

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

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Introduction

In 1990 the Oil Pollution Act (OPA) was promulgated under the direction of the National Oceanic and Atmospheric Administration (NOAA) following the Exxon Valdez oil spill in March of 1989. These regulations require a Natural Resource Damage Assessment (NRDA) following a release of oil into the nation's waterways. Currently NOAA is conducting a NRDA to determine the impact of the Deepwater Horizon oil spill. There are several NRDA technical working groups (TWGs) assembled to determine; baseline conditions before the oil spill, impacts to plant and animals following the spill and the current conditions of the marine ecosystem. The trustees are also evaluating impacts from the response, to include use of dispersants.

Aquatic toxicity of crude oil is critical to providing estimates of damage following a spill. Determinations of acute toxicity of crude oils require an understanding of the total composition of the source material. Measurements of the water-accommodated fractions (WAF) for semi-volatiles focus mostly on polyaromatic hydrocarbons (PAHs). While this approach is effective in making chronic toxicity determinations it falls short of measuring the initial exposure to the marine ecosystem. Less emphasis has been placed on the forensic chemistry of light distillates since the time of exposure to marine life is significantly less than middle-distillate products. Toxicity of crude oil WAFs varies with oil type and animal species tested. A study by Gala, et al. tested PAHs, BTEX, total volatile petroleum hydrocarbons (VPH) and total extractable petroleum hydrocarbons (EPH) and found that the toxicity followed the listed order from most toxic, PAHs to least toxic EPH. Therefore the most toxic constituents of oil are PAHs & BTEX ^{1,2}.

Purge-and-trap techniques using EPA 8260B will be used to determine the following:

1. Recoveries of crude in salt water versus fresh water.
2. Dispersed oil versus non-dispersed oil analysis.
3. Feasibility of detecting ppb levels of total crude oil by analyzing BTEX in ppt using GC-MS-SIM.
4. Comparison of WAFs of different crude oils; Mississippi Canyon, Maya and California crude.

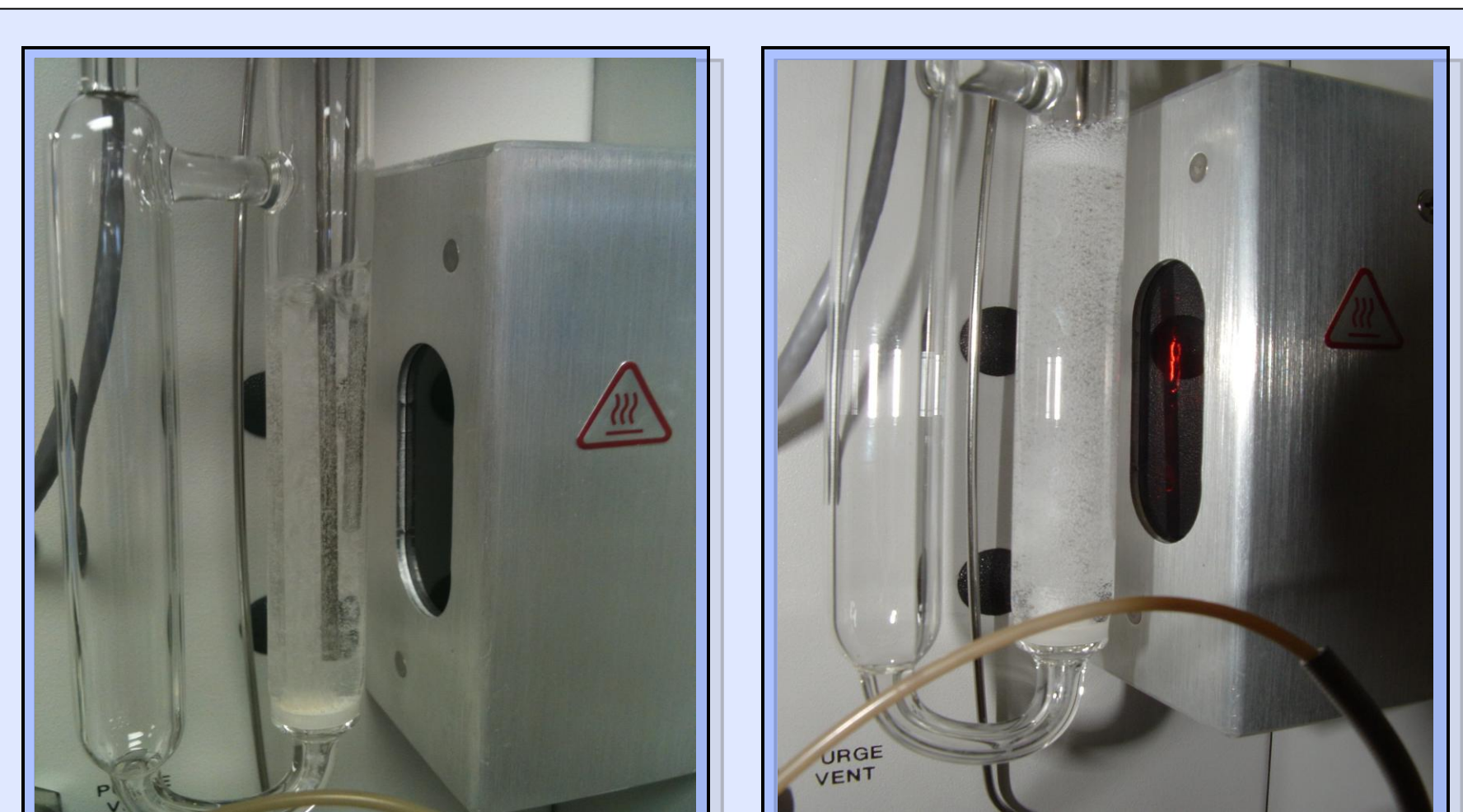


Photo #1 (left): A typical water sample purged at 40ml/min. Photo #2 (right) Salt water sample; notice the increase in the number and size of the helium bubbles compared to a fresh water sample. Does this increase purging efficiency for light distillates?

Crude Oil Analysis by Cool-on-column Injection.

Oil from the Macondo Prospect (MC252) is loosely classified as a type A --Louisiana light sweet crude oil. Sweet crudes are low in sulfur and have a higher percentage of gasoline/kerosene fractions over the heavier oils, such as Maya & California crudes. Weathering of crude can occur within the first 24-48 hours with up to a 40% loss (by weight) within a week. Our analysis of the Mississippi Canyon crude oil determined the majority of the compounds to be in the range of C3 to C36 (See figure 1). The use of purge and trap will address C3 to C12 ending with 1-methylnaphthalene as shown in the shaded area in figure 1.

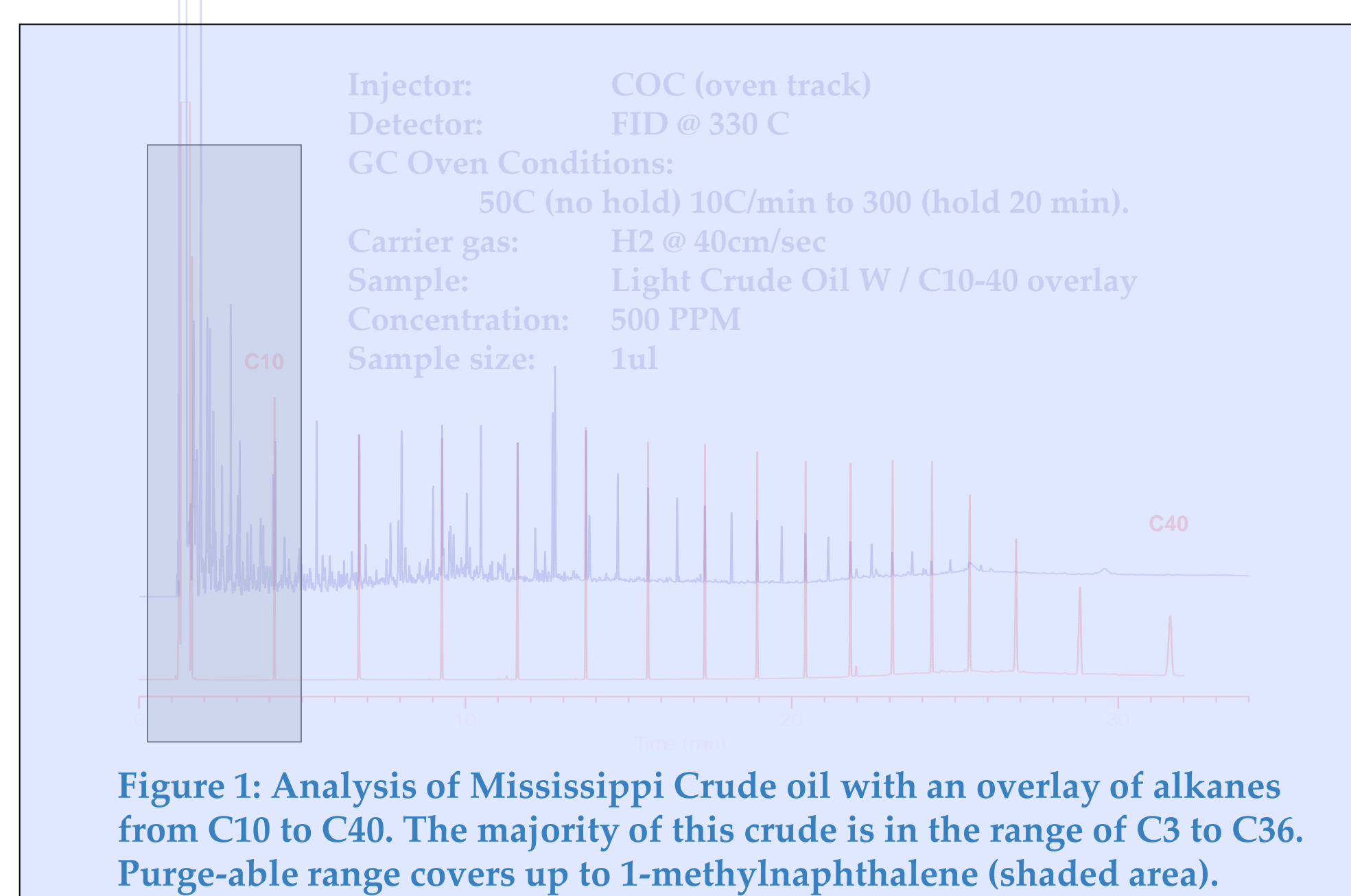


Figure 1: Analysis of Mississippi Crude oil with an overlay of alkanes from C10 to C40. The majority of this crude is in the range of C3 to C36. Purge-able range covers up to 1-methylnaphthalene (shaded area).

Salt Water versus Fresh Water Analysis:

A five point salt water curve was prepared and analyzed for eleven target compounds using 1,4-difluorobenzene as an internal standard and 4-bromofluorobenzene as a surrogate. A second source of BTEX was spiked as a quality control sample with adequate recoveries. A 1ppm gasoline composite standard and a 10ppm crude oil sample were analyzed both in fresh water and salt water (see Table 1).

Target Compound	%RSD	Salt		Fresh	
		%Rec.	ppb	%Rec.	ppb
1,4-difluorobenzene	12%	121%	ND	121%	ND
2-methyl pentane	8%	107%	44.2	43.9	66.8
benzene	9%	107%	12.6	13.0	22.2
2,2,4-trimethylpentane	10%	ND	28.1	27.7	0.0
n-heptane	10%	ND	12.8	11.1	132.6
toluene	10%	106%	ND	98.0	101.9
ethylbenzene	11%	109%	ND	21.2	22.2
m/p-xylene	12%	109%	ND	77.7	81.5
o-xylene	12%	109%	ND	31.5	32.8
1,2,4-trimethylbenzene	16%	ND	35.9	36.7	33.5
naphthalene	21%	ND	1.9	2.1	9.7
bromofluorobenzene	12%	110%	106.8%	102.4%	100.3%

Table 1: Comparison between equal concentrations of sample in fresh versus salt water. No differences were observed.

Replicates of these runs were conducted with the same results. Since the non-polar analytes have a low affinity for the aqueous phase; dissociation of water with salt has no effect on concentration.

Dispersed Oil versus Non-Dispersed Oil Analysis:

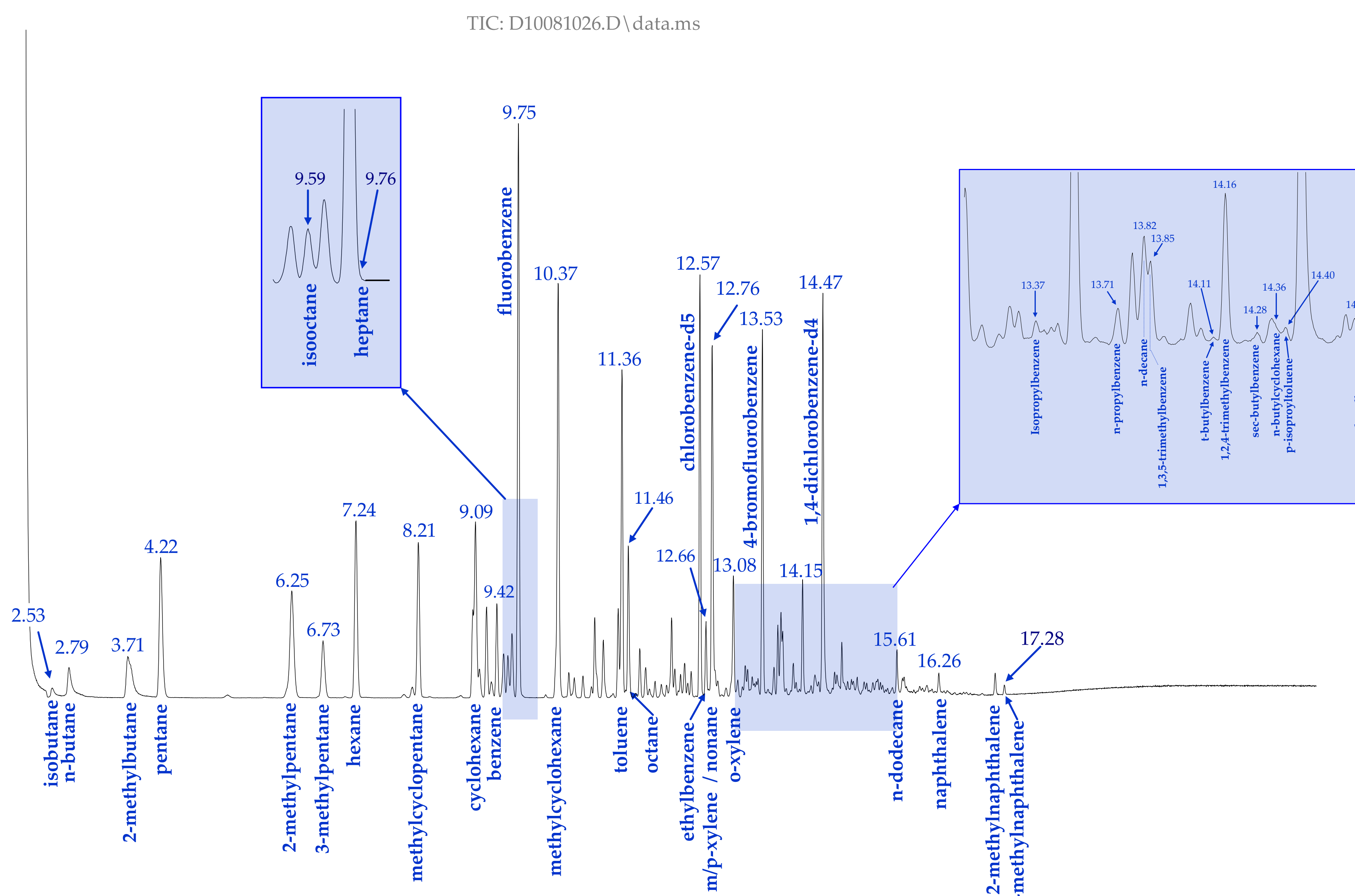
The non-dispersed sample consisted of dissolving oil into methanol at a concentration of 5000 ppm. Dispersed oil included both propylene glycol and 2-butoxyethoxy ethanol at an equal concentration of 5000 ppm each. These analytes are the active ingredients listed in Nalco Corexit EC9527A. The surfactants were not used as part of this study given the potential for instrument damage as a result of foaming.

Target Compound	%RSD	Salt		Salt	
		%Rec.	ppb	%Rec.	ppb
1,4-difluorobenzene (IS)	10%	ND	51.0	53.2	22.1
2-methyl pentane	5%	119%	ND	19.9	22.1
benzene	5%	ND	0.0	0.0	0.0
2,2,4-trimethylpentane	9%	ND	99.3	118.3	69.5
n-heptane	11%	114%	ND	58.2	69.5
toluene	3%	121%	ND	13.0	15.3
ethylbenzene	13%	125%	ND	67.7	87.1
m/p-xylene	10%	111%	ND	24.7	30.5
o-xylene	13%	ND	30.6	40.2	2.0
1,2,4-trimethylbenzene	20%	ND	9.8	12.2	1.2
bromofluorobenzene	7%	110%	107.1%	92.1%	95.8%

Table 2: Comparison between equal concentrations of sample with and without dispersant. No differences were observed.

There appears to be no significant difference between crude with dispersant and without (Table 2). BTEX and other volatile petroleum distillates are soluble in water independent of dispersants. The dispersants are effective for PAHs and higher molecular weight analytes but have no effect on the volatile organics. This is further confirmed by the ingredients of the other dispersant Nalco Corexit EC9500A which contains petroleum distillates in the estimated range of C10 to C12.

Figure 2: Purge & trap analysis of the riser pipe oil taken from the well head of the Macondo Prospect, Mississippi Canyon 252 using a Remotely Operated Vehicle (ROV). Crude oil concentration at 10ppm in salt water. Analysis performed using EPA Method 8260.



Analysis of 100ppb Total Crude Oil Using Single Ion Monitoring (SIM):

The analysis of crude oil by purge and trap full scan GC-MS is relatively straightforward. Parts per trillion (ppt) level analysis of BTEX requires careful optimization. Benzene RSDs were 25% and the quality control (QC) standard failed low for benzene; therefore it was dropped and we focused on the TEX (toluene, ethylbenzene & xylenes). 4-Bromofluorobenzene was a poor choice for a surrogate since it elutes in the middle of the hydrocarbon pattern. Surrogate recoveries were high even after manual integration. Surrogates that elute before cyclohexane are best suited for low level analysis since interference is minimal in this range. Water was salted to a density of 1.01, boiled for one hour and additional aquarium salt was added to bring the final density to 1.023. Even with these procedures our background toluene was 50ppt requiring our curve to start at 100ppt. Ethylbenzene, M/P & O xylene were calibrated for 50 to 2000 ppt. With this curve we were able to report concentrations of TEX in 100ppb of crude oil (Table 3).

1. Gala, W. R., G. A. Rausina, M.J. Ammann, E. A. Harvey, P. Krause. 2001. Predicting the Aquatic Toxicity of Crude Oils. In Proceedings of the 2001 Oil Spill Conference. American Petroleum Institute, Washington, D.C. pp935-940.
2. Uhler, A. D., S. A. Stout, K. J. McCarthy, J. A. Seavey, and R. M. Uhler. 1998. Identification and Differentiation of Light- and Middle-Distillate Petroleum for NRDA Using Chemical Forensics. In Proceedings of the 1998 Oil Spill Conference. Battelle, Duxbury, MA.

Target Compound	%RSD	%Rec.	ppb		
			ppb	ppb	ppb
1,4-difluorobenzene (IS)	12%	121%	ND	574.2	544.8
toluene	8%	99%	ND	119.9	121.2
ethylbenzene	10%	102%	ND	322.3	324.7
m/p-xylene	8%	112%	ND	238.2	238.2
o-xylene	10%	82%	106%	122.9%	124.2%
bromofluorobenzene	7%	110%	107.1%	92.1%	95.8%

Table 3: Analysis of 100ppb total crude oil with toluene, ethylbenzene, m/p, o-xylene within range.

Comparison of SIM to Full Scan for Crude Analysis:

In Table 4 we took recoveries from full scan analysis and compared them to values we achieved at much lower levels. The values were corrected by multiplying the concentration to normalize all values to 1ppm crude oil. The data shown in this table represents 4 different calibration curves. It is interesting to note the accuracy of the values listed especially ethylbenzene which is represented at the lower end of the curve by full scan analysis at 1.51 ppb (Table 4). This curve is 6 points from 0.5ppb to 200ppb with 9% RSD. The SIM values corrected from 100ppb to 1ppm (multiplied by 10X) show a value for ethylbenzene of 1.19ppb.

Target Compound	ppb			
	ppb	ppb	ppb	ppb
1,4-difluorobenzene (IS)	2.56	2.40	5.50	5.47
benzene	7.45	6.98	6.00	6.44
toluene	1.51	1.38	1.06	1.19
ethylbenzene	8.40	7.66	6.00	6.44
m/p-xylene	3.00	2.68	2.20	2.38
o-xylene	104%	93.4%	142.5%	122.9%
bromofluorobenzene	104%	93.4%	142.5%	122.9%

Table 4: Corrected values from four different curves. The 100ppb crude oil sample was corrected to 1ppm by multiplying the recoveries by 10X to allow for a direct comparison to the full scan data.

Comparisons of MC252, Maya and California Crude Oil:

The MC252 Crude oil is the lightest crude tested. It was the only crude oil that could be drawn up into a syringe needle with a density of 0.81. Maya crude is considered a medium sour crude, that is composed of higher molecular weight fractions and contains sulfur (density 0.93) California crude is rich in asphaltene; not too dissimilar from Prudhoe bay crude oil and is considered a heavy sour crude oil with a density of 0.97. It is interesting how completely different these crude oils are. For instance Maya and MC252 are lacking the presence of 2,2,4-trimethylpentane. N-heptane is another interesting pattern since it is almost non-existent in the California crude (Table 5).

Target Compound	%RSD	ppb		
		ppb	ppb	ppb
1,4-difluorobenzene (IS)	10%	ND	51.0	22.6
2-methyl pentane	5%	ND	19.9	5.5
benzene	5%	ND	0.0	0.0
2,2,4-trimethylpentane	11%	ND	99.3	35.6
n-heptane	3%	ND	58.2	16.6
toluene	13%	ND	13.0	5.3
ethylbenzene	14%	ND	67.7	16.2
m/p-xylene	10%	ND	24.7	6.9
o-xylene	13%	ND	30.6	7.8
1,2,4-trimethylbenzene	20%	ND	9.8	1.1
naphthalene	7%	107.1%	92.1%	110.4%
bromofluorobenzene	7%	107.1%	92.1%	110.4%

Table 5: There are a variety of differences between these crude oils, for instance 2,2,4-trimethylpentane is not detected in the lighter crudes and yet is found in the heaviest crude oil.

Column Choice

The Rxi-624Sil MS column can handle GC programmed temperature of 320 C allowing rapid heating with a minimal hold time. The naphthalene shown in Figure 2 is at a concentration of 9.8 ppb as a reference to the column bleed. This is a good choice for difficult samples that require high bake-out temperatures.

Overview:

Volatile petroleum hydrocarbons in crude oil can be analyzed with current purge and trap systems. Matrix, i.e. salt water, has no effect on compound recoveries, but can be problematic with autosamplers. Frequent freshwater blanks are necessary to prevent clogging of valves prior to the purge vessel. GC-MS analysis using SIM is an effective way to determine ppb levels of crude in ocean water. Purge and trap is a necessary tool in assessing acute exposure of crude oil to marine biota.