

# **Evaluation of Analytical Methods for Pharmaceuticals and Personal Care Products**



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# Pharmaceuticals and Personal Care Products as Pollutants (PPCPs)

- ❖ Prescription and over-the counter therapeutic drugs, hormones
- ❖ Veterinary drugs, esp. antibiotics and steroids
- ❖ Antibacterial/microbial soaps/detergents
- ❖ Fragrances, Cosmetics
- ❖ Nutraceuticals (e.g., vitamins)



# Sources of PPCPs:



- ❖ Human activity
- ❖ Residues from hospitals, nursing homes
- ❖ Veterinary drug use, especially antibiotics and steroids
- ❖ livestock wastes
- ❖ Residues from pharmaceutical manufacturing (well defined and controlled)



## Problems from PPCPs

- ❖ 1999-2000, USGS surveyed 139 streams across 30 states - 80 percent of water samples contained residues of PPCPs
- ❖ “**Intersex**” fish in the Potomac River : male carried eggs in their testes
- ❖ Research at Great Lakes Water Institute in Milwaukee shown Lipitor or Zocor, are causing **fish to deposit fat into their eggs**





# Research Needs for PPCPs

- ❖ **Monitoring/Surveys in Illinois:** NE IL (Chicago area) and Central IL data (Bloomington area)
- ❖ **Analytical Methods:** More Labs can analyze at sub-ppb levels and standardized methods for data comparison
- ❖ **Point Source Studies** to the wastewater treatment plant in the urban environment (hospitals and nursing homes)





## PPCP Target List

Based on findings in Central Illinois surface waters near Bloomington (Caughey et al. 2006)

❖ List: analgesic, antiinflammatory, antibiotics, antiepileptic, antimicrobial, and antacids.

❖ Acetaminophen, Ibuprofen, Naproxen, Caffeine, Ciprofloxacin, Erythromycin, Oxytetracycline, Tetracycline, Sulfamethazine, Sulfamethoxazole, Trimethoprim, Carbamazepine, Triclocarban, Triclosan, Cimetidine, Ranitidine



# USEPA Method 1694: PPCPs by HPLC/MS/MS – Dec 2007

- ❖ 4 methods for groups of target analytes, positive and negative ion modes
- ❖ Optimize to use less methods for the list
- ❖ HPLC – Waters Symmetry C8 column  
– 2.1 x 100 mm column,  
Flow Rate:0.2 ml/min
- ❖ MS – Waters Micromass Quattro micro Tandem Mass Spectrometry System

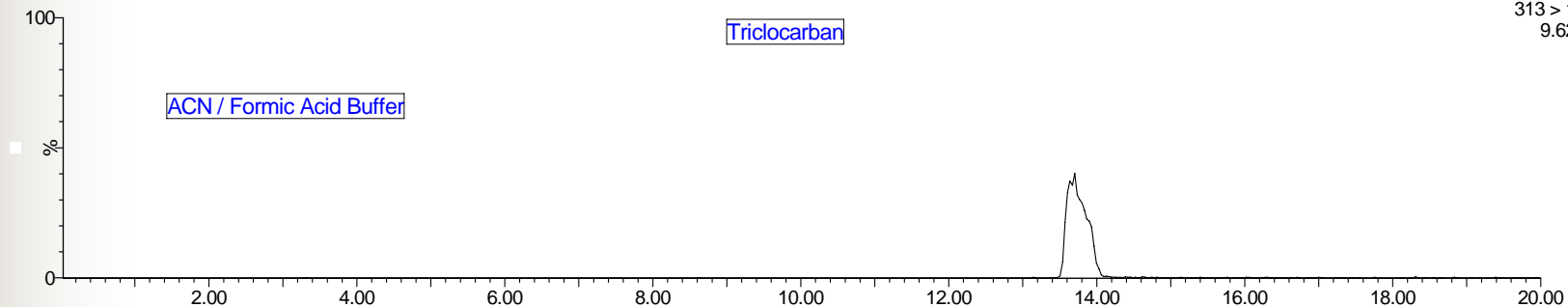
# Solvent Effect on Elution and Response

Mix 14 cpds

20080414-18

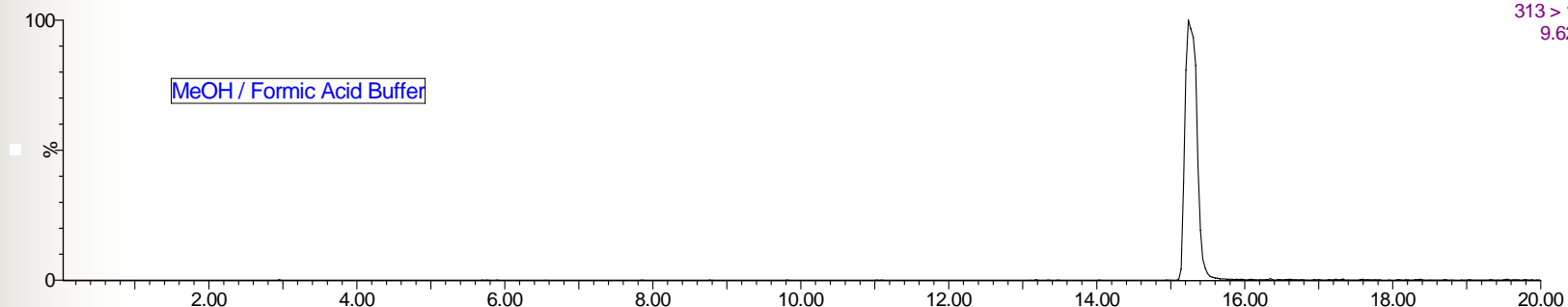
14-Apr-2008

1: MRM of 3 Channels ES-  
313 > 160  
9.62e4



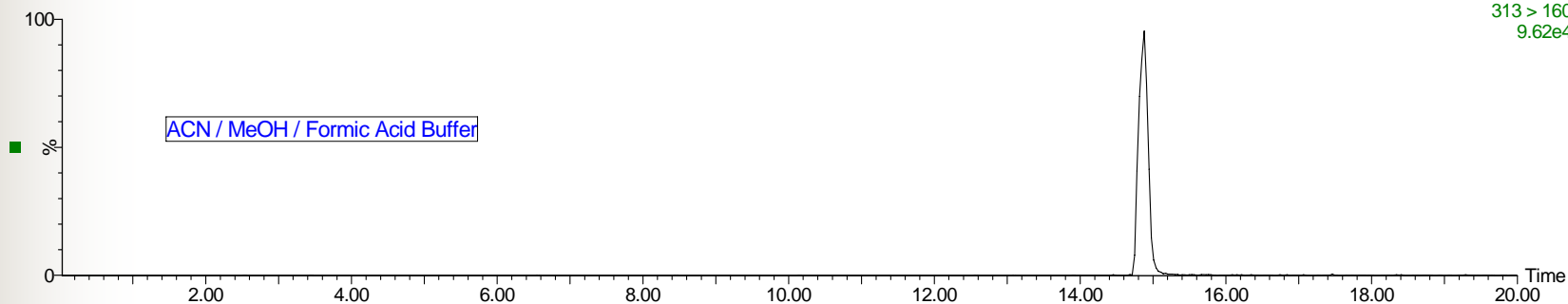
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1: MRM of 3 Channels ES-  
313 > 160  
9.62e4



20080414-21

1: MRM of 3 Channels ES-  
313 > 160  
9.62e4





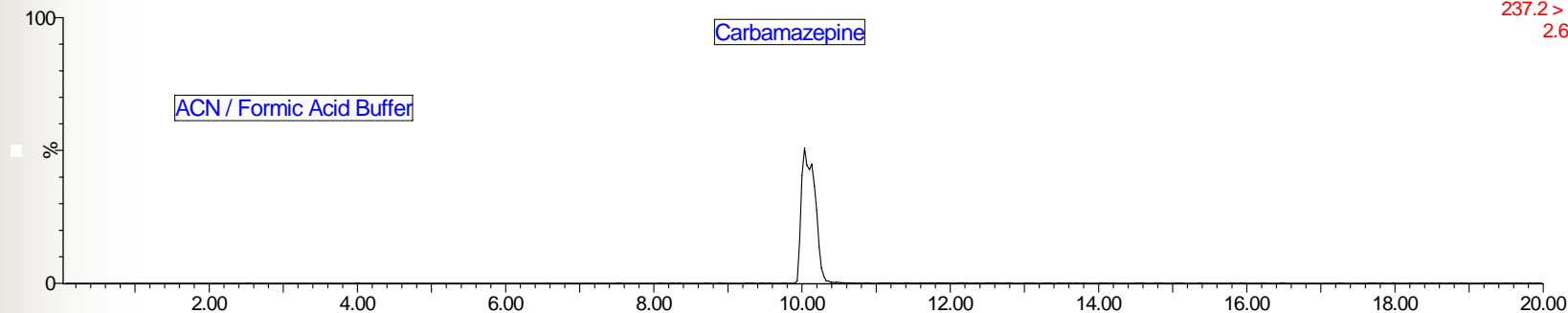
# Solvent Effect on Elution and Response

Mix 14 cpds

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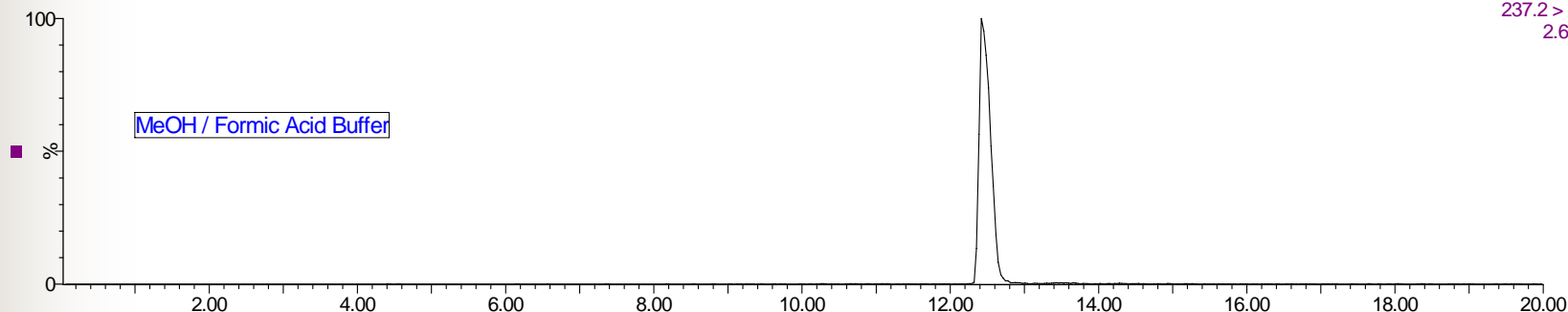
14-Apr-2008

2: MRM of 11 Channels ES+  
237.2 > 194  
2.64e5



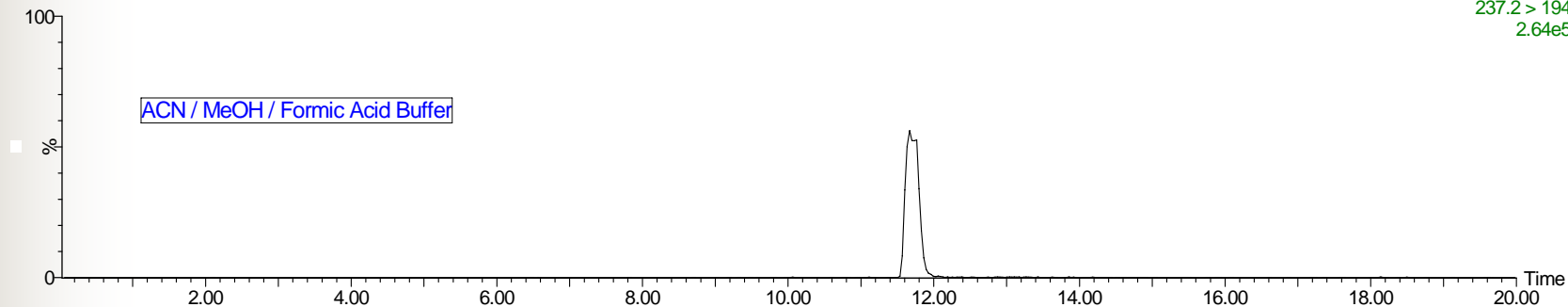
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2: MRM of 11 Channels ES+  
237.2 > 194  
2.64e5



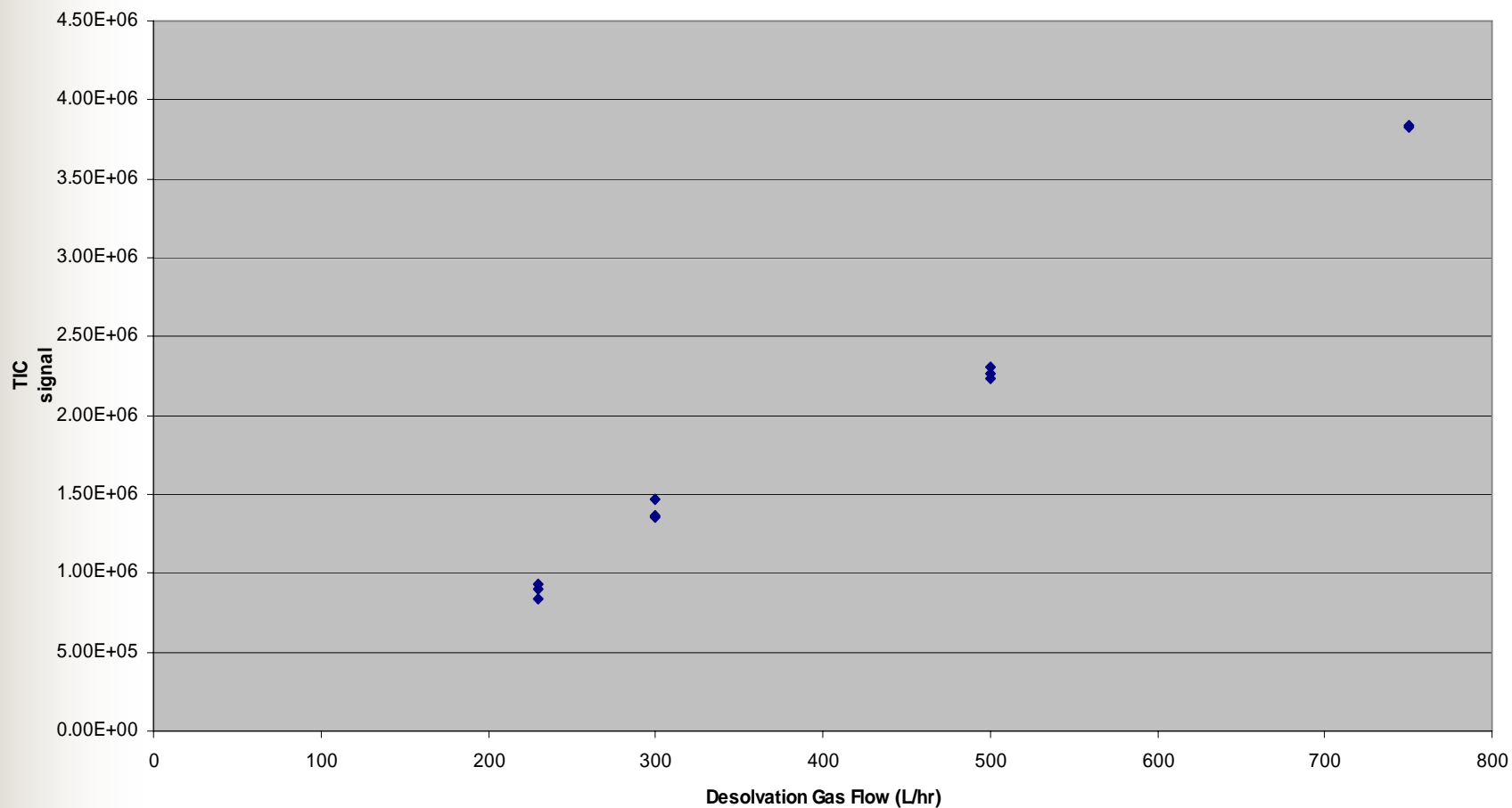
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2: MRM of 11 Channels ES+  
237.2 > 194  
2.64e5



# Desolvation Gas Effect on TIC Response

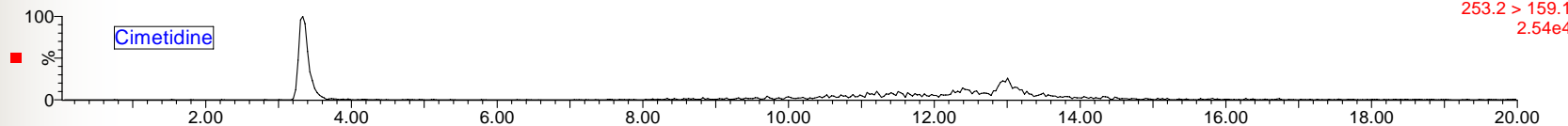
Effect of Desolvation Gas Flow on TIC response of PPCP Mix



# Method 1: Formic Acid/NH4 formate Buffer/ACN/MeOH

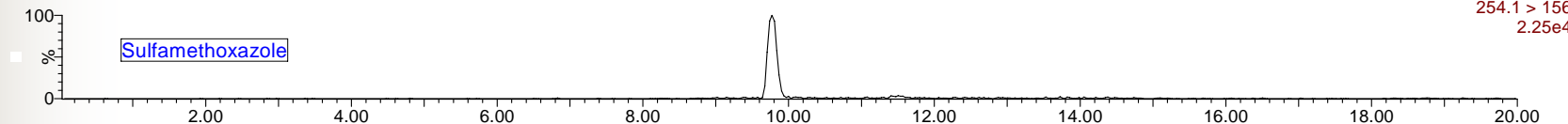
Mix 14 cpds

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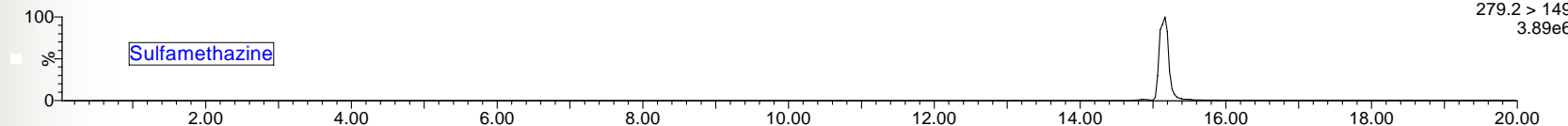
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2: MRM of 11 Channels ES+  
253.2 > 159.1  
2.54e4

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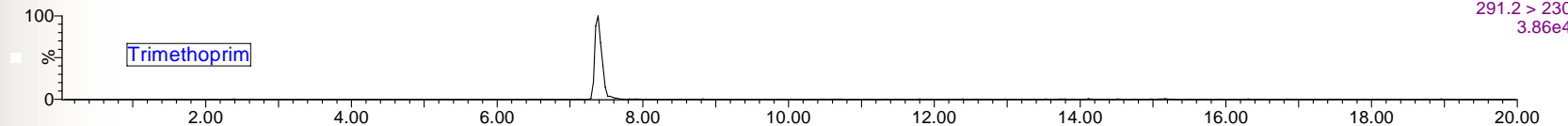
2: MRM of 11 Channels ES+  
254.1 > 156  
2.25e4

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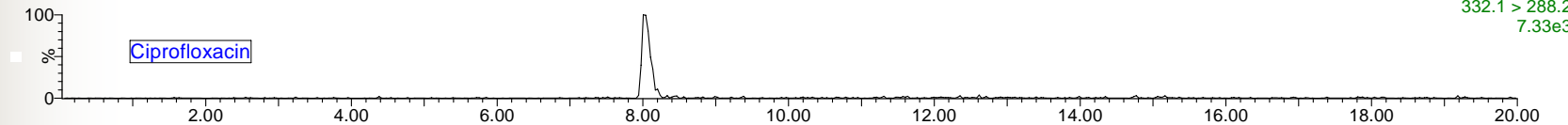
2: MRM of 11 Channels ES+  
279.2 > 149  
3.89e6

20080414-21



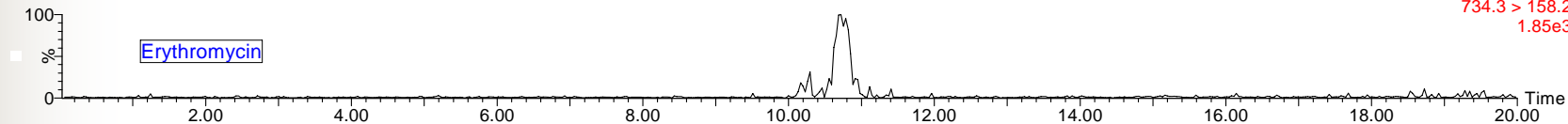
2: MRM of 11 Channels ES+  
291.2 > 230  
3.86e4

20080414-21



2: MRM of 11 Channels ES+  
332.1 > 288.2  
7.33e3

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2: MRM of 11 Channels ES+  
734.3 > 158.2  
1.85e3

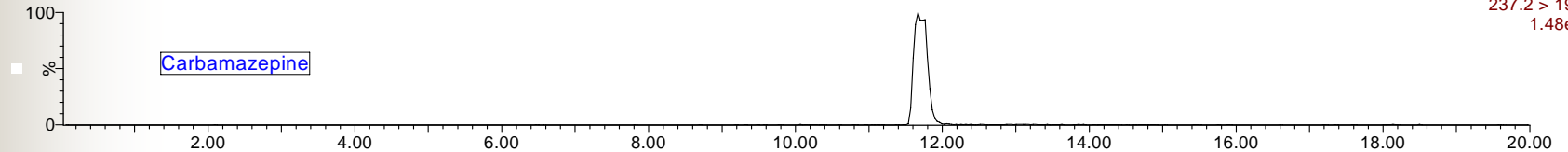
# Method 1: Formic Acid/NH4 formate Buffer/ACN/MeOH

Mix 14 cpds

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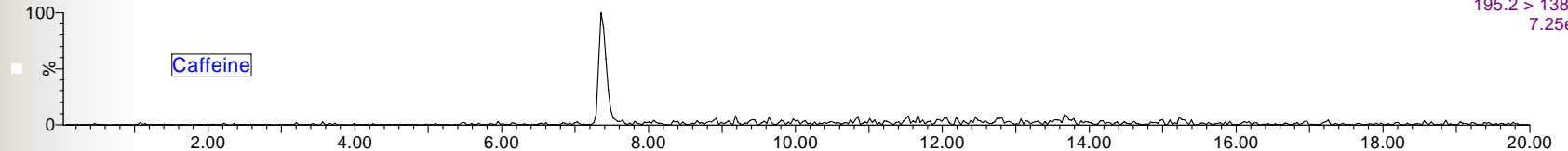
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2: MRM of 11 Channels ES+  
237.2 > 194  
1.48e5



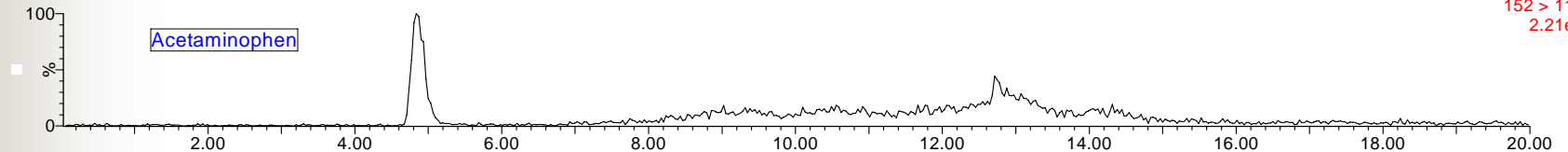
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2: MRM of 11 Channels ES+  
195.2 > 138.1  
7.25e3



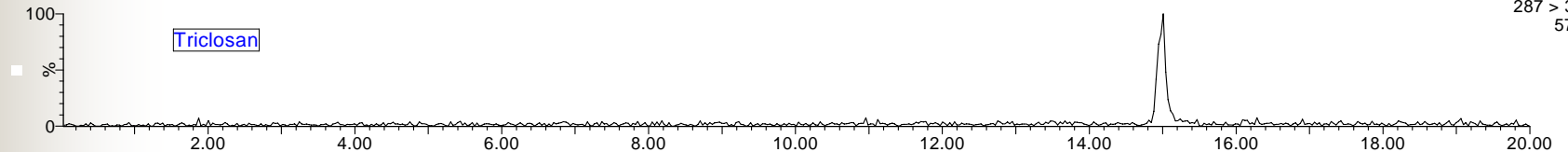
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2: MRM of 11 Channels ES+  
152 > 110  
2.21e4



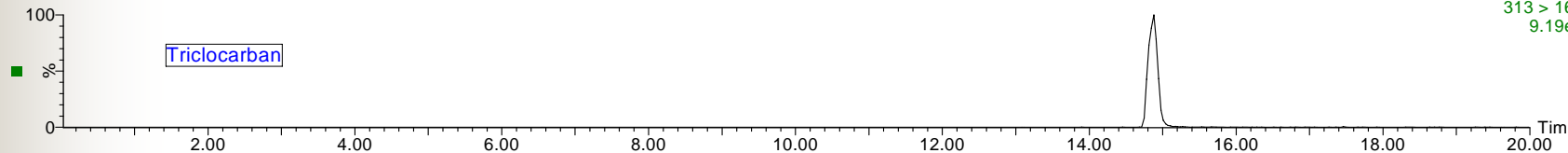
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1: MRM of 3 Channels ES-  
287 > 35  
575



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1: MRM of 3 Channels ES-  
313 > 160  
9.19e4

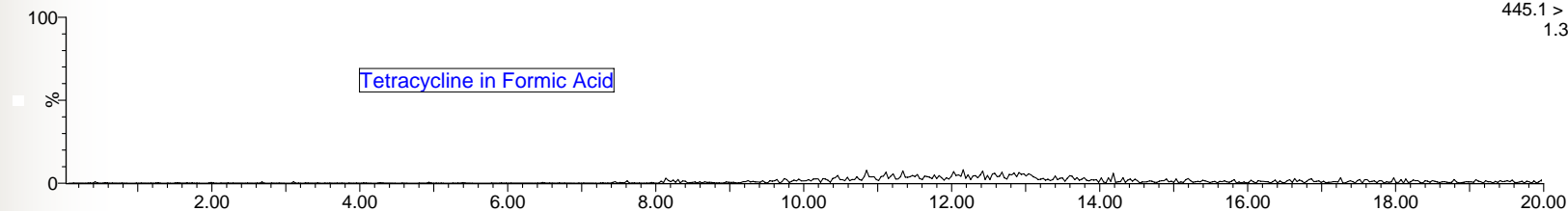


# Method 2: Oxalic Acid/ACN/MeOH

20 ppb Oxytetra, tetra  
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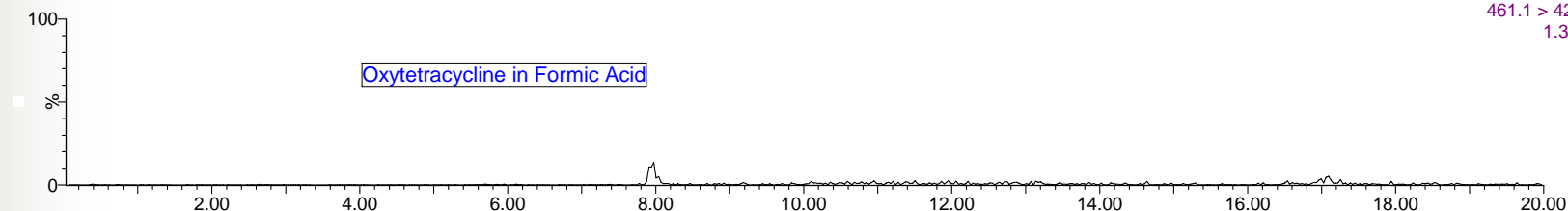
17-Apr-2008

2: MRM of 11 Channels ES+  
445.1 > 410  
1.36e4



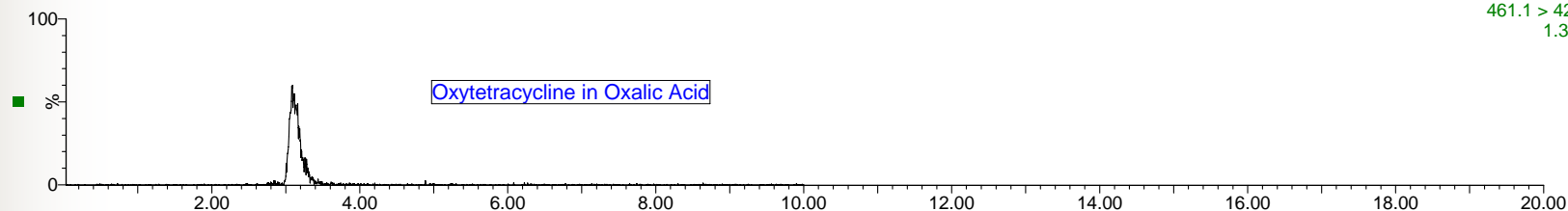
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2: MRM of 11 Channels ES+  
461.1 > 426.1  
1.36e4



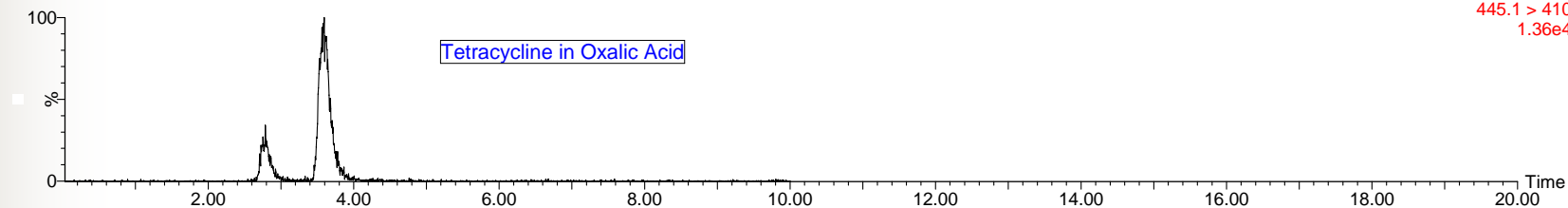
20080417-06

MRM of 2 Channels ES+  
461.1 > 426.1  
1.36e4



20080417-06

MRM of 2 Channels ES+  
445.1 > 410  
1.36e4





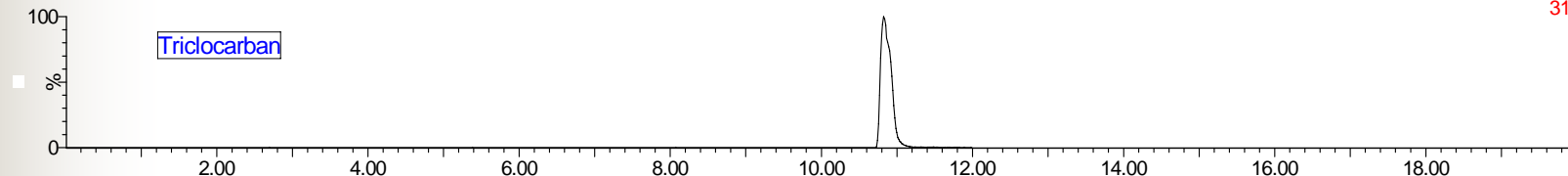
# Method 3: Water/ACN/MeOH

6 cpd in water, 100 ppb

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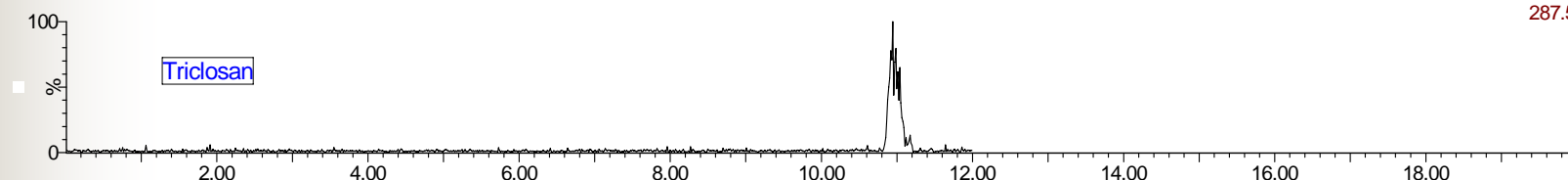
23-Apr-2008

MRM of 6 Channels ES-  
313 > 160  
3.86e5



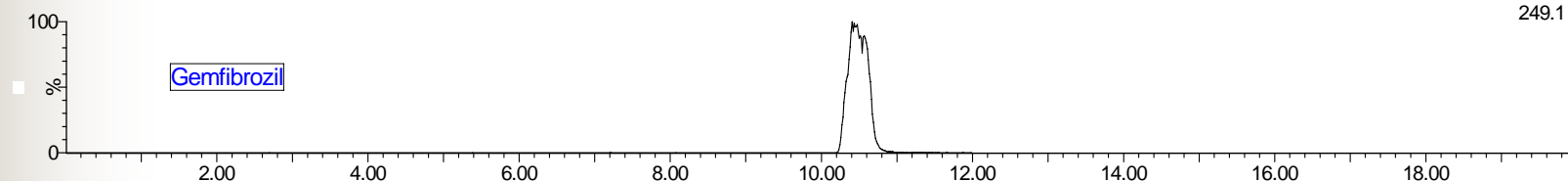
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MRM of 6 Channels ES-  
287.5 > 34.5  
1.43e3



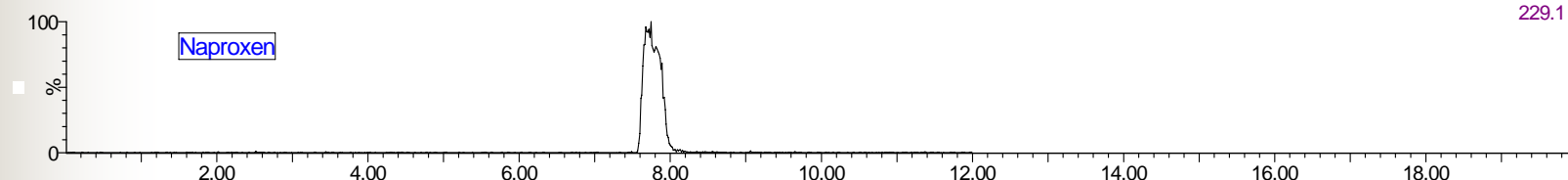
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MRM of 6 Channels ES-  
249.1 > 120.9  
1.45e5



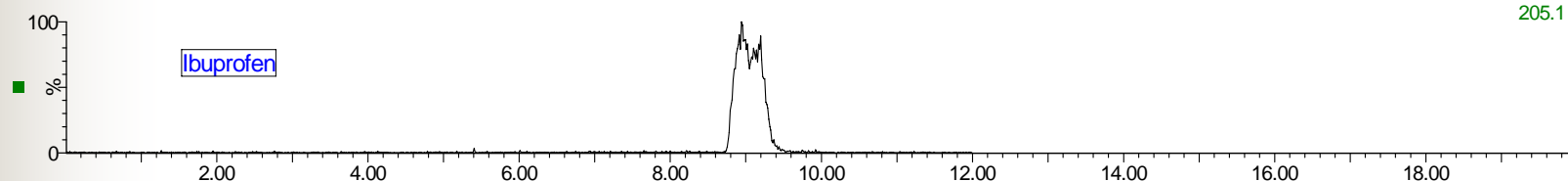
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MRM of 6 Channels ES-  
229.1 > 169.1  
1.16e4



20080423-08

MRM of 6 Channels ES-  
205.1 > 161.1  
1.92e4



Time

# PPCPs instrument detection limits

<u>PPCP analytes</u>	<u>instrumental reporting limits</u>
Acetaminophen	2 ppb
Caffeine	5 ppb
Ciprofloxacin	2 ppb
Erythromycin	5 ppb
Triclosan	1 ppb
Triclocarban	<1 ppb
Sulfamethazine	<1 ppb
Sulfamethoxazole	1 ppb
Trimethoprim	<1 ppb
Carbamazepine	<1 ppb
Cimetidine	<1 ppb
Ranitidine	1 ppb
Metformin	2 ppb
Ibuprofen	1 ppb
Naproxen	2 ppb
Gemfibrozil	1 ppb
Tetracycline	5 ppb
Oxytetracycline	2 ppb



## Future researches

- Triclosan in Chicago Streams and effects  
- Loyola University, Chicago (Dr. John Kelly)
- AWWA 4167 grant - Evaluation of Analytical Methods for EDCs and PPCPs via Interlaboratory Comparison – Southern Nevada Water Authority (Dr. Brett Vanderford)