**
  - **Little to no variation in retention/signal due to mobile phase composition, column lot #, MS (has worked on 1946D, 1956A, 1956B) or MS conditions**

**but.....**

- **Get TAT under 15 minutes**
  - **Different mobile phases, different lengths of columns**
- **Explore unsuppressed mobile phases**



# 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

# Alternate mobile phases

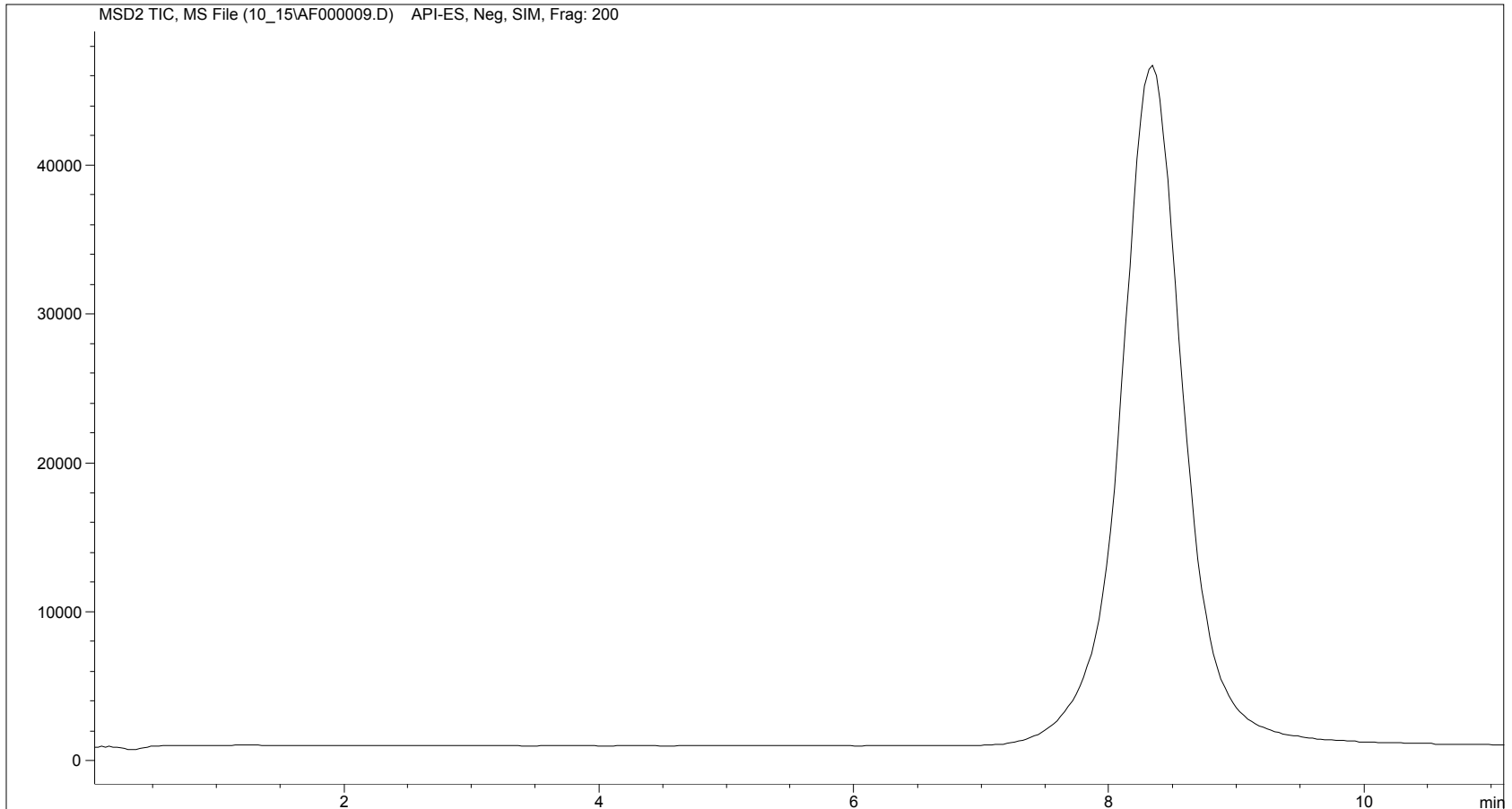
- **NaOH/MeOH works but...**
  - **Peak shape**
  - **Sulfate tail**
  - **Turn around time**

# Analysis Parameters

- **Agilent 1100 binary LC/1100 MSD**
  - **ESI**
  - **Drying Gas, 11L/min**
  - **Nebulizer pressure, 20 psi**
  - **SIM**
  - **Capillary voltage, 2500 V**
- **80mM Ammonium Formate adjusted to pH 9 with ammonia**
- **0.7ml/min**
- **5cm x 3mm Alltech NovaSep A2**

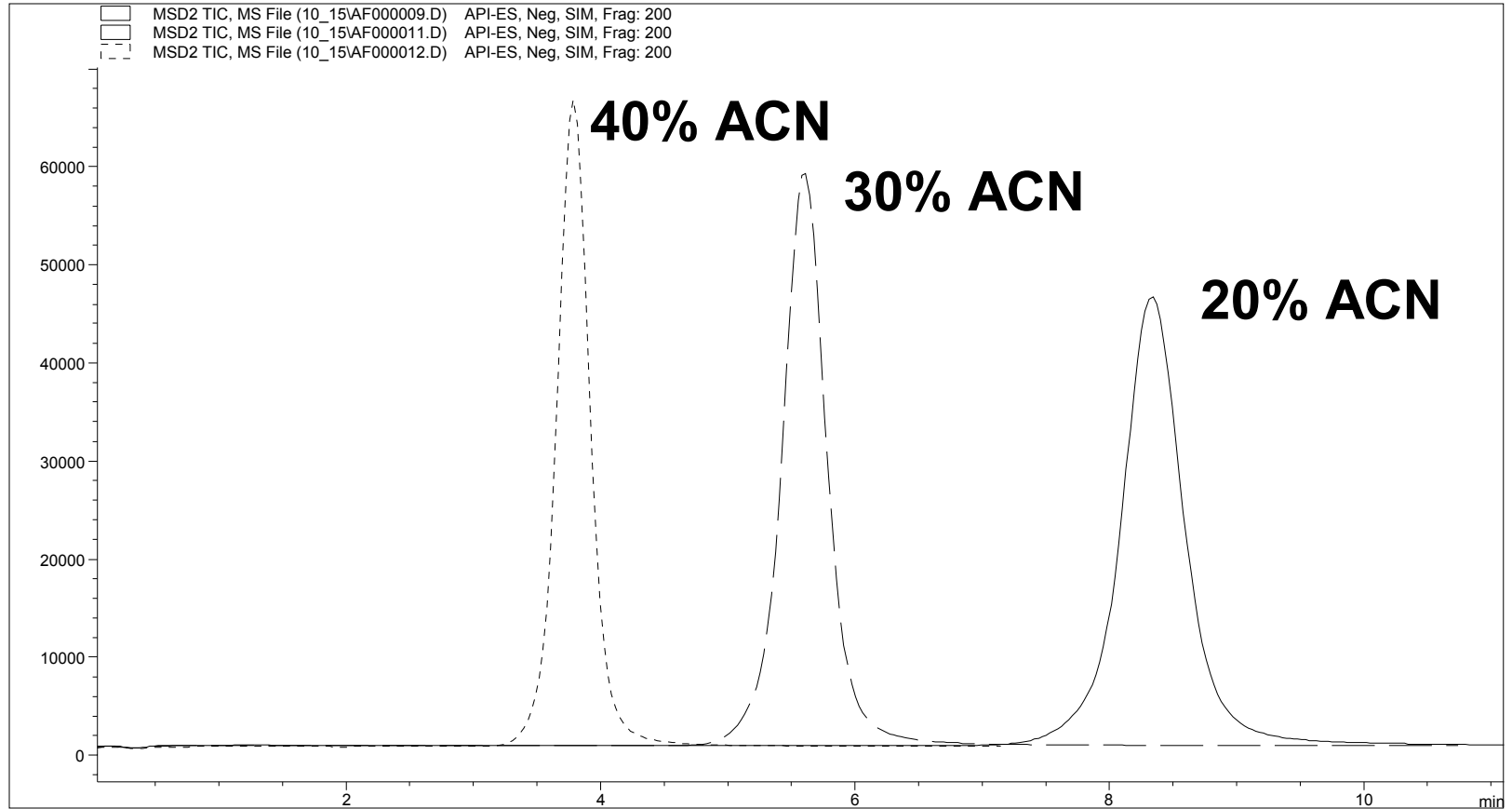


# 80mM Ammonium Formate pH9 20% ACN 5uL injection, 1 ppm Perchlorate

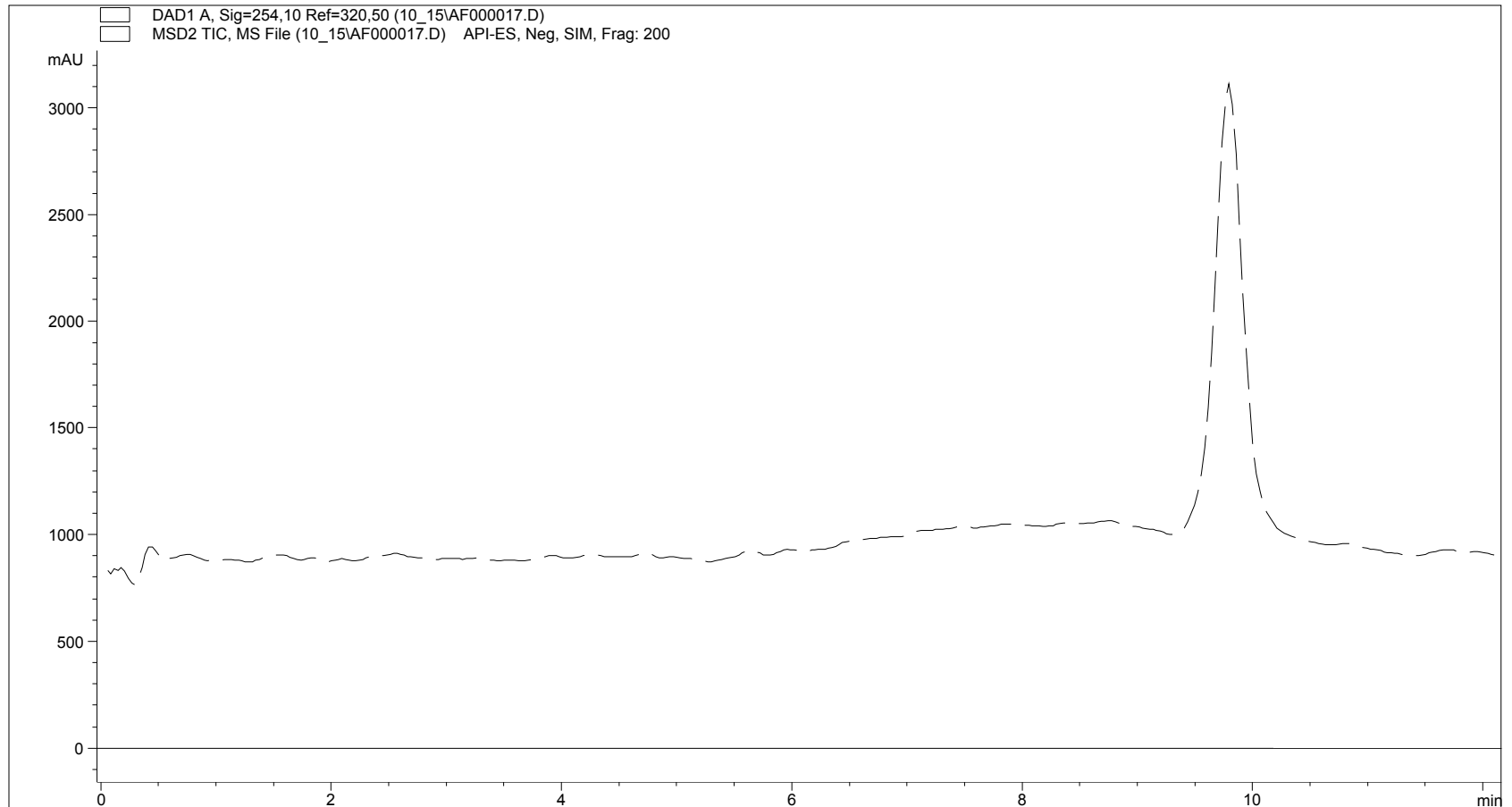




# 80mM Ammonium Formate pH9

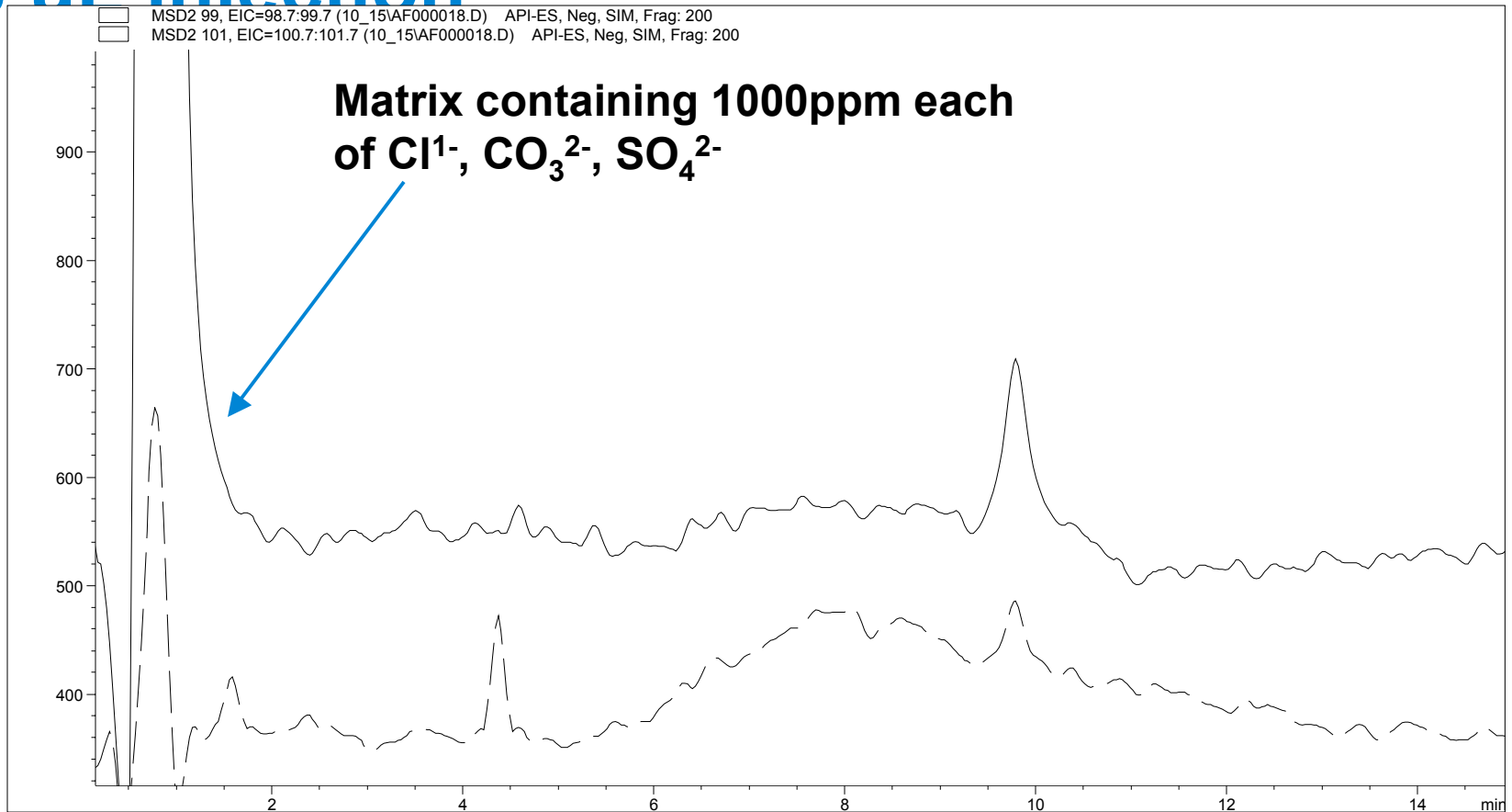


# 10 ppm perchlorate using ACN gradient (10-50% in 10 minutes) and 8 uL injection

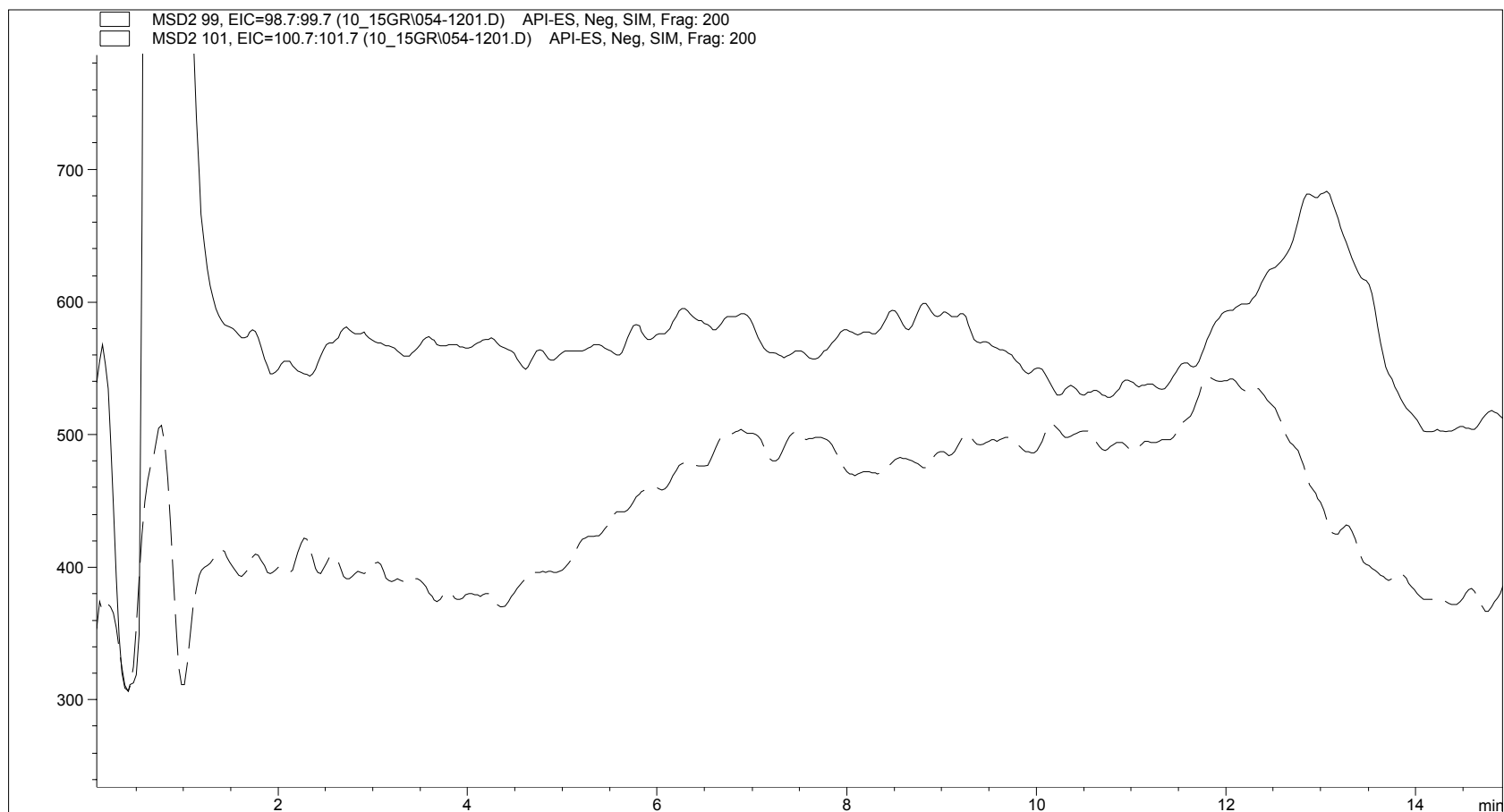


# Synthetic matrix with 0.5ppb Perchlorate spike

## 8 $\mu$ l injection



# Well Water from College Station



# Can the injection size be scaled up?

- **Peak width effects**
- **Matrix effects on retention time**
- **Sulfate behavior**

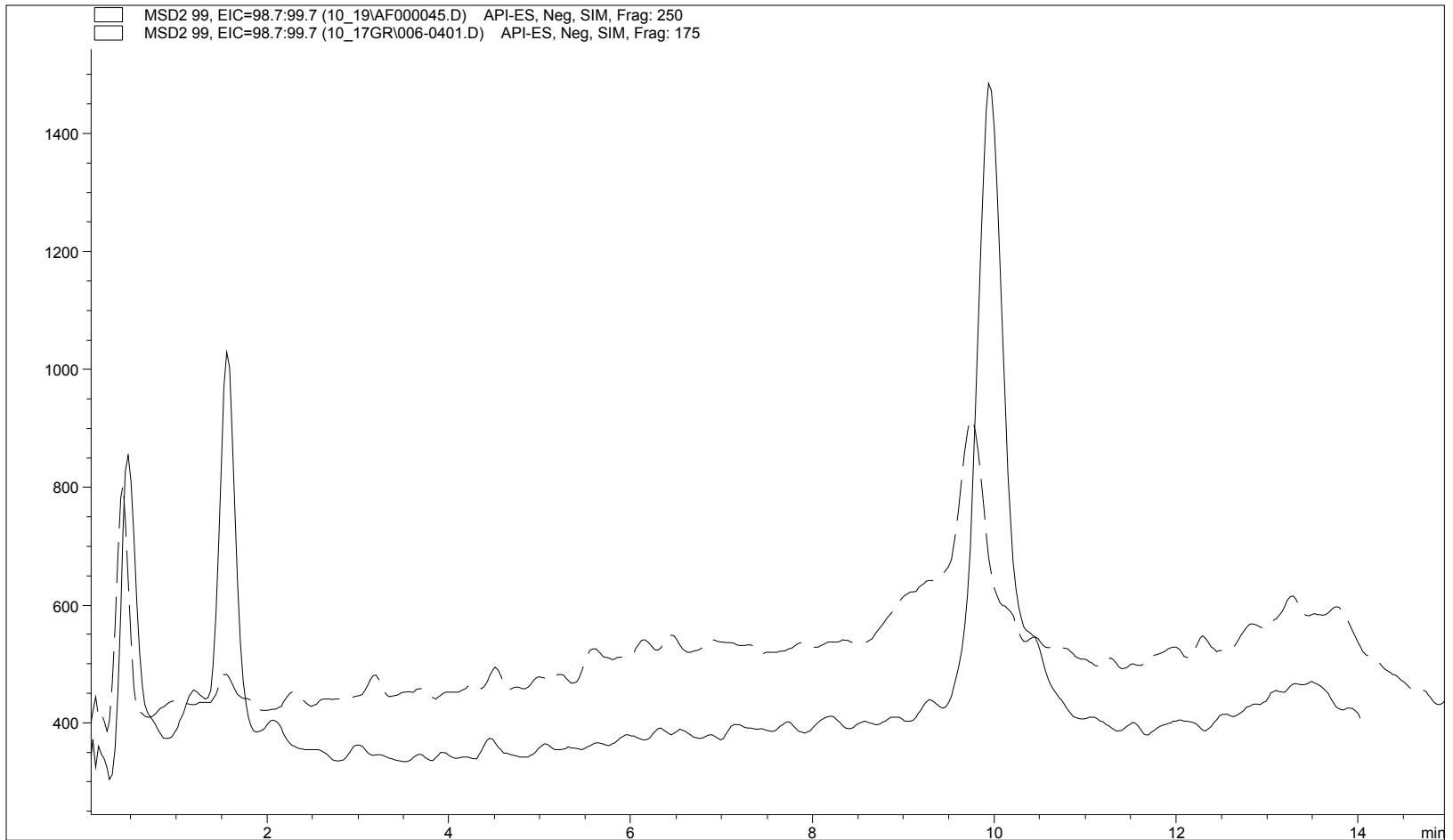


# Stability during a run without internal standard for 8 $\mu$ L injection

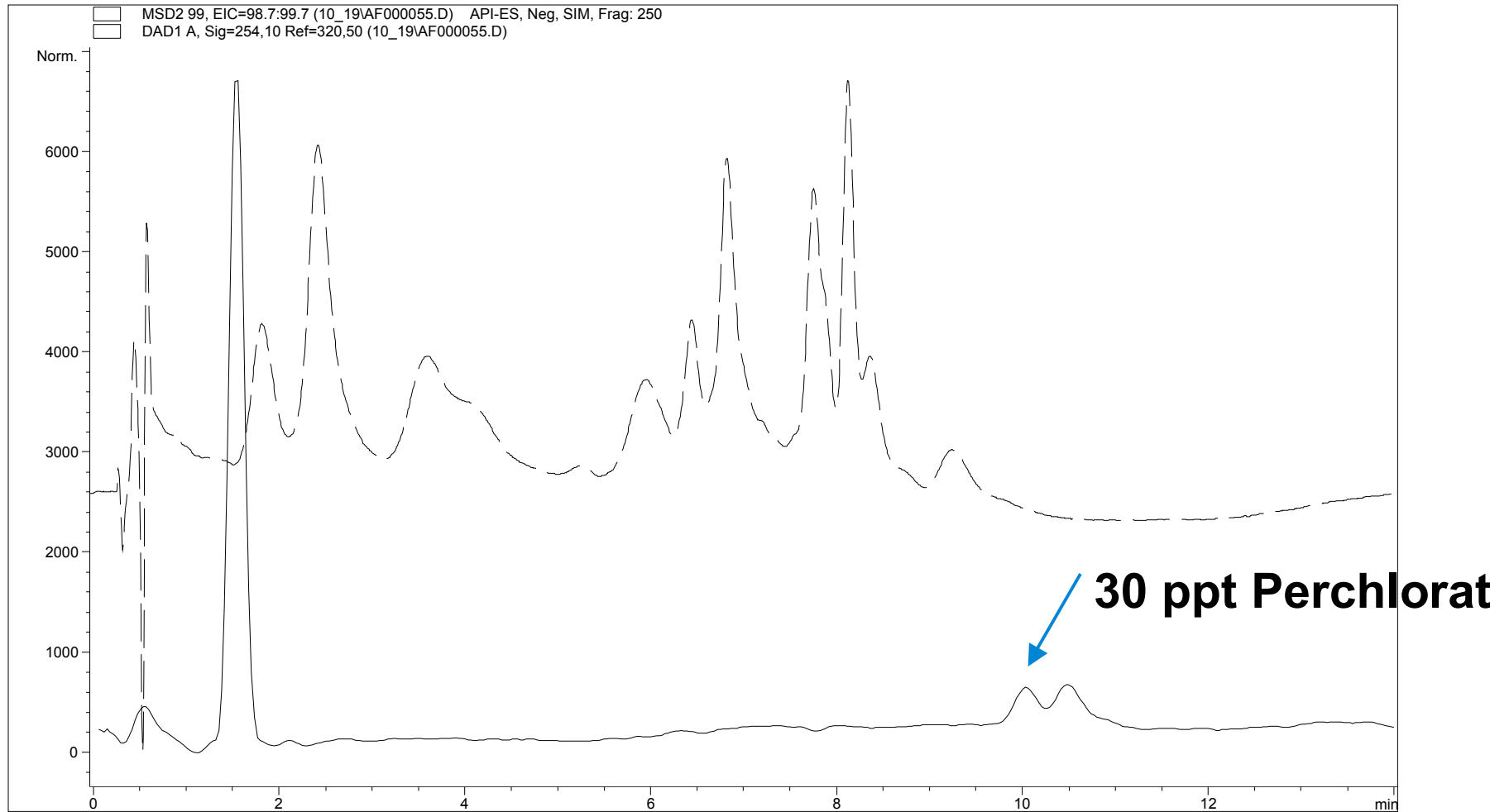
- Over 50 samples of “high matrix” , Houston and College Station tap
- CCV recovery (0.5 ppb) for 5 checks ranged from 92 to 107%
- All CCB’s (5) were neg.
- No Perchlorate was found in CS “blanks” 5 samples
- Recovery of 1 ppb in “high matrix” for 30 samples averaged 90% with RSD or 6%
- Recovery of 0.5 ppb in college station water (5 samples) ranged from 90 to 106%



# 8uL vs 50uL injections of 0.95 ppb Perchlorate on a 3 mm id column



# Armand Bayou surface water





# Short term observations of using an ammonium formate/ acetonitrile buffer

- Retention behavior and peak shape for perchlorate is excellent
- Retention time for perchlorate appears to be independent of matrix
- Interference from organic material appears to be minimal
- Daughter ions at 83/85 can be used for confirmation
- Different injection sizes can be used to fit the needed detection limit



# 1 ppb Perchlorate extracted ion chromatogram

