Schlumberger Reservoir Laboratories

Fluid Analysis Report

Water Analysis

Well: OCS-Y-2321 Burger J 001 Well API/UWBI 55-352-00004-00 Block: Posey 6912 Lease OCS-Y-2321

For

Shell Gulf Of Mexico, Inc

Report No: 2015USPB-P004-J0001 Houston, Texas, US 14th January 2016



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Schlumberger Reservoir Laboratories 16115 Park Row, Suite 150 Houston, TX, 77084

14-Jan-2016

Shell Gulf Of Mexico, Inc

 Attention:
 Mrs. Esra Inan Villegas

 Subject:
 Fluid Analysis Report – Water samples

Report No: 2015USPB-P004-J0001

Dear Mrs. Esra,

Schlumberger Reservoir Laboratories has performed laboratory analysis of MDT bottom hole samples taken from OCS-Y-2321 Burger J 001 well of Posey 6912 block for Shell Gulf of Mexico, Inc. The samples were received at our lab facility on 28-Sep-2015.

Presented in the report are the results of the water samples as per the scope of work agreed with Shell.

Schlumberger is very pleased to have been of service to Shell Gulf Of Mexico, Inc. Should any questions arise concerning the data presented in the report, or if may be of any assistance in any other matter, Please do not hesitate to contact us.

Sincerely,

Rizwan Ahmed Khan, Project Manager Schlumberger Reservoir Laboratories

Email: rkhan4@slb.com Phone: +12812856381



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A rigorous program of quality assurance, continuous employee training and enforcement of strict safety standards maintains our compliance with Quality, Health, Safety and Environment (QHSE) requirements. Proactive integration of QHSE objectives and management goals at every level supports the communication and implementation of QHSE policies and standards.

Schlumberger requires that qualified engineering technologists perform all laboratory measurements according to specified analytical procedures designed for obtaining accurate and reliable data. Rigorous quality assurance programs and instrument calibration protocols are in place to ensure and maintain the accuracy of the procedures. Details of these programs are available upon request.

The results of all laboratory work are interpreted and reported by the Project Engineer responsible for supervision of the project. The completion of each project requires that a second Engineer/Manager/Scientist carry out an independent review of all technical data to confirm the consistency and accuracy of the report. Raw data may be adjusted within experimental error tolerances to minimize material balance error. All property measurements and calculation procedures are maintained in company archives for a period of 5 years. This information is available for review by clients upon request.

The file and laboratory records information as listed below, provide access reference to all records related to this project. For answers to any questions, please do not hesitate to contact the undersigned Project Engineer.

Data Reporting

Rizwan Khan Project Engineer

Overall Report Quality

x_____ Joseph P

. Lab Manager

ph N.A. **Data Quality**

Joseph Thomas Manakalathil Data Quality Team Lead

1. Executive Summary

1.1 Objectives

The objective of this study is to evaluate fluid properties of reservoir fluid from well OCS-Y-2321 Burger J 001.

1.2 Introduction

Schlumberger Reservoir Laboratories were contacted by Esra Inan of Shell with a request to conduct sample validations on MDT samples collected from rig Polar Pioneer for the Block Posey 6912, Well OCS-Y-2321 Burger J001. Other details pertaining are Well API/UWBI 55-352-00004-00 with Lease detail as OCS-Y-2321. These samples were collected in MPSR cylinders and were delivered on an urgent basis by air cargo.

Validation analyses were conducted on the following samples;

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Sample Point #1 – Water (MDT Fluid Analyzer); at 5922.1 ft MD; sample 1.01
Sample Point #2 – Water (MDT Fluid Analyzer); at 6478.9 ft MD; sample 1.02, 1.03, 1.04.
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Table 1 summarizes the list of samples received from OCS-Y-2321 Burger J 001 MDT operations, including bottomhole samples received in pressurized cylinders. In addition atmospheric drilling fluid was received for compositional analysis.

1.3 Scope of Work

Analysis was conducted on selected pressurized samples 1.01, 1.02, 1.03, 1.04, including:

- Opening pressure of each sample was measured upon receipt.
- Restoration of all samples for 24 hrs at reservoir temperature and 6,000 psia without rocking and sample side up.
- Push 10 cc from sample side to confirm nature of sample as water prior to proceeding with below scope of work.
 - Push 20 ml, with no headspace, preserved to <2 pH with hydrochloric acid and ship the samples to Geochemistry lab in Shell in cooler with ice packs. (Addressed to Ileana Rhodes, Lab EC 401)
- Flash remaining sample for GWR measurements and composition of flash gas. Flashed water obtained from the samples was be subsampled as below.
 - o 30 mL for pH and conductivity (filtered)
 - 10 mL filtered into amber vial for organic acids
 - 25 mL into glass vial for shipment to Isotech
 - Remainder stays in HDPE bottle, stored refrigerated and hotshot to water lab for additional testing and for further subsampling 50-100 ml for Shell.
- Conduct full analysis on water based mud filtrate
- No analysis was requested/conducted for the mud sample collect from MDT pump

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1.4 Summary of Samples Received

Field	Field Sampling Cylinder Sample Type		Sampling Data and Time	Reservoir Conditions				
Sample ID	ID	Sample Type	Sampling Date and Time	Pressure	Temperature	Formation	Depth	
				psia	°F		ft MD	
1.01	MPSR - 30002	Bottom hole MDT	09-23-2015, 11:01	3168.0	147.3	C/A	5922.1	
1.02	MPSR - 1370	Bottom hole MDT	09-23-2015, 19:55	3387.3	159.3	D	6478.9	
1.03	MPSR- 1399	Bottom hole MDT	09-23-2015, 20:22	3387.3	159.3	D	6478.9	
1.04	MPSR - 4360	Bottom hole MDT	09-23-2015, 20:30	3387.3	159.3	D	6478.9	
1.05	1000 cc Glass	Mud from pump*	9/23/15	NA	NA	NA	NA	
1.06	1 Gallon	Water based mud sample *	9/23/15	NA	NA	NA	NA	

Table 1 : Sample Identification

*Sample received at Houston Laboratory as atmospheric sample.

MPSR -30002 was expected to be mostly WBM filtrate water

MPSR -1370 was sampled after MDT pumping for 7 L

MPSR-1399 was sampled after MDT pumping for 12 L

MPSR-4360 was samples after MDT pumping for 13 L

Table 2: Initial Sample Validation Results

Laboratory Sample ID	Client Sample ID	Sample Cylinder ID	Chamber Opening Conditions*	Transfer Cylinder ID	Transfer Conditions	Field Reported Sample Volume	Remaining Sample Volume
			psia at °C		psia at °F	cc	cc
2015USPB-P004- J0001-S1	AKO-T-2, FPC_1159051.1 (1.01)	MPSR - 30002	500 @ 39	5772-MA	8000 at 147F	420	0
2015USPB-P004- J0001-S2	AKO-T-3, FPC_1159052.1 (1.02)	MPSR - 1370	1000 @ 39	8613-QA	8000 at 159.3F	420	0
2015USPB-P004- J0001-S3	AKO-T-4, FPC_1159053.1 (1.03)	MPSR- 1399	1000 @ 39	17449-IB	8000 at 159.3F	420	0
2015USPB-P004- J0001-S4	AKO-T-5, FPC_1159054.1 (1.04)	MPSR - 4360	800 @ 39	5503-IB	8000 at 159.3F	420	0
2015USPB-P004- J0001-S6	1.06	IATA can	NA	NA	NA	3780	0

*Opening pressure were measured on field and as listed on sampling sheet.

2. Pressurized Water Sample Analysis

2.1 Sample Preparation and Analysis

Pressurized bottomhole water samples 2015USHO-P004-J0001-S1 (1.01), 2015USHO-P004-J0001-S2 (1.02), 2015USHO-P004-J0001-S3 (1.03), 2015USHO-P004-J0001-S4 (1.04) were used for analysis. Firstly, sample cylinder opening pressures were measured upon sample bottle receipt followed by 24 hours of thermal restoration at reservoir temperature and 8,000 psia. Samples restored at reservoir temperature were not kept rocking and sample side was kept up with an objective to capture light fluid / hydrocarbons.

Following 24 hour restoration, each sample was then checked for sample nature by pushing out 10 cc from top. All samples were found to be water. A subsample was taken from each for benzene, toluene, ethylene and xylene (BTEX) and sent to Shell for analysis. Each sample was then submitted to a single-stage flash, where flashed gas and flashed liquid volumes were measured and collected. The measured gas-water ratio for each sample is presented in Table 3. The collected flashed gas was submitted for compositional analysis, as presented in Table 3. The collected flashed water was immediately submitted for water analysis by Schlumberger. A 25 mL subsample of each was sent to Isotech for isotope analysis at the request of Shell. Table 4 presents results of flashed water from pressurized bottomhole samples. Figure 1 shows images of each flashed water sample.

A portion of unpreserved water (~75 mL) was set aside for Shell laboratories.

2.2 Discussion

The calculated and measured total dissolved solids and ion imbalance are less than 10% for all samples. The elemental sulfur was roughly 25% higher due to the matrix. The sample dilution was minimized to 100x but depressed the internal standards. The internal standard recovery was within acceptance range however the spikes recovered around 25%. The spikes were diluted 1000x. The elemental sulfur was repeated with a higher dilution to remove the matrix interference. The sample 1.01 result remained the same while all others were lower and match well with the sulfate.

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Component	Samples	AKO-T-2, FPC_1159051.1 (1.01)	AKO-T-3, FPC_1159052.1 (1.02)	AKO-T-4, FPC_1159053.1 (1.03)	AKO-T-5, FPC_1159054.1 (1.04)
	MW (g/mol)	Mole%	Mole %	Mole %	Mole %
CO2	44.01	0.009	0.295	0.545	0.475
H2S	34.08	0.000	0.000	0.000	0.000
N2	28.01	11.675	6.611	3.204	3.263
C1	16.04	85.770	90.978	92.855	94.423
C2	30.07	1.292	1.355	1.309	1.329
C3	44.10	0.058	0.089	0.092	0.090
i-C4	58.12	0.002	0.006	0.004	0.004
n-C4	58.12	0.004	0.011	0.009	0.009
i-C5	72.15	0.004	0.002	0.029	0.003
n-C5	72.15	0.001	0.017	0.002	0.002
C6	84.00	0.004	0.009	0.019	0.007
Mcyclo-C5	84.16	0.000	0.001	0.000	0.000
Benzene	78.11	0.023	0.036	0.037	0.020
Cyclo-C6	84.16	0.001	0.002	0.001	0.000
C7	96.00	0.006	0.009	0.784	0.080
Mcyclo-C6	98.19	0.001	0.002	0.000	0.000
Toluene	92.14	1.142	0.558	1.098	0.292
C8	107.00	0.003	0.004	0.003	0.001
C2-Benzene	106.17	0.000	0.001	0.000	0.000
m&p-Xylene	106.17	0.001	0.002	0.001	0.000
o-Xylene	106.17	0.000	0.001	0.000	0.000
C9	121.00	0.001	0.004	0.001	0.000
C10	134.00	0.002	0.003	0.001	0.000
C11	147.00	0.000	0.003	0.001	0.000
C12+	161.00	0.001	0.002	0.005	0.000
Calculated MW		18.55	17.64	18.33	17.09
GLR (scf/stb)		1.89	5.45	6.35	6.78
Water Density (g/cc)		1.1487	1.0935	1.0756	1.0723
Gas Gravity (Air = 1)		0.6404	0.609	0.634	0.590

Table 3: Compositional Analysis Flashed Gas





Figure 1 : Collected Water Samples (From L to R: MPSR 30002 (AKO-T-2), MPSR 1370 (AKO-T-3), MPSR 1399 (AKO-T-4) and MPSR 4360(AKO-T-5))

General Analysis	Method	AKO-T-2, FPC_1159051.1 (1.01)	AKO-T-3, FPC_1159052.1 (1.02)	AKO-T-4, FPC_1159053.1 (1.03)	AKO-T-5, FPC_1159054.1 (1.04)	Units
Specific Gravity at 15.56°C	Modified ASTM 4052	1.1497	1.0953	1.0776	1.0739	
Density at 15.56°C	Modified ASTM 4052	1.1485	1.0943	1.0765	1.0729	g/cm3
Observed pH	EPA 150.1	9.00	8.18	7.83	7.81	
pH temperature		23	21	25	25	°C
Resistivity	ASTM 1125/EPA 120.1	5.314	6.930	6.854	7.117	ohm•cm
Conductivity	ASTM 1125/EPA 120.1	188.2	144.3	145.9	140.5	mS/cm
Conductivity temperature		20	20	25	25	°C
Total Alkalinity	Rice	1797	1150	1275	1677	mg/L as HCO ₃ -
Carboxylic acids	Rice	887	622	612	947	mg/L acetate equivalent
Total Dissolved Solids						
Evaporated	ASTM 5907/EPA 160.1	237000	140600	115200	110000	mg/L
Calculated		237542	152560	118369	109767	mg/L
Anions:	ASTM 4327/EPA 300.1					
Fluoride (F-)		ND	ND	ND	ND	mg/L
Chloride (CI-)		136000	89500	67300	60800	mg/L
Nitrite (NO ₂ -1)		ND	ND	ND	ND	mg/L
Bromide (Br-)		590	370	294	245	mg/L
Nitrate (NO3-)		ND	ND	ND	ND	mg/L
Phosphate (PO43-)		ND	ND	ND	ND	mg/L
Sulfate (SO ₄ ²⁻)		2360	1110	843	764	mg/L
Hydroxide (OH-) at measured pH	Rice	ND	ND	ND	ND	mg/L
Carbonate (CO ₃ ²⁻) at measured pH	Rice	223	55	35	31	mg/L
Bicarbonate (HCO ₃ -) at measured pH	Rice	346	355	550	614	mg/L
Cations:	ASTM 6919		r	r	1	
Sodium (Na ⁺)		96600	59000	47200	45400	mg/L
Potassium (K+)	-	516	<u>290</u>	<u>240</u>	<u>310</u>	mg/L
Magnesium (Mg*)		ND	<u>500</u>	<u>490</u>	<u>150</u>	mg/L
Calcium (Ca+)		340	450	400	400	mg/L

Dissolved Metals:	ASTM 5673/EPA 200.8	AKO-1-2, FPC_1159051.1 (1.01)	AKO-1-3, FPC_1159052.1 (1.02)	AKO-1-4, FPC_1159053.1 (1.03)	AKO-1-5, FPC_1159054.1 (1.04)	Units
Barium (Ba2+)		8.83	1.87	2.06	2.33	mg/L
Boron (B)		6.10	23.6	31.2	30.8	mg/L
Copper (Cu ²⁺)		0.405	1.55	0.03	0.627	mg/L
Iron (Fe dissolved)		0.57	0.20	0.73	0.40	mg/L
Lead (Pb ²⁺)		0.46	0.81	<u>0.11</u>	0.19	mg/L
Lithium (Li⁺)		0.36	1.22	1.14	1.12	mg/L
Manganese (Mn2+)		0.29	0.58	0.72	0.33	mg/L
Silica (Si4+)		12.0	10.9	12.8	13.9	mg/L
Strontium (Sr2+)		2.1	17.9	15.4	15.0	mg/L
Sulfur (S)		884	398	279	285	mg/L
Zinc (Zn ²⁺)		0.50	0.11	0.70	1.34	mg/L
Organic Acids	ICE					
Glycolate		227	296	315	311	mg/L
Formate		47.9	47.0	36.5	39.5	mg/L
Acetate		164	457	540	541	mg/L
Propionate		ND	39.3	56.9	59.1	mg/L
Butyrate		ND	4.5	6.6	<u>6.5</u>	mg/L
Valerate		ND	ND	ND	ND	mg/L

ND

1.27%

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ND

6.82%

% Ion Difference

ND= Not Detected

<MDL = Less than method detection limits

ND

3.95%

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NS = Not enough Sample

ND

4.36%

NM = Not Measured

Underlined samples were <RL but > MDL

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3. Water Based Mud Sample Analysis

3.1 Sample Preparation and Analysis

Sample 2015USHO-P004-J0001-S6 (1.06) was a water based mud (WBM) sample collected from the active mud pit and given to onsite Schlumberger Reservoir Sampling and personnel. The received container is in Figure 2. The mud was pressed to obtain 50 mL of filtrate. The filtrate was subsampled and used to perform full water analysis. A 15 mL subsample was sent to Isotech for isotope analysis at the request of Shell. Due to the limited sample volume the total dissolved solids on this sample were not measured, only calculated. The results are in Table 5.

3.2 Discussion

The calculated and measured total dissolved solids and ion imbalance are less than 10% for mud filtrate sample. The elemental sulfur is roughly 25% too high due to the matrix. The sample dilution was minimized to 100x but depressed the internal standards. The internal standard recovery was within acceptance range however the spikes recovered around 25%. The spikes were diluted 1000x. The elemental sulfur will be repeated with a higher dilution to remove the matrix interference.



Figure 2: Water based mud sample (1.06)

Table	5.	Water	Analy	vsis	Results
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General Analysis	Method	1.06	Units	
Specific Gravity at 15.56°C	Modified ASTM 4052	1.1571		
Density at 15.56°C	Modified ASTM 4052	1.1560	g/cm3	
Observed pH	EPA 150.1	8.79		
pH temperature		22	°C	
Resistivity	ASTM 1125/EPA 120.1	5.30	ohm•cm	
Conductivity	ASTM 1125/EPA 120.1	188.6	mS/cm	
Conductivity temperature		20	°C	
Total Alkalinity	Rice	1613	mg/L as HCO₃-	
Carboxylic acids	Rice	282	mg/L acetate equivalent	
Total Dissolved Solids				
Calculated		246213	mg/L	
Anions:	ASTM 4327/EPA 300.1			
Fluoride (F [.])		ND	mg/L	
Chloride (Cl-)		142000	mg/L	
Nitrite (NO ₂ -1)		ND	mg/L	
Bromide (Br [.])		486	mg/L	
Nitrate (NO ₃)		<u>34</u>	mg/L	
Phosphate (PO ₄ ³⁻)		ND	mg/L	
Sulfate (SO ₄ ²⁻)		1990	mg/L	
Hydroxide (OH) at measured pH	Rice	ND	mg/L	
Carbonate (CO32-) at measured pH	Rice	193	mg/L	
Bicarbonate (HCO3) at measured pH	Rice	905	mg/L	
Cations:	ASTM 6919			
Sodium (Na⁺)		98500	mg/L	
Potassium (K⁺)		860	mg/L	
Magnesium (Mg⁺)		ND	mg/L	
Calcium (Ca⁺)		<u>640</u>	mg/L	

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Dissolved Metals:	ASTM 5673/EPA 200.8	1.06	Units	
Barium (Ba ²⁺)		0.520	mg/L	
Boron (B)		<u>1.7</u>	mg/L	
Copper (Cu ²⁺)		1.07	mg/L	
Iron (Fe dissolved)		1.85	mg/L	
Lead (Pb ²⁺)		1.12	mg/L	
Lithium (Li+)		0.18	mg/L	
Manganese (Mn ²⁺)		0.40	mg/L	
Silica (Si4+)		<u>0.8</u>	mg/L	
Strontium (Sr ²⁺)		1.91	mg/L	
Sulfur (S)		668	mg/L	
Zinc (Zn ²⁺)		3.59	mg/L	
Organic Acids	ICE			
Glycolate		343	mg/L	
Formate		51.4	mg/L	
Acetate		194	mg/L	
Propionate		ND	mg/L	
Butyrate		ND	mg/L	
Valerate		ND	mg/L	

% Ion Difference

3.03%

ND= Not Detected

<MDL = Less than method detection limits

NS = Not enough Sample

NM = Not Measured

Underlined samples were <RL but > MDL



Figure 3: Mud sample collected from Pump (No Analysis was conducted on this sample)

Appendix A: Nomenclature and Definitions

MDL Method detection limit

RL Reporting limit

VSMOW Vienna Standard Mean Ocean Water

Method detection limit is the minimum concentration that a specified analyte can be identified, measured and reported as above zero with 99% confidence. One is defined for each analyte by ion chromatography and inductively coupled plasma mass spectroscopy.

Reporting Limit is defined as the lowest standard from the analytical curve. It is considered the lowest concentration that an analyte can be quantitatively identified.

Appendix B: Procedure for Water Analysis

Water Analyses

Unless otherwise specified all water analyses are performed according to, or adapted from, ASTM and/or EPA methods. Samples are preserved and holding times observed according to these methods. The following is a brief summary of the methodology. EPA procedures are available for free download online while ASTM requires purchase.

<u>pH, EPA 150.1</u>: This method uses a glass electrode with a reference potential to electrometrically determine pH in all types of unfiltered water. The pH is precisely measured by calibrating the probe with at least 3 certified buffer solutions and verifying the calibration with a separate certified buffer. Triplicate sample readings are taken and the average reported. The sample must be $\pm 2^{\circ}$ C of the calibration buffers.

<u>Alkalinity, ASTM 1067-06 Method A/ EPA 310.1</u>: This method is used to determine the total alkalinity based on carbonic acid in many unfiltered water types using electrometric titration. The hydroxide, carbonate and bicarbonate species are calculated from the titrations. Oil, organic acid salts and mineral acids interfere. This method utilizes standardized hydrochloric acid to neutralize the hydroxyl species. The amount of acid needed to completely neutralize the sample is used to calculate the total calcium carbonate alkalinity. The laboratories use an automated titrator capable of dispensing 0.0001 mL and recording the titration plot of titrant volume vs. pH. Defined endpoints are used to determine the buffering capacity of the water. The sample is first titrated to a pH of 8.3 then to 3.0. The final endpoint is determined by inflection around 4.5. In the presence of organic acids such as acetate this endpoint is masked. A default endpoint of 4.5 is used which overestimates alkalinity and bicarbonate. In most oilfield water samples Rice Alkalinity is recommended.

<u>Rice Alkalinity</u>: This method is applicable to determine total alkalinity based on multiple species found in oilfield waters that affect alkalinity using electrometric titration methods. This method removes the alkalinity contribution from organic acid salts and mineral acid and determines the true total alkalinity attributed to bicarbonate. The bicarbonate, carbonate and hydroxide species are calculated from the titration based on the sample pH. Optimal results are obtained from samples with minimal oil. The standard 4.5 inflection point is difficult to determine in the presence of organic acids. The Rice Alkalinity method is advised in oilfield waters unless the TDS and organic acids are low. The method utilizes standardized hydrochloric acid to neutralize the hydroxyl species. A pH curve is made in in the software plotting titrant volume vs. pH. The sample is filtered with a 0.45 µm nylon filter and titrated to pH 3.0. The filter is digested in a 2% nitric acid solution and the solution is measured for iron and calcium. Iron indicates the level of oxidation the sample experienced while calcium accounts for oxidation and precipitation of calcite. This key information increases the sample holding time for standard alkalinity from 24 hours to at least 7 days. The Rice Alkalinity macro file takes the titration points and extracts 20 evenly spaced titration data points between a pH of 8.3 and 3.0. Several other inputs are needed such as sample pH, TDS and conductivity, temperature, titrant strength, % CO₂ and total Fe and Ca precipitate from the filter. Optional inputs are B, Si, PO4³⁻, and NH4⁺

concentrations. The calculations and software were developed by Rice University for the Brine Chemistry Consortium. The method has been adapted for automated use in Schlumberger Reservoir Laboratories.

<u>Density/specific gravity, M ASTM 4052</u>: This method is designed for oil samples but is applicable to determine the density and specific gravity of filtered water samples with a digital density meter at atmospheric pressure and 15.56 °C unless otherwise specified. Method ASTM 1429 is designed for water samples but requires a large volume and does not offer a reliable method for maintaining temperature at 15.56 °C. The quality control elements are taken from this method. The digital meter requires air and deionized water checks before starting a sequence. A certified specific gravity standard is then run to verify accuracy before measuring samples.

<u>Conductivity</u>. ASTM 1125-95A/ EPA 120.1: This method uses self-contained 4 and 2 cell conductivity electrodes with a Wheatstone bridge to determine specific conductivity in all types of filtered water. Measurements are made on non-flowing samples ranging from 10 μ S to 200 mS/cm using a 4 cell and 200 mS/cm to 2000 mS/cm using a 2 cell electrode. The measurements are made at ambient temperature and adjusted to the nearest reference temperature of 20 or 25 °C. The inverse of conductivity is resistivity and is calculated from the conductivity reading. The conductivity reading is used by the electrode to estimate the dissolved ions (TDS) by assuming all conductivity and thus TDS is from sodium chloride, NaCI. The salinity is calculated by the electrode in a similar manner. These values are considered estimates and only accurate in pure NaCI solutions.

<u>Sulfide, EPA 376.1:</u> This method is applicable to unfiltered waters to determine total soluble and dissolved sulfide in concentrations above 1 mg/L. Insoluble sulfides like copper sulfide are not measured by this method. A known concentration of 0.025N iodine is added to a sample. The sample is then acidified with 12.22M hydrochloric acid. Once acidified, the iodine oxidizes all sulfide to sulfur. The remaining iodine is back titrated with 0.025N sodium thiosulfate. The sulfide is then calculated from the iodine.

<u>Sulfide, Methylene Blue</u>: Individual pre-weighed packets of N,N-dimethyl-p-phenylenediamine sulfate are added to unfiltered water samples to react with hydrogen sulfide and acid-soluble metal sulfides. When sulfide is present the reaction results in a blue color from the formation of methylene blue. A spectrophotometer using 665 nm wavelength or colorimeter using 610 nm wavelength determine the concentration of sulfide according to the level of blue color. Hydrogen sulfide concentrations are calculated from this assuming all sulfide is from H₂S.

<u>Dissolved CO₂, Titration</u>: A known volume of unfiltered water sample is titrated with sodium hydroxide to a pH of 8.3. The titrant molarity depends on expected sample concentrations. All acidity in the sample is assumed to be from carbon dioxide. The presence of other acids or sulfide will interfere.

<u>Total Suspended Solids, ASTM D5907-10/ EPA 160.2</u>: This method uses filtration, evaporation and weighing to determine the amount of non-filterable material in all types of water. Measurements are made by homogenizing a sample and passing it through a glass fiber filter. The material that is unable to pass through the filter is dried at 103-105 °C until a constant weight is achieved. The dried material and volume of sample are used to determine the amount of non-filterable total suspended solids (TSS). Oil and grease are interferants.

Total Dissolved Solids, ASTM D5907-10/ EPA 160.1: This method uses filtration, evaporation and weighing to determine the amount of filterable dissolved material in all types of water. Measurements are made by homogenizing a sample and passing it through a glass fiber filter. The filtrate is then evaporated at 103-105 °C with continued drying to 180°C until a constant weight is achieved. The dried material and volume of sample are used to determine the amount of filterable total dissolved solids (TDS). Oil and grease are interferants.

<u>Anions, ASTM D4327-11/ EPA 300.1 and Cations, ASTM D6919-09</u>: This method uses ion chromatography to determine the concentration of inorganic anions and cations in filtered water. Cation samples are preserved with nitric acid to a pH less than 2. A small volume is introduced onto a guard column and then a specified ion chromatography column by the eluent mobile phase. The analytical column separates the analytes based on their affinity to the column resin. The aliquot passes through a suppressor reducing baseline noise from the eluent. The aliquot proceeds to the conductivity detector that measures analyte conductance, which is converted to a final concentration. Quantification is performed by comparing peak areas to a calibration curve constructed by analytical standards. Peak identity is confirmed by comparing the retention times to analytical standards.

<u>Cations, Metals and other species, ASTM D5673-10/ EPA 200.8</u>: This method is applicable to determine trace elements dissolved in water using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Samples are filtered and preserved with nitric acid, except for silica and boron analysis where only filtered samples are used. When the total suspended solids in the sample exceed 1%, the sample must be digested. In addition total recoverable metals are determined through the same digestion process. In preparation for analysis, nitric acid is added to a homogeneous sample aliquot. It is introduced to the system where it is aspirated into argon plasma by a nebulizer. The molecules are dried, dissociated, and ionized. The charged particles are filtered, focused, and directed into the quadrupole of the mass spectrometer where they are detected by impact to a dynode on an electron multiplier. The quadrupole uses the mass-to-charge ratio to filter the particles and thereby define a specific ratio to be detected by the dynode. The collision causes a surge of electrons that are amplified and measured as a pulse. The pulse intensity or counts are used to determine the elemental concentration from a selected isotope. The counts are quantified through calibration of known standards concentrations. Various internal standards are selected to correct for instrument drift and fluctuations in response caused by the sample introduction system, plasma or sample matrix. Collision and collision/reaction systems introduce a gas to reduce interference caused by the matrix. The appropriate system depends on the element of interest and the desired level of sensitivity.

<u>Organic acids, Ion Exclusion Chromatography</u>: This method uses ion exclusion chromatography (ICE) to determine the concentration of dissociated anions from organic acids and volatile fatty acids in filtered water. Samples are preserved with glutaraldehyde or sodium hydroxide. The pH is adjusted to neutral prior to analysis. Then the samples are passed through a cleanup cartridge to remove chloride, bromide, iodide, alkaline earth and transition metals. High concentrations of these ions interfere with the integration of glycolate and formate. A small volume is introduced onto a guard column and then a specified ion chromatography column by the eluent mobile phase. The analytical column excludes anions and cations then separates the analytes based on their affinity to the column resin. The aliquot passes through a suppressor reducing baseline noise from the eluent. The aliquot proceeds to the conductivity detector that measures analyte conductance, which is converted to a final concentration. Quantification is performed by comparing peak areas to a calibration curve constructed by analytical standards. Peak identity is confirmed by comparing the retention times to analytical standards.

Appendix C: Molecular Weight Data

No Component		Katz	Whitson	
	Component	g/mol	g/mol	Different
1	CO2	44.0	44.0	
2	H2S	34.1	34.1	
3	N2	28.0	28.0	
4	C1	16.0	16.0	
5	C2	30.1	30.1	
6	C3	44.1	44.1	
7	i-C4	58.1	58.1	
8	n-C4	58.1	58.1	
9	i-C5	72.2	72.2	
10	n-C5	72.2	72.2	
11	C6	84.0	84.0	
12	Mcyclo-C5	84.2	84.2	
13	Benzene	78.1	78.1	
14	Cyclo-C6	84.2	84.2	
15	C7	96.0	96.0	
16	Mcyclo-C6	98.2	98.2	
17	Toluene	92.1	92.1	
18	C8	107.0	107.0	
19	C2-Benzene	106.2	106.2	
20	m&p-Xylene	106.2	106.2	
21	o-Xylene	106.2	106.2	
22	C9	121.0	121.0	
23	C10	134.0	134.0	
24	C11	147.0	147.0	
25	C12	161.0	161.0	
26	C13	175.0	175.0	
27	C14	190.0	190.0	
28	C15	206.0	206.0	
29	C16	222.0	222.0	
30	C17	237.0	237.0	
31	C18	251.0	251.0	
32	C19	263.0	263.0	
33	C20	275.0	275.0	
34	C21	291.0	291.0	
35	C22	305.0	300.0	*
36	C23	318.0	312.0	*
37	C24	331.0	324.0	*
38	C25	345.0	337.0	*
39	C26	359.0	349.0	*
40	C27	374.0	360.0	*
41	C28	388.0	372.0	*
42	C29	402.0	382.0	*
43	C30+	750.0	750.0	

Table 6: Molecular Weight Data of Katz and Whitson

'MW values for C30+ are industry average which do not reflect the actual MW values of C30+ measured in this study.

Appendix D: Procedure for Sample Restoration and Flashes

Procedure for Sample Restoration and Integrity Check

Fluid Sample Restoration & Quality Check

Upon arrival, a sample bottle is connected to a high pressure displacement pump to check the opening pressures at ambient temperature. Next, the sample is conditioned at appropriate pressure and temperature conditions to restore it to its original conditions. For a bottomhole sample, the sample bottle is heated to Tres, pressurized to at least Pres and allowed to equilibrate. As advised, samples were not rocked and were kept under restoration with sample side up. 10 cc of sample was purged to check nature of the sample contained in the bottle.

Compositional Analyses

Following the sample restoration described above, a sample of each equilibrated live fluid is isobarically displaced, one at a time, into a pre-cleaned and evacuated pycnometer for density, GWR, and compositional analysis of flash gas using a flash procedure. In this technique, sample is flashed into evacuated flash apparatus to which pycnometer is connected. Flashed water gets collected into flash apparatus whereas flash gas evolved will be sampled into pycnometer. Pressure in the pycnometer prior and after the flash is measured which will determine amount of gas evolved in the process for GWR measurement. The vapor phase is analyzed to C15, and GWR is calculated once density of water is measured by densitometer.

The compositional analysis of gaseous mixtures is performed using two separate gas analysis detectors: one with a natural gas configuration and the other with an extended gas configuration. The natural gas configuration consists of packed columns, a Thermal Conductivity Detector (TCD) detector and uses helium as a carrier gas. The detection range covers N2, CO2, H2S, C1 to nC4. The extended gas configuration consists of a capillary column, a Flame Ionization Detector (FID) detector and uses helium as a carrier gas. The temperature programming is non-isothermal (ramping to 464.0 °F) and the detection range covers C1 to C15 including the associated common isomers.