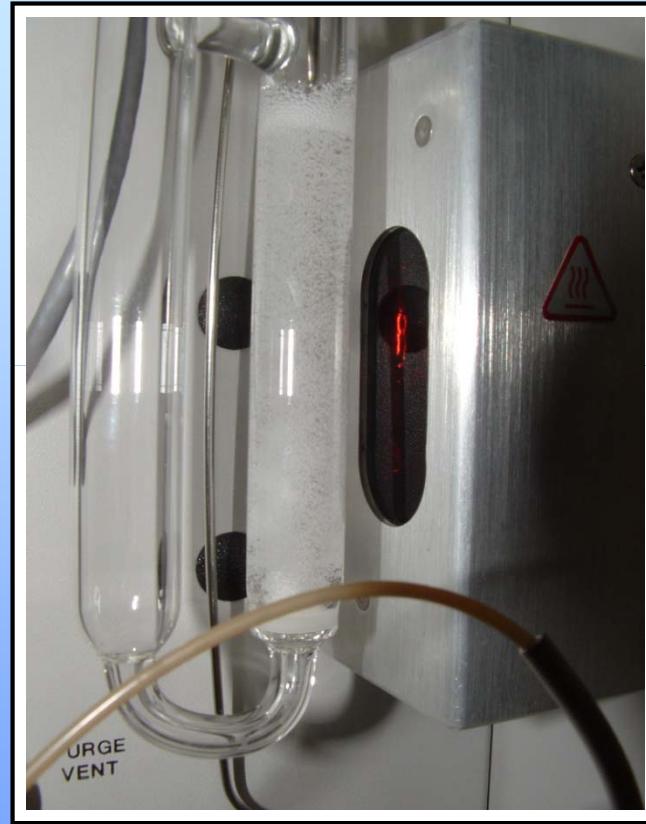


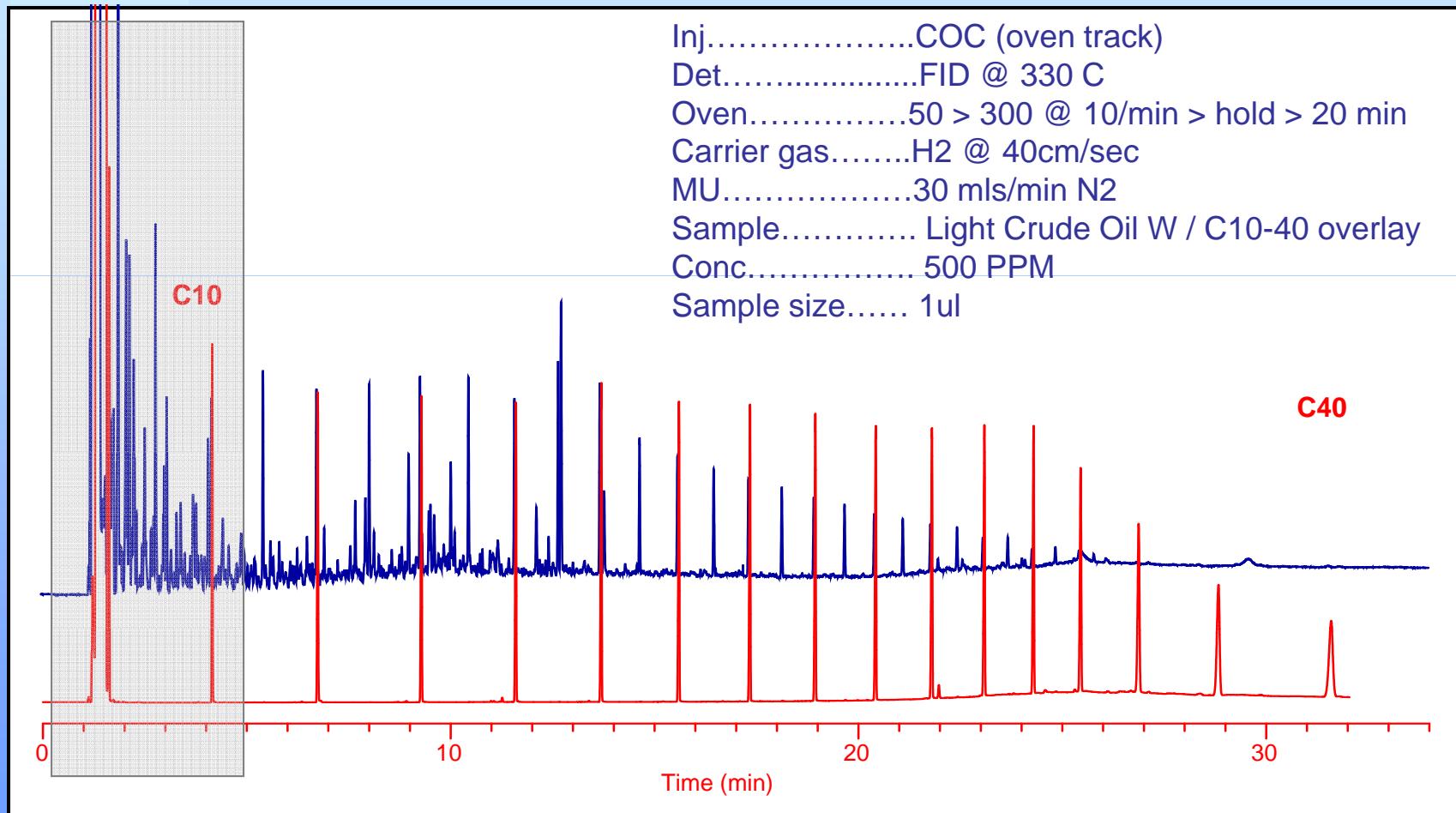
BP Gulf Oil Spill: Modified EPA Method 8260 for the Analysis of Crude Oils by Purge-and-Trap GC-MS.



C. English, J. Konschnik, J. Cochran, M. Misselwitz, R. Lautamo, and G. Stidsen

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823

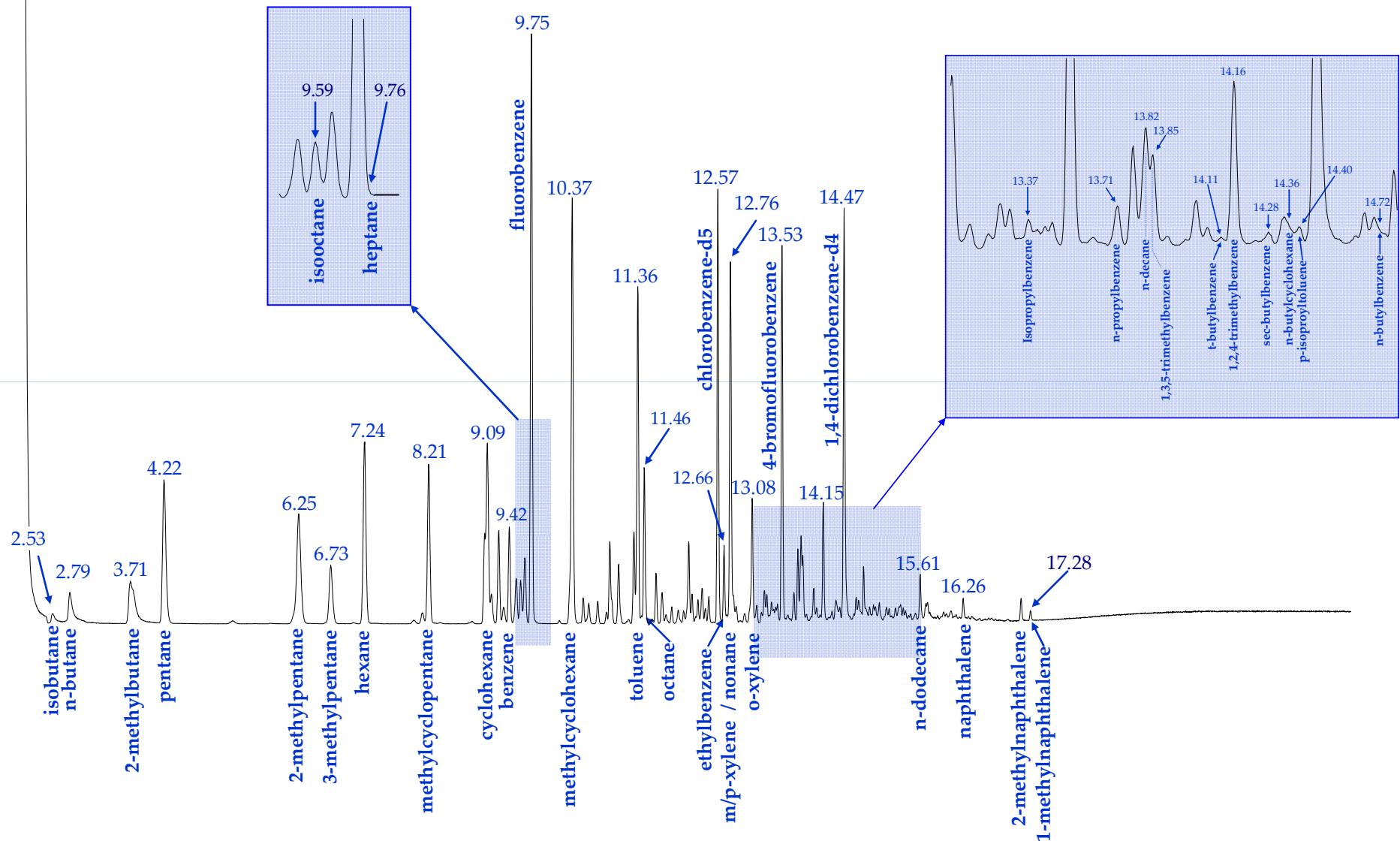
Typical Crude Oil Analysis



Target Compounds

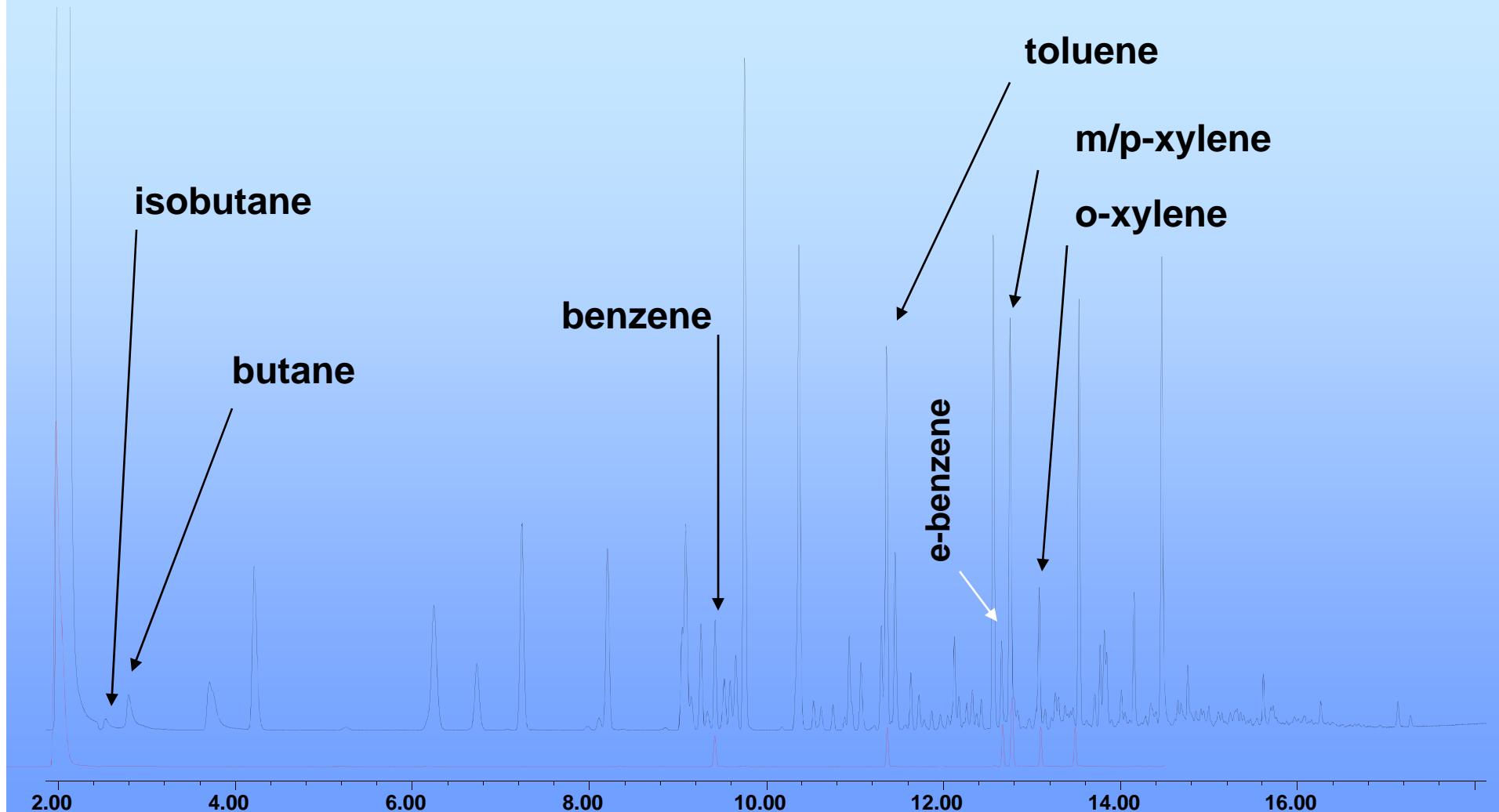
1	1,4-Difluorobenzene
2	isobutane
3	n-butane
4	2-methylbutane
5	pentane
6	2-methylpentane
7	3-methylpentane
8	hexane
9	methylcyclopentane
10	cyclohexane
11	benzene
12	2,2,4-trimethylhexane
13	heptane
14	methylcyclohexane
16	toluene

17	n-octane
18	ethylbenzene
19	m/p-xylene
20	n-nonane
21	o-xylene
22	isopropylbenzene
23	n-propylbenzene
24	n-decane
25	sec-butylbenzene
26	n-butylcyclohexane
27	p-isopropyltoluene
28	n-butylbenzene
29	n-dodecane
30	naphthalene
31	2-methylnaphthalene
32	1-methylnaphthalene

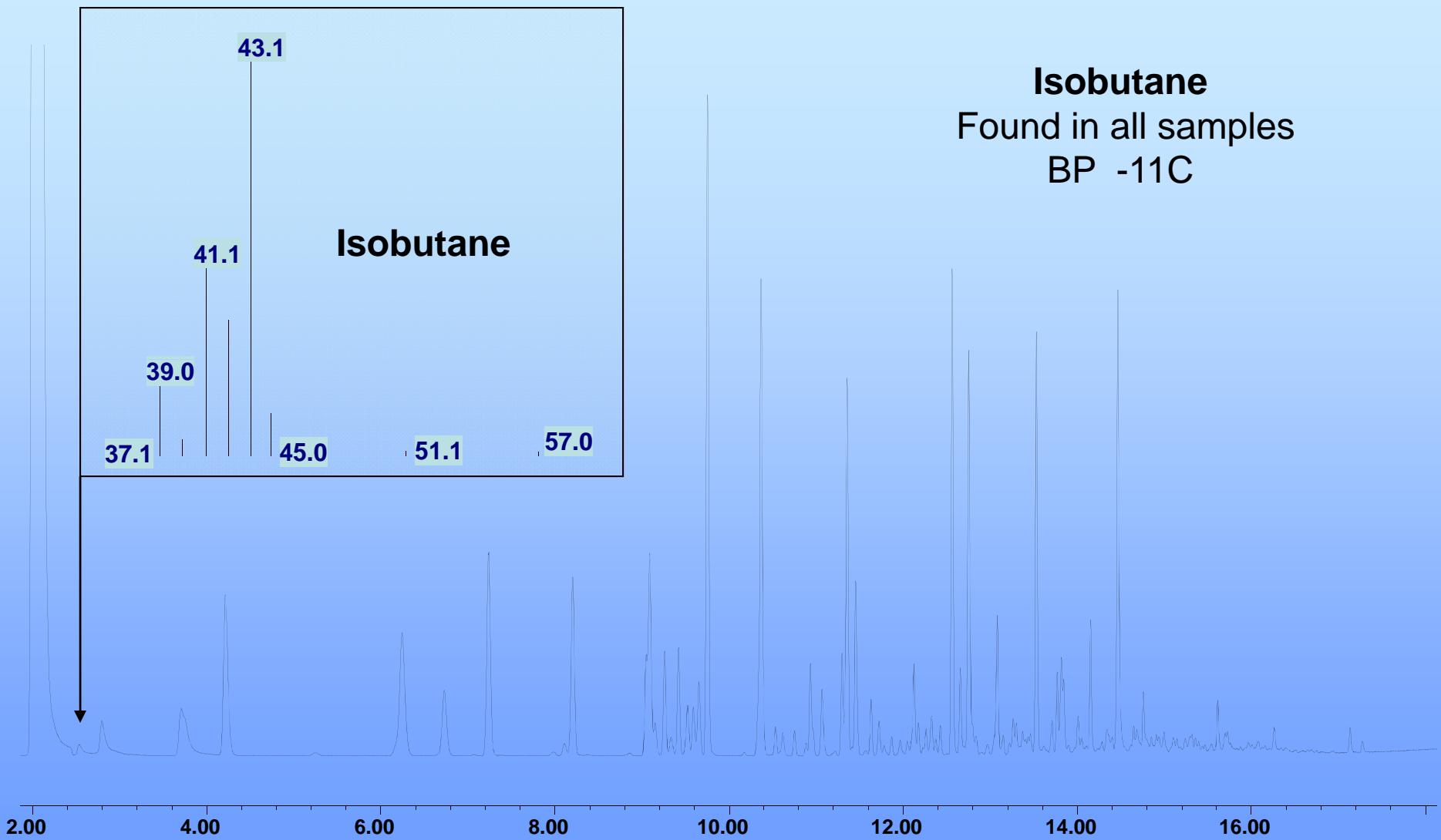


Rxi-624Sil MS 30m x 0.25mm x 1.4df, 1ml/min, 45C heated 5ml purge
Oven: 35C(hold 5min) 11C/60C (0 hold) 20C/320C (hold 1)

Crude Oil Chromatogram at 10 ppm



Crude Oil Chromatogram at 10 ppm



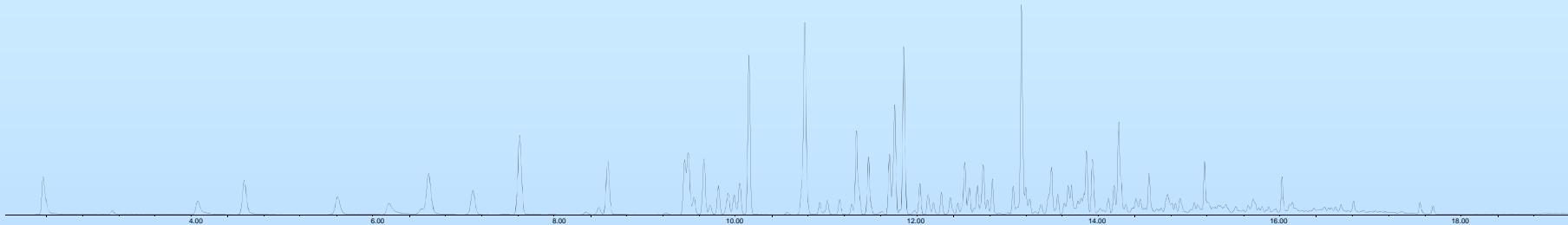
Study:

- **Salt water vs. fresh water**
- **Dispersed oil vs. non-dispersed oil**
- **Feasibility of detecting ppb levels of total crude**
Require ppt levels of single analytes
- **Comparison of WAFs of different crude oils**
Mississippi Canyon, Maya & California

Salt Water vs. Fresh Water Purge



Fresh Water vs. Salt Water Analysis



Curve
Points
1, 10, 50,
100, 200

100 ppb BTEX

Method Blank

1ppm Composite
Gasoline

1ppm Composite
Gasoline

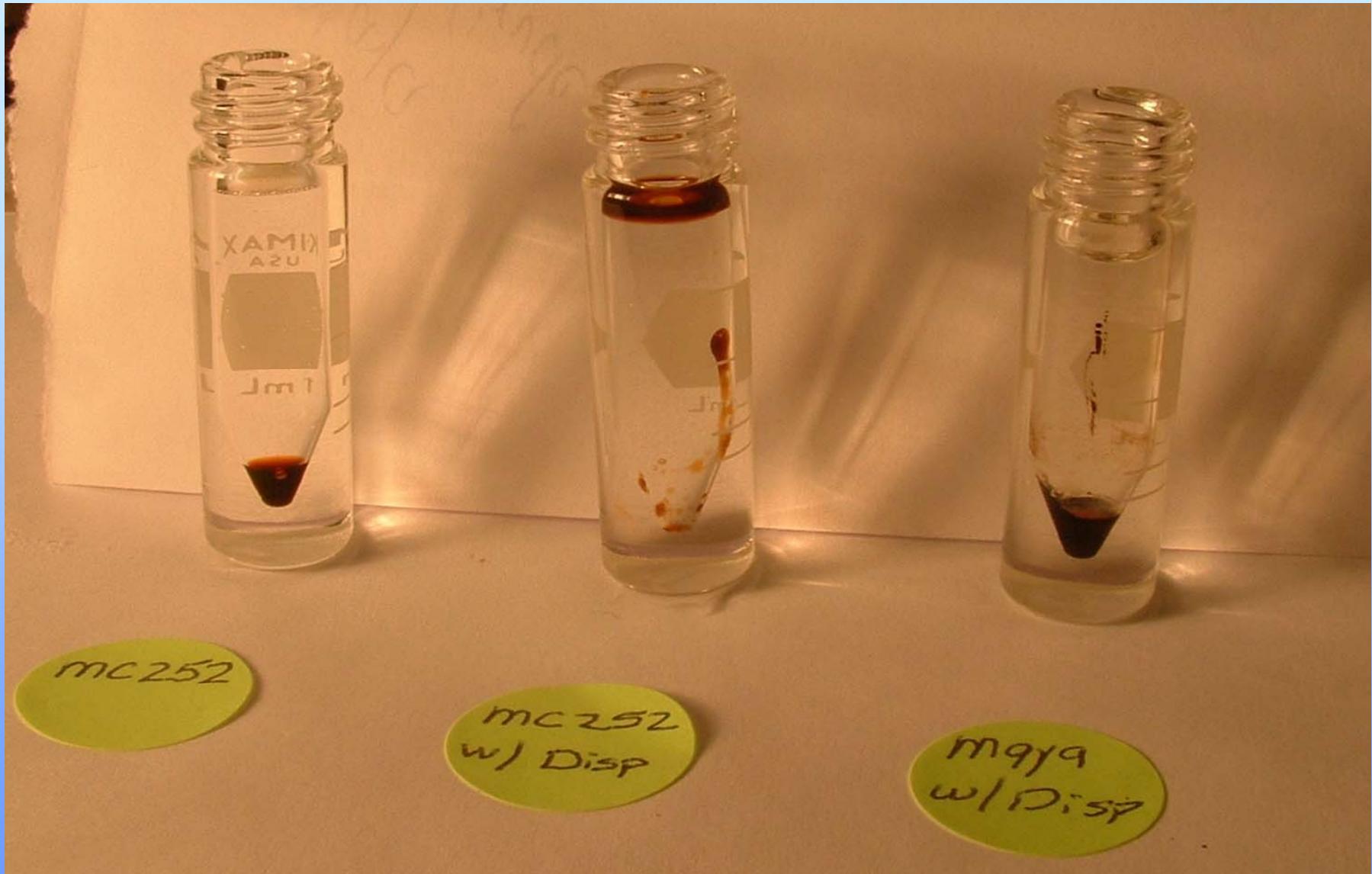
10ppm MC252
Crude

10ppm MC252
Crude

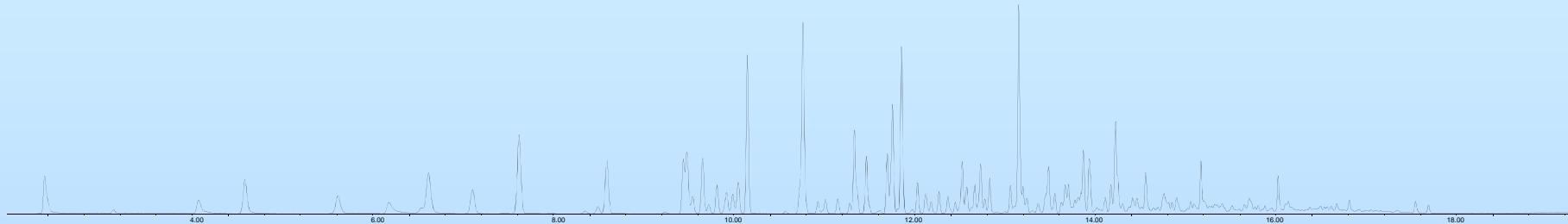
Target Compound	%RSD	Salt	Salt	Fresh	Salt	Fresh	Salt
1,4-difluorobenzene							
2-methyl pentane	8%		ND	44.2	43.9	66.8	63.2
benzene	9%	107%	ND	12.6	13.0	22.2	22.1
2,2,4-trimethylpentane	10%		ND	28.1	27.7	0.0	0.0
n-heptane	10%		ND	12.8	11.1	132.6	121.2
toluene	10%	106%	ND	98.0	101.9	63.2	61.3
ethylbenzene	11%	109%	ND	21.2	22.2	13.5	13.8
m/p-xylene	12%	109%	ND	77.7	81.5	70.1	68.0
o-xylene	12%	109%	ND	31.5	32.8	25.4	25.6
1,2,4-trimethylbenzene	16%		ND	35.9	36.7	33.5	33.1
naphthalene	21%		ND	1.9	2.1	9.7	11.2
bromofluorobenzene	12%	110%	106.8%	102.4%	100.3%	96.1%	89.1%

Curve: D100818

Dispersed Oil vs. Non-Dispersed Oil



Dispersed Oil vs. Non-Dispersed Oil



Points:
0.5, 10, 50,
100, 200

100 ppb BTEX

Method Blank

10ppm MC252 Crude

10ppm MC252 Crude
Dispersant Added

Target Compound	%RSD	%Rec.	ND	Salt ppb	Salt ppb
1,4-difluorobenzene (IS)					
2-methyl pentane	10%		ND	51.0	63.2
benzene	5%	119%	ND	19.9	22.1
2,2,4-trimethylpentane	5%		ND	0.0	0.0
n-heptane	11%		ND	99.3	118.3
toluene	3%	114%	ND	58.2	69.5
ethylbenzene	13%	121%	ND	13.0	15.3
m/p-xylene	11%	125%	ND	67.7	87.1
o-xylene	10%	111%	ND	24.7	30.5
1,2,4-trimethylbenzene	13%		ND	30.6	40.2
naphthalene	20%		ND	9.8	12.2
bromofluorobenzene	7%	110%	107.1%	92.1%	95.8%

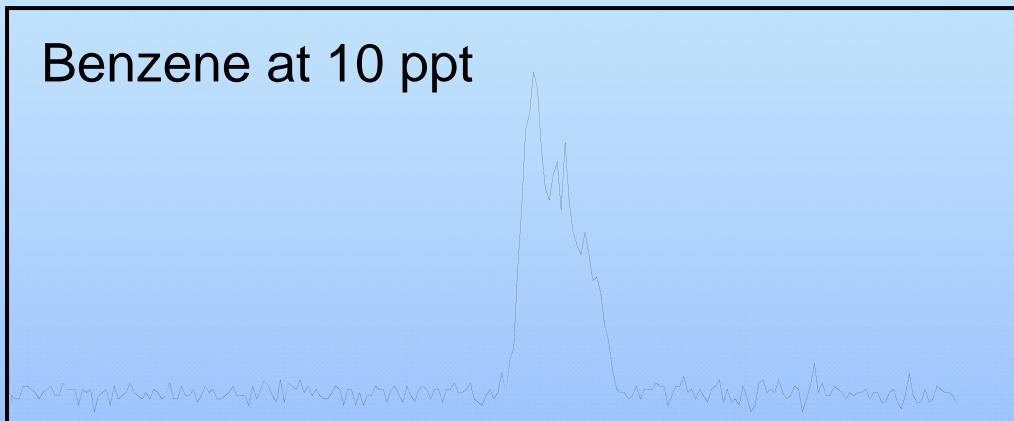
curve: D100819

P&T-GC/MS-SIM



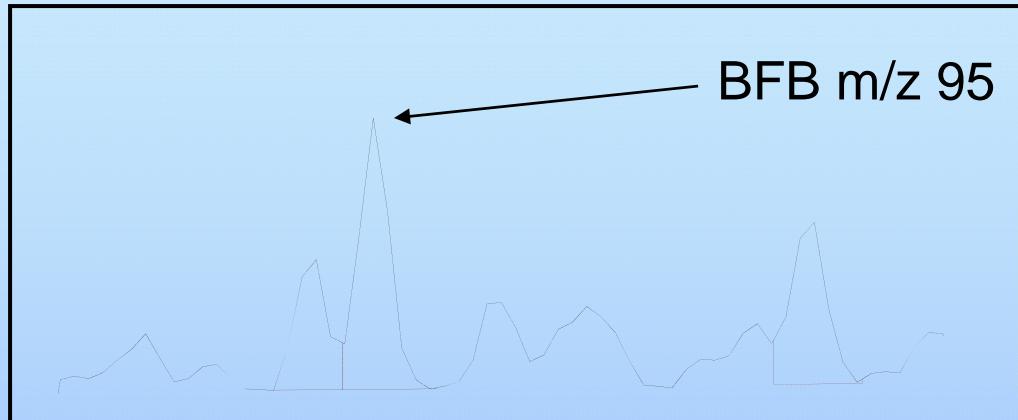
P&T-GC/MS-SIM: toluene, ethylbenzene, m, p, o, xylene

Detection of TEX crude volatiles to 100 ppb total crude



- calibration: 50, 100, 500, 1000, 2000 ppt
- benzene did not pass calibration
- toluene Low Point 100ppt (background ~ 75 ppt)
- e-benzene low point 50ppt
- m/p xylene Low Point 100ppt
- o-xylene Low Point 50ppt

SIM: toluene, ethylbenzene, m, p, o, xylene Recoveries of volatiles in 100ppb total crude.

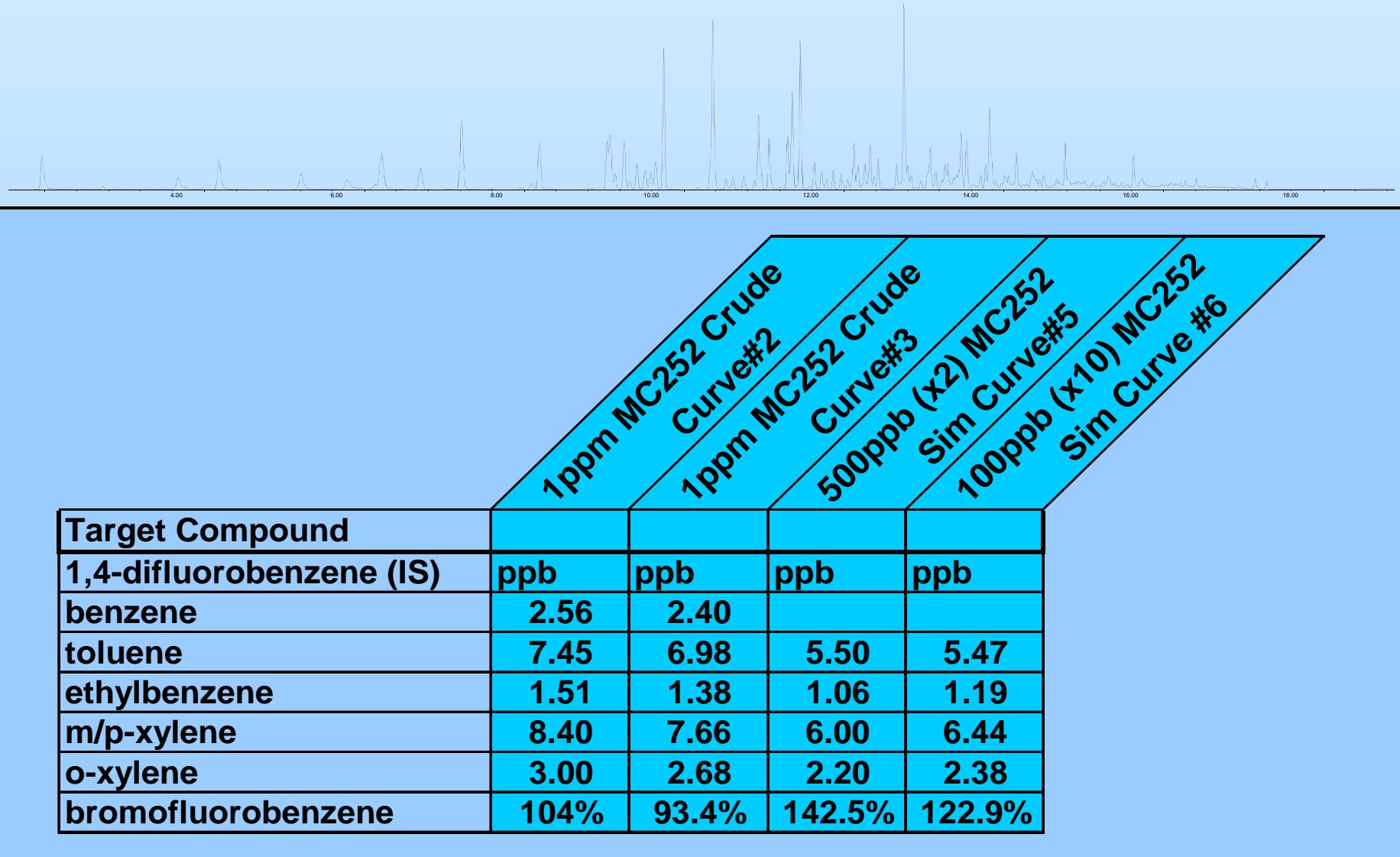


Points: 50,
100, 500,
1000, 2000
ppt.

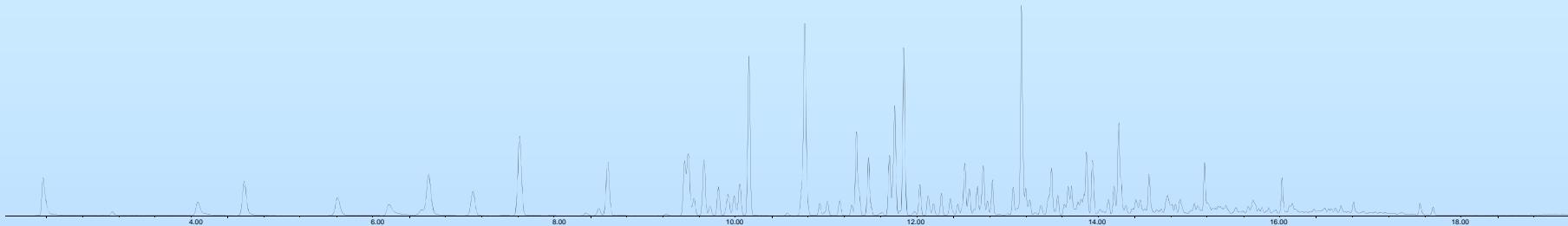
Target Compound	%RSD	%Rec.	ND	100 ppt BTEX		
				100 ppt BTEX	Method Blank	100 ppb MC252 Crude
1,4-difluorobenzene (IS)						
toluene**	12%	121%	ND	574.2	544.8	355.1
ethylbenzene	8%	99%	ND	119.9	121.2	116.7
m/p-xylene	10%	102%	ND	322.3	324.7	170.0
o-xylene	8%	112%	ND	238.2	238.2	138.2
bromofluorobenzene	10%	82%	106%	122.9%	124.2%	103.8%

** 50 ppt point dropped.

Comparison Between SIM & Full Scan



Comparisons of MC252, Maya and California Crude Oil



Points:
0.5, 10, 50,
100, 200

Method Blank
10ppm MC252 Crude
10ppm Maya Crude
10ppm California Crude

Target Compound	%RSD	ppb	ppb	ppb	
1,4-difluorobenzene (IS)					
2-methyl pentane	10%	ND	51.0	22.6	12.0
benzene	5%	ND	19.9	5.5	3.2
2,2,4-trimethylpentane	5%	ND	0.0	0.0	5.6
n-heptane	11%	ND	99.3	35.6	3.7
toluene	3%	ND	58.2	16.6	20.6
ethylbenzene	13%	ND	13.0	5.3	4.6
m/p-xylene	11%	ND	67.7	16.2	16.1
o-xylene	10%	ND	24.7	6.9	6.4
1,2,4-trimethylbenzene	13%	ND	30.6	7.8	7.0
naphthalene	20%	ND	9.8	1.1	0.5
bromofluorobenzene	7%	107.1%	92.1%	110.4%	100.8%

Analytical Challenges

- Salt Clogging Autosamplers
- Making up standards
- Background BTEX limits this method
- Proper choice of SS & IS is critical

Observations

- Salt water vs. fresh water
- Dispersed oil vs. non-dispersed oil
- Total crude detected at 100 ppb
- Crude showed measurable differences
- Butanes present in all crudes

Questions ?

