

New Method for Stock-Tank Oil Compositional Analysis

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Abstract

A new method for accurately determining stock-tank oil composition to normal pentatriacontane using gas chromatography is developed and validated. The new method addresses the potential errors associated with the traditional equipment and technique employed for extended hydrocarbon gas chromatography outside a controlled laboratory environment, such as on an offshore oil platform. In particular, the experimental measurement of stock-tank oil molecular weight with the freezing point depression technique and the use of an internal standard to find the unrecovered sample fraction are replaced with correlations for estimating these properties. The use of correlations reduces the number of necessary experimental steps in completing the required sample preparation and analysis, resulting in reduced uncertainty in the analysis.

Introduction

During the development of innovative wellsite pressure, volume, and temperature (PVT) analysis equipment, the need for a rugged, yet accurate, gas chromatograph (GC) and methodology was identified. Understanding the composition of stock-tank oil is essential for the characterization of a petroleum reservoir fluid. In many cases, it is desirable to have this knowledge as early as possible in the oil exploration process so that key operational decisions can be made. As a result, performing compositional analysis at the wellsite as soon as possible after bringing a reservoir fluid sample to the surface is often of critical importance.

Compositional analysis techniques applied to stock-tank oil in the laboratory require relatively delicate equipment and precise procedures designed for controlled conditions. The internal standard (ISTD) technique is the traditional method used to find the "lost" fraction of the stock-tank oil (STO) sample that, because of its high boiling point, does not elute from the column during a GC analysis and cannot be directly quantified. (1)

The ISTD technique requires the preparation of a solution of stock-tank oil sample and a pure component not naturally present in the sample, such as 1-hexene in the case of oil. The mass of each liquid must be accurately measured and the solution

made homogenous to achieve accurate results. The solution is analyzed by GC, and the ratio of sample detected to pure standard detected is compared to the known ratio used to prepare the solution. The difference between the two ratios allows for the calculation of the unrecovered fraction. (2)

The molecular weight of the stock-tank oil sample is traditionally measured using freezing point depression (FPD). (3) This method requires the preparation of a solution of a known weight of stock-tank oil and benzene. The temperature of the solution is gradually lowered in a cryoscope until the liquid freezes. The solute molar concentration is directly proportional to the freezing point depression of benzene. The mass of each component in the solution is measured directly. The molecular weight and cryoscopic constant of pure benzene are known, and, by experiment, the molar concentration of each component is found, allowing for the calculation of the sample molecular weight.

Because the ISTD and FPD experiments were designed for laboratory use, they are generally not suitable for field applications. To overcome the limitations associated with these experiments, a new hardware platform and data processing method were needed for liquid compositional analysis. The new field method described and validated here was designed to be relatively operator-independent, easy to perform, and faster than the traditional laboratory methods.

Hardware platform

As noted previously, traditional GC equipment designed for laboratory use is fragile. For field applications, a more rugged gas- and liquid-analyzing GC specifically designed for field conditions was required. The hardware platform was designed to use metal columns, rather than fragile fused-silica columns, to prevent column damage during shipment. In addition, both the gas and liquid columns and ovens were contained in a single hardware unit that weighed a total of 30 kg and had a small footprint of 67 cm by 53 cm. To avoid the health and safety issues associated with the use of compressed hydrogen in a rig environment, helium ionization detectors (HIDs) were chosen for both the gas and liquid analyses. Because helium was also used as the carrier gas, only one cylinder of inert compressed gas was required, making shipping safer and easier and the operation less complex. With only one type of detector used in the field, GC for both the liquid and gas analyses, fewer spare parts and less troubleshooting knowledge were required.

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New methodologies

To complement the hardware modifications previously described and to address the unique nature of the analysis environment in the field, a new analysis method was also needed. The ISTD method and its associated molecular weight estimation by FPD prove difficult on an offshore oil platform, as they require the preparation of gravimetric solutions using several solvents and toxic chemicals.

The first limitation addressed was the use of benzene in the FPD experiment. As a known carcinogen, benzene requires special permits and procedures for safe transport and storage. The second limitation to the laboratory method was the requirement to measure an accurate mass of internal standard. Accurate measurement is difficult to achieve in a field environment, particularly offshore where the impact of rig heave on mass measurement must be corrected for. Finally, the potential problems associated with poorly mixed oil/internal-standard solutions, as well as errors in the determination of the internal-standard area from an overall chromatogram, were more difficult to address in the field environment.

Recognizing these limitations and difficulties of applying the traditional ISTD techniques to the field environment, it was desired that any new method would have the following characteristics: (i) no requirement for molecular weight measurements, eliminating any health risks associated with the use of benzene; (ii) minimal sample preparation with no requirement for mass measurement.

One traditional laboratory measurement that did not exhibit limitations in a field environment was STO density. Because of the confidence in the STO density measurement, the new compositional method was designed to estimate the molecular weights of the oil and plus fractions by correlating them against oil density. The plus-fraction correlation was assumed to be a linear function, while the oil molecular weight correlated to density in the form of a fourth degree polynomial function. After determination of the molecular weights by correlation and measurement of the component concentrations of the recovered fraction by GC, the plus-fraction concentration was calculated.

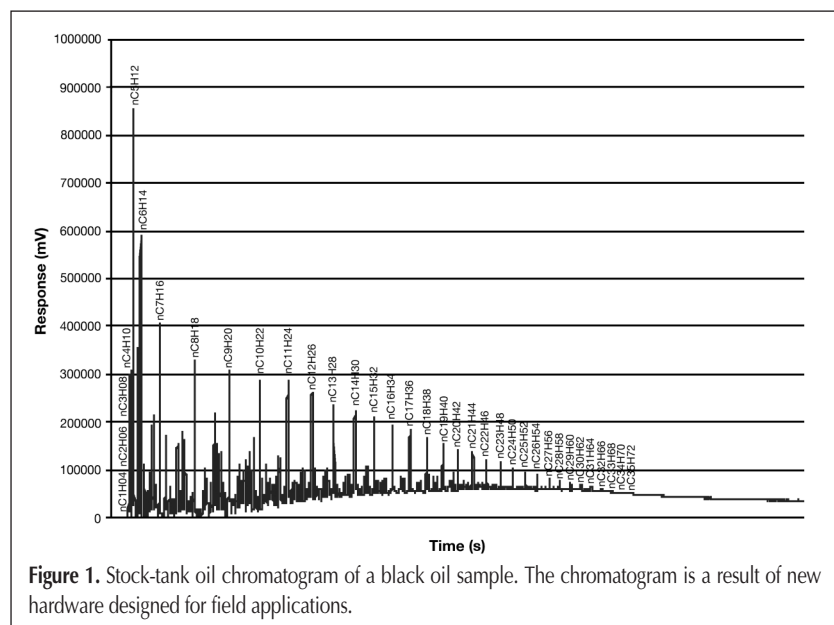


Figure 1. Stock-tank oil chromatogram of a black oil sample. The chromatogram is a result of new hardware designed for field applications.

Experimental

Compositional analysis for the field method was performed using manual direct injection into a modified, dual-oven SRI Instruments GC (Torrance, CA) using a Restek MXT-1 30 m, 0.28 mm i.d., 0.5 μ m film column. Grade 5.5 helium was used as both the carrier gas and the ionized HID gas. A two-stage stainless steel regulator was used to regulate a stable helium pressure to 60 psi. A stable 220 V power supply was also required. A temperature program ramping from 40°C to 320°C was used to shorten GC run-time. Black oil samples were diluted with carbon disulfide in the proportion 50:50, while for volatile oil and condensates, sample dilution was not necessary. Comparative crude oil compositional analysis was performed in the laboratory on an Agilent Technologies GC (Palo Alto, CA) using a flame ionization detector (FID).

The resulting field-generated chromatogram, shown in Figure 1, was integrated up to normal pentatriacontane, C₃₅. The light ends, from methane to normal pentane, were identified and integrated as individual peaks. The heavier components were grouped into pseudocarbon groups. Each group consisted of all components eluting after the normal hydrocarbon C_(n-1)H_{2(n-1)+2} until the normal hydrocarbon C_(n)H_{2(n)+2}, including the last normal hydrocarbon peak.

To calculate the molecular weight of the C₃₅-fraction (oil fraction: C₃₅ and below), average molecular weights were applied to each group, from pseudo-C₆ to pseudo-C₃₅. The values applied were the Whitson-modified Katz molecular weights displayed in Table I (4,5).

The experimental stock-tank oil molecular weight measurements were performed on a Crette WR, Wide Range, Precision Systems, cryscope (Natick, MA). The liquid density measurements were performed using an Anton Paar handheld density

Table I. Whitson-modified Katz Molecular Weights Defined for Each Pseudocarbon Group (4,5)

Pseudo group	MW (g/mol)	Pseudo group	MW (g/mol)	Pseudo group	MW (g/mol)
C ₆	84	C ₁₆	222	C ₂₆	349
C ₇	96	C ₁₇	237	C ₂₇	360
C ₈	107	C ₁₈	251	C ₂₇	372
C ₉	121	C ₁₉	263	C ₂₉	382
C ₁₀	134	C ₂₀	275	C ₃₀	394
C ₁₁	147	C ₂₁	291	C ₃₁	404
C ₁₂	161	C ₂₂	300	C ₃₂	415
C ₁₃	175	C ₂₃	312	C ₃₃	426
C ₁₄	190	C ₂₄	324	C ₃₄	437
C ₁₅	206	C ₂₅	337	C ₃₅	445

	Density (g/mL)	C ₃₆₊ MW (g/mol)
Condensate liquid	0.75	500
Heavy oil	0.95	750

meter, DMA 35N. The chemicals used were of analytical grade.

The molecular weight of the unrecovered C₃₆ (normal hexatri-acontane) + fraction was determined by correlating a linear function between oil density and the molecular weight of the C₃₆₊ fraction (oil fraction: C₃₆ and above) (Equation 1). The average molecular weight values of the C₃₆₊ fraction and liquid densities of two extreme types of oil, condensate liquid and heavy oil, were applied (Table II). Similar values have historically been used in laboratories to validate the FPD measurement by calculating the sample molecular weight using an assumed plus-fraction molecular weight similar to those assumed here.

$$MW_{36+} = 1250 \cdot \rho_{STO} - 437.5 \quad \text{Eq. 1}$$

The molecular weight of the stock-tank oil sample was estimated by a correlation (Equation 2) based on more than 500 stock-tank oil molecular weights measured by FPD. The coefficient of determination or R^2 of this fourth order polynomial is roughly 0.92, demonstrating a good curve fit to the data.

$$MW_{STO} = 131386 \cdot \rho_{STO}^4 - 414789 \cdot \rho_{STO}^3 + 491393 \cdot \rho_{STO}^2 - 258065 \cdot \rho_{STO} + 50688 \quad \text{Eq. 2}$$

Once the stock-tank oil and C₃₆₊ fraction molecular weights were estimated, the molar ratios of the C₃₅₋ (x_{C35-}) and C₃₆₊ (x_{C36+}) were calculated with Equations 3 and 4.

$$MW_{STO} = MW_{C35-} \cdot x_{C35-} + MW_{C36+} \cdot (1 - x_{C35-}) \quad \text{Eq. 3}$$

$$\uparrow$$

$$x_{C35-} = \frac{(MW_{C36+} - MW_{STO})}{(MW_{C36+} - MW_{C35-})}$$

$$x_{C35-} + x_{C36+} = 1 \quad \text{Eq. 4}$$

The concentration of each individual component was calculated as follows:

$$C_i = Y_i \times x_{C35-} \quad \text{Eq. 5}$$

where C_i = Concentration (mol%) of component i in oil and Y_i = Concentration (mol%) of component i in C₃₅₋ fraction. Finally, the C₃₆₊ concentration in mole percent was calculated as follows:

$$C_{36+} = 100 \cdot (1 - x_{C35-}) \quad \text{Eq. 6}$$

Example calculation

$\rho_{STO} = 0.85$ g/mL: measured.

$MW_{35-} = 200$ g/mol: result from integrated chromatograph and Katz-Whitson molecular weights for individual pseudo-components.

$$MW_{36+} = 1250 \cdot 0.85 - 437.5 = 625 \text{ g/mol}$$

$$MW_{STO} = 131386 \times 0.85^4 - 414789 \times 0.85^3 + 491393 \times 0.85^2 - 258065 \times 0.85 + 50688 = 216 \text{ g/mol}$$

$$x_{C35-} = \frac{(625 \text{ g/mol} - 216 \text{ g/mol})}{(625 \text{ g/mol} - 200 \text{ g/mol})} = 0.962$$

$$x_{C36+} = 1 - 0.96 = 0.038$$

Results and Discussion

Extensive validation of the field method was performed during and after its development. STO samples were analyzed using both the standard laboratory method and the new field method. The test samples covered a wide range of densities, from 0.807 g/cm³ to 0.963 g/cm³, and molecular weights, from 165 g/mol to 449 g/mol.

The C₃₆₊ molecular weight correlation was validated by applying the measured FPD STO molecular weight to the two methodologies, lab and field. Table III displays the 22 results from this validation. The minus fractions, or moles eluted by each method, were compared, showing that the average deviation in the weight percent and mole percent of eluted sample, or C₃₅₋ fraction, was 3.29% and 3.23%, respectively.

Table IV displays the results of the second validation, in which the molecular weight of the sample measured by FPD was

Table III. Validation of C₃₆₊ MW Correlation: Results of Field and Lab Methods Using Measured STO MW by FPD

Density (g/mL)	MW		Wt% Field	Eluted Lab	Mol% Field	Eluted Lab	C ₃₆₊ Field	MW Lab
	FPD (g/mol)							
0.807	165		87.7	86.5	96.4	95.1	571	456
0.815	174		100.0	100.0	100.0	100.0	581	456
0.830	194		80.5	80.6	93.7	93.9	600	612
0.832	201		86.9	82.4	95.6	90.7	602	378
0.845	207		82.6	82.0	94.2	93.9	619	596
0.851	215		74.8	74.4	91.3	90.8	626	601
0.852	216		76.2	73.9	91.8	89.0	628	512
0.864	220		79.7	79.2	93.1	92.4	643	601
0.869	226		72.5	67.0	90.4	83.6	649	455
0.870	234		71.6	70.9	89.8	88.8	650	610
0.883	247		66.3	66.8	87.5	88.2	666	695
0.886	259		62.3	65.9	85.4	90.5	669	924
0.895	279		68.5	72.3	97.1	91.2	681	898
0.895	272		60.1	60.7	84.0	85.0	681	711
0.907	261		64.7	63.9	86.8	85.7	697	661
0.911	316		51.3	49.4	78.0	75.1	702	643
0.913	327		48.4	51.1	76.0	80.3	703	811
0.923	338		46.0	48.6	74.5	78.8	716	817
0.936	339		64.2	67.0	83.4	87.1	732	866
0.942	398		51.1	49.4	73.7	71.3	741	701
0.948	368		53.1	54.9	76.9	79.6	748	813
0.963	449		34.7	39.1	61.7	69.5	766	896

applied only to the laboratory method, as this is the traditional analysis, while the molecular weight estimated by Equation 2 was applied to the field method. The comparison showed that the average deviation in the weight percent and mole percent of the C_{35-} fraction was 6.45% and 3.88%, respectively.

The accuracy of the new method in estimating the sample molecular weight proved better for lighter fluids. Heavier oils contain a larger C_{36+} fraction; therefore, any error in the C_{36+} molecular weight estimation contributes to the total error more than it would for oils with less heavy ends. Figure 2 displays the sample molecular weight distribution versus the sample density using both the FPD and correlation methods. It was apparent that there was more deviation between the two molecular weights as density increased.

Table IV. Validation of STO MW Correlation: Results of Field Method Applying STO MW by Correlation and Lab Results Applying STO MW by FPD

Density (g/mL)	MW corr. (g/mol)	MW FPD (g/mol)	WT% Field	Eluted Lab	Mol% Field	Eluted Lab
0.807	177	165	79.2	86.5	93.6	95.1
0.815	184	174	92.3	100.0	97.6	100.0
0.830	197	194	78.6	80.6	93.0	93.9
0.832	199	201	88.2	82.4	96.1	90.7
0.845	212	207	79.7	82.0	93.1	93.9
0.851	217	215	74.1	74.4	91.0	90.8
0.852	218	216	75.0	73.9	91.3	89.0
0.864	231	220	73.6	79.2	90.5	92.4
0.869	236	226	67.5	67.0	88.1	83.6
0.870	237	234	70.0	70.9	89.0	88.8
0.883	254	247	63.5	66.8	86.1	88.2
0.886	257	259	62.9	65.9	85.7	90.5
0.895	270	279	71.9	72.3	88.8	91.2
0.895	271	272	60.4	60.7	84.3	85.0
0.907	291	261	53.9	63.9	80.7	85.7
0.911	299	316	56.9	49.4	81.7	75.1
0.913	301	327	56.1	51.1	81.2	80.3
0.923	322	338	50.1	48.6	77.5	78.8
0.936	352	339	59.7	67.0	80.6	87.1
0.942	371	398	59.2	49.4	79.6	71.3
0.948	387	368	47.8	54.9	73.0	79.6
0.963	436	449	37.3	39.1	64.3	69.5

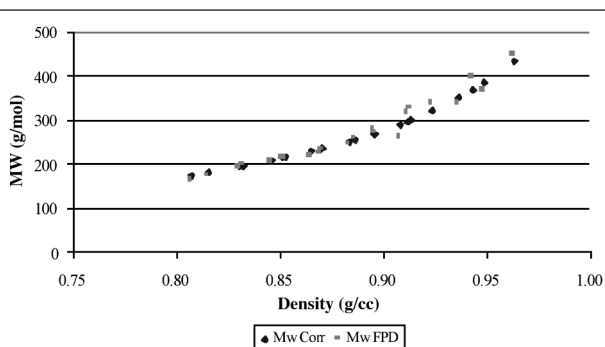


Figure 2. Molecular weight by FPD and by STO molecular weight correlation versus STO density.

In the laboratory method, the molecular weight of the plus fraction could only be calculated once the stock-tank oil molecular weight and plus fraction were measured. Therefore, the plus-fraction molecular weight accumulated the error generated by these experiments. As a result, the molecular weight of the plus fraction would occasionally result in an unrealistic value for

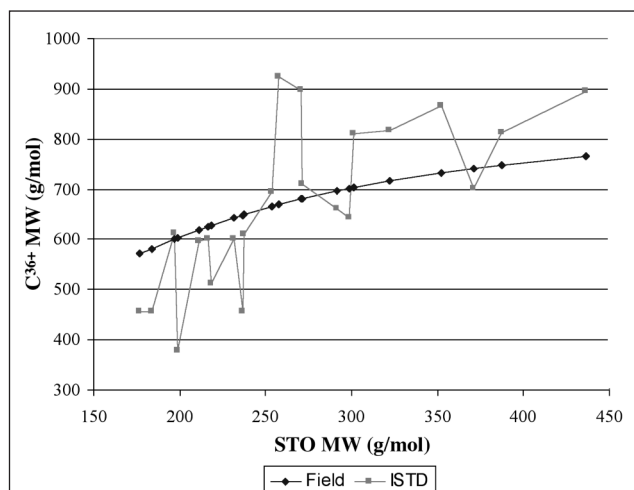


Figure 3. C_{36+} molecular weights found by traditional laboratory methods (ISTD) and by correlation (field) versus STO molecular weight.

Table V. Composition Comparison of Lab and Field Method Results

	Lab (wt%)	Field (wt%)	Deviation (%)	Lab (mol%)	Field (mol%)	Deviation (%)	
1	C_{7+}	95.0	96.8	1.9	86.8	91.1	4.9
	C_{20+}	45.2	46.4	2.6	22.5	24.6	9.1
	C_{30+}	24.9	24.0	3.7	9.9	9.9	0.1
	C_{36+}	17.4	17.6	1.5	6.3	6.7	6.3
2	C_{7+}	94.2	95.8	1.6	83.7	87.6	4.6
	C_{20+}	49.1	49.1	0.0	24.1	25.0	3.8
	C_{30+}	30.0	28.9	3.8	12.0	11.7	2.5
	C_{36+}	22.4	23.2	3.9	8.3	8.9	7.2
3	C_{7+}	90.6	93.0	2.6	79.4	84.2	6.1
	C_{20+}	29.3	28.5	2.8	13.2	13.1	0.9
	C_{30+}	10.6	10.3	2.8	3.7	3.5	4.8
	C_{36+}	4.7	6.4	37.4	1.4	1.9	41.1
4	C_{7+}	91.3	94.3	3.2	77.7	84.2	8.3
	C_{20+}	41.7	44.2	5.9	19.0	22.0	15.4
	C_{30+}	22.5	22.6	0.9	8.1	8.7	7.9
	C_{36+}	15.9	16.7	4.8	5.3	5.9	12.9
5	C_{7+}	94.6	94.0	0.6	87.9	84.3	4.1
	C_{20+}	41.5	42.4	2.2	20.4	20.5	0.7
	C_{30+}	21.4	22.4	4.6	8.3	8.6	3.2
	C_{36+}	14.3	15.2	6.5	5.0	5.3	5.6
6	C_{7+}	94.5	95.4	1.0	83.7	86.3	3.0
	C_{20+}	50.1	50.4	0.6	25.1	25.8	2.6
	C_{30+}	29.7	30.0	1.0	12.1	12.3	1.4
	C_{36+}	21.7	24.6	13.4	8.1	9.5	16.7

the given sample molecular weight. In the worst cases, the C₃₆₊ fraction molecular weight was actually found to be lower than the molecular weight of C₃₅. The molecular weight–density correlation used here resulted in some errors, but the results were always realistic. A comparison of the correlated and experimentally found C₃₆₊ molecular weights versus the STO molecular weight can be seen in Figure 3.

Compositional analysis by the field method and the traditional laboratory method, which uses both ISTD and FPD, on stock-tank oil samples showed relatively comparable results. The hardware platform designed for the field, as well as the two density–molecular weight correlations, were used to produce the chromatograms and compositions for the field results. The laboratory-generated compositions were found by traditional laboratory methods and equipment, including the ISTD and FPD experiments. Table V displays the grouped compositions of six samples analyzed by both methods. The field method analysis and data processing time was less than 3 hours. The duration of compositional analysis using laboratory equipment and experimental procedure was at least double that of the field method.

Conclusion

A new method for determining stock-tank oil composition in a field environment was developed to replace the internal-standard and freezing point depression techniques that are typically used in the laboratory. Two correlations were introduced to estimate the molecular weights of the stock-tank oil and the plus fraction. The compositional analysis results by both the laboratory and field methods were compared and showed good agree-

ment. The new field method was shown to be easier to perform and faster than the traditional laboratory method, while maintaining an acceptable level of accuracy, which were added benefits when performing compositional analysis as part of fast-paced oil rig operations.

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