Tool for Monitoring Viscosity Content and Brand Authentication of Petroleum Products

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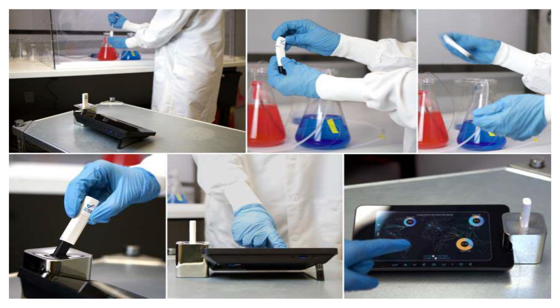
Abstract

Time-Domain nuclear magnetic resonance (TD-NMR) represents an attractive alternative method for analyzing petroleum products such as motor oil and diesel fuel. This is due to its ability to analyze samples with little or no sample preparation, allowing fast data collection, and being a nondestructive and noninvasive method. Current TD-NMR methods that have been developed to analyze petroleum product samples utilize very large and expensive TD-NMR benchtop equipment. WaveGuide is developing a portable TD-μNMR (Time-Domain micro-NMR) that can be utilized in the field to determine the viscosity and authenticity of branded petroleum products.

TD-NMR was explored as a rapid method for simultaneous assessment of the quality parameters in conventional and synthetic motor oil samples. Data obtained with the relaxation decay curves employing a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence revealed tight and well-separated clusters of the motor oils, allowing discrimination of the motor oil samples according to their viscosity content and brand: 0W-30, 5W-30, 10W-30 and 10W-40.[1] A set of 10 ASI standards for sulfur in diesel fuel was also analyzed, using a CPMG pulse sequence.[2] The resulting data also showed well-separated clusters, allowing discrimination among the standards with sulfur weight percentage (wt %): 0, 0.1, 0.25, 0.5, 1, 1.5, 2, 3, 4, 5.

WaveGuide's portable TD-μNMR is the first battery powered instrument that is fully automated and robust enough to operate in the field without the need for a trained NMR technician. The device is 22x smaller, ~80x lighter, and 30x lower cost than contemporary commercial analytical systems.



How Does This Fit with PANIC's Mission?

WaveGuide's portable TD-NMR (time domain micro-NMR) provides solutions for field testing of petroleum products for counterfeiting. Testing can now be conducted on site at ports of entry where counterfeit products are likely to enter the supply chain. WaveGuide's TD-NMR allows non-scientists to conduct field testing of counterfeit motor oils as well as high sulfur contaminated diesel products. WaveGuide is providing a practical industry-focused solution by bringing TD-NMR to the masses.

Introduction

On a global scale, the counterfeiting business is highly profitable across multiple retail markets. Retail goods that are routinely counterfeited include high end clothes, jewelry, and cell phones. Counterfeiters create these fake replicas to answer the growing consumer demand for these products. The business of creating fake goods is not just for the luxury items as it extends into the energy industry, specifically with motor oil and other automotive lubricants. Operations of massive oil counterfeiting can be seen within the United States as well as countries like Russia, where in December of 2015, a large counterfeit oil ring was discovered outside of Moscow by Russian law enforcement, collecting a profit of $164 million a year.[3,4] Large brand names became damaged with the illegal activity such as Mobil, Castrol, Shell, and others.[5] The individuals behind the ring even faked OEM oil with major car brands such as Toyota, Ford, and Mazda, selling the inauthentic oil under their brand names. The frequency of such counterfeits is both detrimental to the brands' reputations but also could pose potentially catastrophic and deadly consequences to the consumers.[6] The risk of damage can be minimized if products can be analyzed and authenticated prior to falling into the customers hands. A device that can test a sample on the spot and within minutes determine if the product is genuine or counterfeit can save customers, vendors, corporations, and law enforcement significant time and money typically used to derail such counterfeit operations.[4] The WaveGuide Formμla ™ is a truly portable, handheld device that can be used by nearly anyone.

The WaveGuide Formμla™ portable μNMR
Little to no sample preparation required
Sample analysis take only minutes
Less than 50μL of sample typically used per test

Materials & Methods

Objective 1: Analyze a set of 19 commercially available motor oil samples (Table 1) and explore correlation between T2 and reported viscosity to correctly identify commercial samples.

Experiment Methods: Each sample was freshly prepared and tested (using 40μL sample volume) using the protocol: 3 runs each sample, accumulating 4 scans per run, scan duration of 0.4 seconds, a recycle delay of 2 seconds, and 400 μs for the echo period in the CPMG[4] pulse sequence at 25°C. The magnetic field of the μNMR was at 0.50 Tesla. The data was fitted using a bi-exponential algorithm.

Objective 2 Analyze a set of crude oil samples (Table 3) to correlate T2 with the determined wt% asphaltene which is a crude oil contaminant that usually requires a 24-hour labor intensive method to determine to create a fast replacement test.

Objective 3: Analyze a set of crude oil samples (Table 2) with determined viscosity and density to provide a faster analytical method for determination of oil extraction process and value of oil asset.

Experimental Methods for 2 & 3: Each sample was freshly prepared and tested (20μL sample volume) two times on the same day: 2 samples accumulating 4 scans per run using a CPMG pulse sequence with a scan duration of 4.0 seconds, a recycle delay of 2.5 seconds, and an echo period of 400 μs at ambient temperature. The data was fitted using a tri-exponential algorithm.

Objective 4: Analyze two sets of sulfur in diesel fuel ASI standards SFD7 (0 to 0.10%) and SFD10 (0 to 5%) to be able to grade diesel oil samples.

Objective 5: Analyze a petroleum distillate set of ONTA standards of Gasoline, Kerosene, and Diesel for differentiation.

Experimental Methods for 4 & 5: Each sample was freshly prepared and tested (50μL sample volume) two times on the same day using a CPMG pulse sequence with a scan duration of 2.0 seconds, a recycle delay of 2.5 seconds, and an echo period of 400 μs at ambient temperature. The data was fitted using mono and bi-exponential algorithms.

Conclusions

Using the WaveGuide Formμla™ μNMR device WaveGuide was able to:

- Show that WaveGuide's μNMR can distinguish between synthetic motor oil grades and non-synthetic motor oils.
- Establish a linear slope for density and viscosity parameters in crude oils and differentiate motor oil samples from the original unused sample and from used samples at different time points.
- Classify wt.% asphaltene in crude oil samples in groups of high, medium and low concentration using T2a as a marker.
- Detect sulfur content in diesel fuel with a dynamic range of 50,000 ppm to 200 ppm.
- Measure distinct petroleum distillate fragments.

References

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Results

Table 1: T2 Values of 19 Commercially Available Motor Oils

SAMPLE Bi-Exponential (T2A &T2B)		AVERAGE (4 samples)	STDEV	VISCOSITY mm2 /(S) @40°C
Pennzoil SAE 5W-30 Bottle #1 (Non-Synthetic)				
	T2A	0.03800	0.00010	63.4
	T2B	0.13065	0.00018	
Proline SAE 5W-30 Bottle #1 (Non-Synthetic)				
	T2A	0.04028	0.00010	67.1
	T2B	0.13555	0.00026	
Pennzoil SAE 10W-40 (Non-Synthetic)				
	T2A	0.02990	0.00012	104.7
	T2B	0.10908	0.00030	
Proline SAE 10W-40 (Non-Synthetic)				
	T2A	0.03028	0.00004	92.8
	T2B	0.10918	0.00015	
Castrol EDGE SAE 5W-30 GDI #1 (Synthetic)				
	T2A	0.04052	0.00010	62.64
	T2B	0.13633	0.00022	
Valvoline Advanced SAE 5W-30 #1 (Synthetic)				
	T2A	0.03622	0.00009	63.17
	T2B	0.12336	0.00016	
Mobil 1 5W-30 Bottle #1 (Synthetic)				
	T2A	0.03712	0.00015	63
	T2B	0.12530	0.00036	
Mobil 1 0W-30 Advanced Fuel Economy (Synthetic)				
	T2A	0.04708	0.00011	11.5
	T2B	0.15318	0.00030	
Castrol EDGE European SAE 0W-30 (Synthetic)				
	T2A	0.03598	0.00008	67.4
	T2B	0.13098	0.00022	
Castrol EDGE 10W-30 (Synthetic)				
	T2A	0.03292	0.00006	64.88
	T2B	0.11517	0.00015	
Mobil 1 5W-30 Bottle #2 (Synthetic)				
	T2A	0.03704	0.00013	63
	T2B	0.12525	0.00037	
Proline SAE 5W-30 Bottle #2 (Non-Synthetic)				
	T2A	0.04033	0.00012	67.1
	T2B	0.13600	0.00036	
Shell Rotella Gas Truck SAE 5W-30 (Synthetic)				
	T2A	0.04310	0.00013	66.4
	T2B	0.14081	0.00041	
Castrol EDGE SAE 5W-30 GDI #2 (Synthetic)				
	T2A	0.04062	0.00010	62.64
	T2B	0.13696	0.00026	
Castrol GTX Ultraclean SAE 5W-30 (Synthetic)				
	T2A	0.03908	0.00013	61.34
	T2B	0.13093	0.00032	
Valvoline Advanced SAE 5W-30 #2 (Synthetic)				
	T2A	0.03622	0.00010	63.17
	T2B	0.12321	0.00018	
Castrol GTX Magnatec SAE 5W-30 (Synthetic)				
	T2A	0.03621	0.00015	61.77
	T2B	0.12545	0.00045	
Pennzoil Platinum SAE 5W-30((Synthetic)				
	T2A	0.03803	0.00006	45.9
	T2B	0.12654	0.00031	
Pennzoil SAE 5W-30 Bottle #2 (Non-Synthetic)				
	T2A	0.03798	0.00014	63.4
	T2B	0.13082	0.00028	

Field Testing of Oil Samples

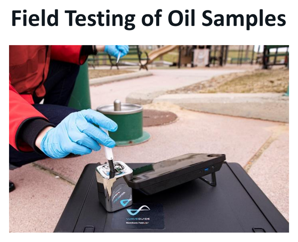
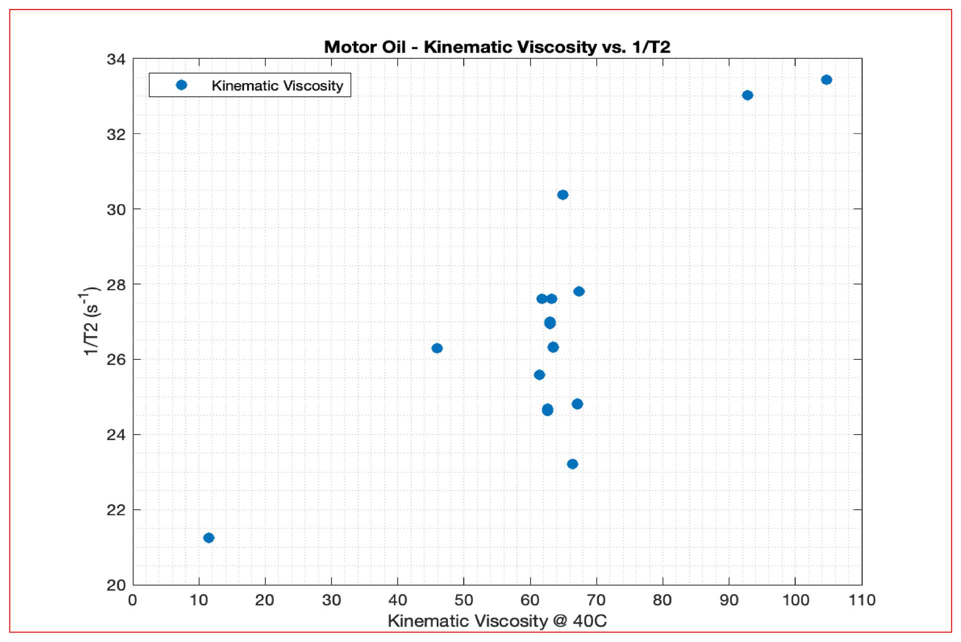


Table 2: 1/T2 vs Viscosity of Conditioned Motor Oils

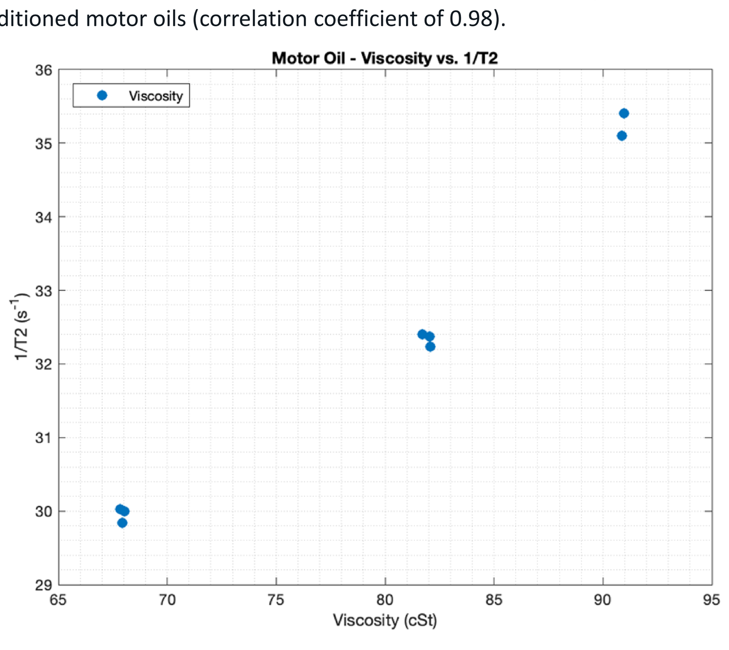
Sample ID	AVG 1/T2 (s)	TIME (Hrs)	Viscosity (cSt)
WG-A1	35.40262	0	90.96
	9.76348		
WG-B1	35.0988	0	90.86
	9.696218		
WG-A2	32.39916	1	81.71
	8.873823		
WG-A3	30.02823	16	67.83
	8.173641		
WG-B2	32.3677	1	82.03
	8.866191		
WG-B3	29.8405	8	67.94
	8.113327		
WG-C1	32.23467	1	82.06
	8.84228		
WG-C2	29.9958	16	68.05
	8.171938		



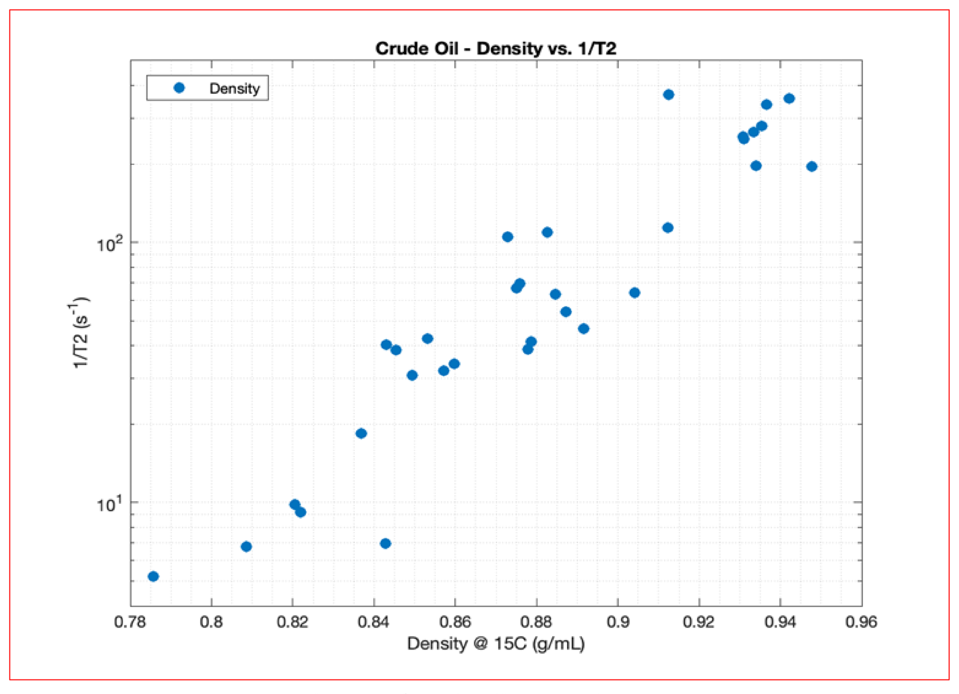
Graph 1: T2 Comparison of Synthetic and Non-Synthetic Commercially Available Motor Oils

Comparing 1/T2 vs density, with 1/T2 on a log scale, one can see a correlation exists with the highest density materials displaying a fast T2, and with the less dense materials yielding a longer T2, as seen in Graph 3 (correlation coefficient of 0.94).

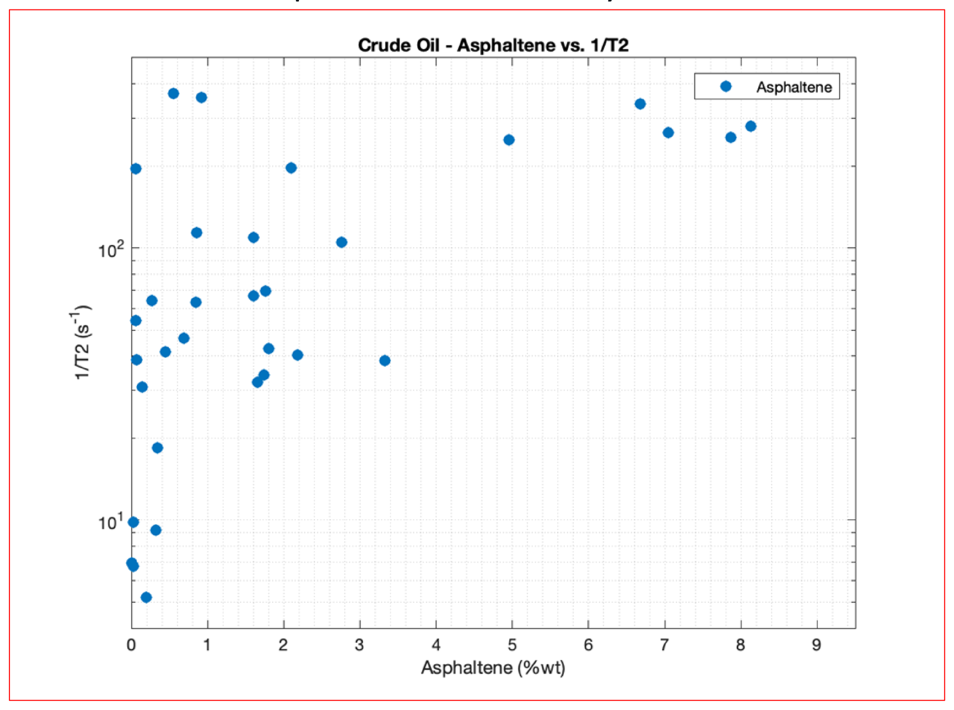
Results Commercial Motor Oil: Synthetic and non-synthetic motor oil samples were differentiated based on the level of viscosity of the different types of motor oil see Graph 1. Comparing 1/T2A vs kinematic viscosity (the time it takes for a specific volume of oil to flow through a capillary tube) with 1/T2A (T2A is the smaller T2 value), one can see correlation coefficient of 0.78 for this data. The high viscous oil samples displaying a fast T2 such as Pennzoil SAE 10W-40 and Proline SAE 10W-40. Table 2 and Graph 2 shows a relationship between conditioned motor oils at different times of use and 1/T2 vs the new viscosity of the conditioned motor oils (correlation coefficient of 0.98).



Graph 2: 1/T2 vs Viscosity of Conditioned Motor Oils



Graph 3: T2 of Crude Oil vs. Density

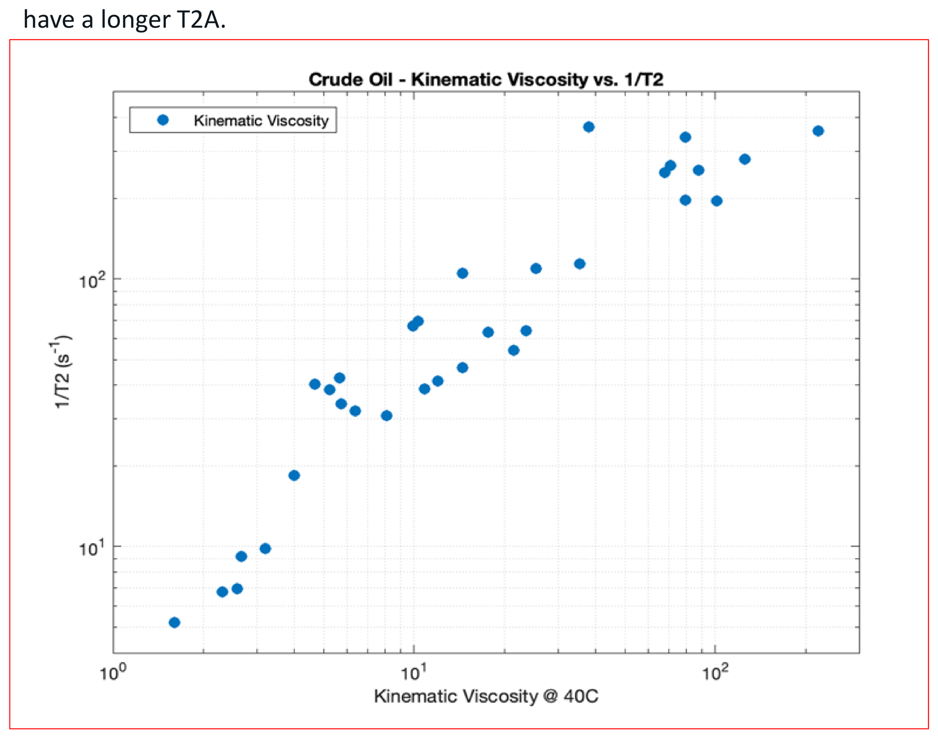


Graph 4: T2 of Crude Oil vs. wt% Asphaltene

Table 3: T2 Values of Crude Oil

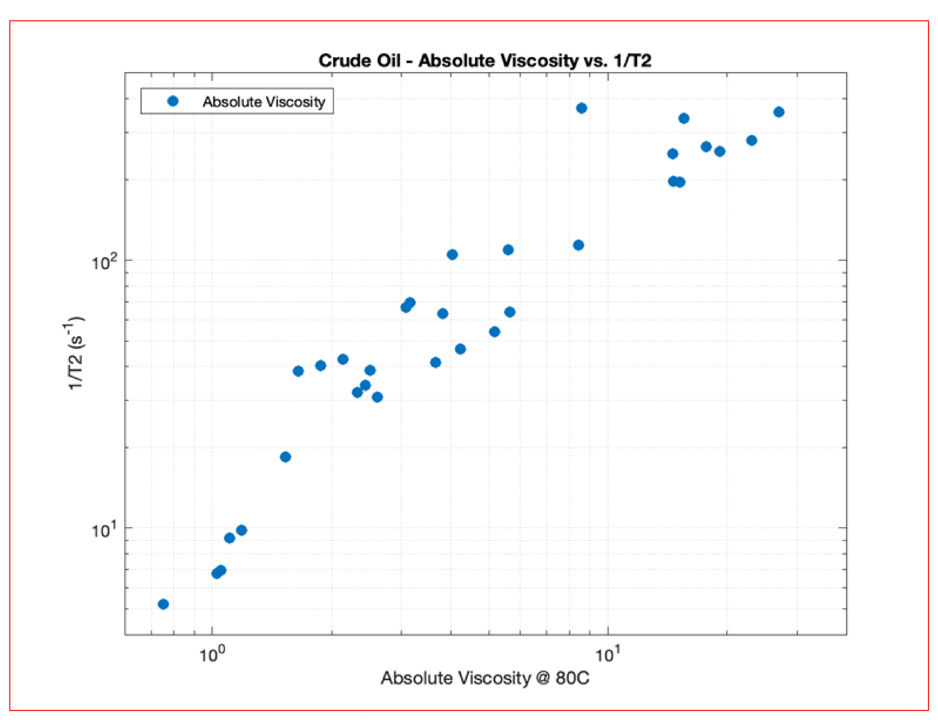
SAMPLE Tri-Exponential (T2A, T2B & T2C)		AVERAGE (2 samples)	STDEV	density @ 15°C(g/ml)	Asphaltene (wt%)	Viscosity (kinematic) 40°C	Viscosity (absolute) 80°C
WG1	T2A	0.00506	0.00006	0.9478	0.05	101.0	15.2
	T2B	0.02178	0.00003				
	T2C	0.06882	0.00056				
WG2	T2A	0.02587	0.00016	0.8779	0.07	10.8	2.5
	T2B	0.12619	0.00097				
	T2C	0.41114	0.00614				
WG3	T2A	0.00268	0.00004	0.9125	0.55	37.9	8.6
	T2B	0.01132	0.00012				
	T2C	0.03158	0.00011				
WG4	T2A	0.02436	0.00034	0.8786	0.45	11.9	3.7
	T2B	0.12296	0.00134				
	T2C	0.38697	0.00333				
WG5	T2A	0.00283	0.00005	0.9422	0.92	219.2	27.0
	T2B	0.01005	0.00022				
	T2C	0.02669	0.00033				
WG6	T2A	0.01843	0.00001	0.8871	0.05	21.4	5.2
	T2B	0.09642	0.00029				
	T2C	0.33080	0.00223				
WG7	T2A	0.00882	0.00002	0.9123	0.85	35.5	8.4
	T2B	0.04074	0.00014				
	T2C	0.12884	0.00006				
WG8	T2A	0.00906	0.00008	0.8826	1.60	25.3	5.6
	T2B	0.04233	0.00014				
	T2C	0.11953	0.00015				
WG9	T2A	0.01593	0.00011	0.8846	0.84	17.6	3.8
	T2B	0.08294	0.00059				
	T2C	0.26809	0.00175				
WG10	T2A	0.00517	0.00012	0.9341	2.10	79.3	14.6
	T2B	0.02141	0.00051				
	T2C	0.06283	0.00134				
WG11	T2A	0.01525	0.00029	0.8751	1.60	9.9	3.1
	T2B	0.07345	0.00139				
	T2C	0.21109	0.00302				
WG12	T2A	0.01440	0.00005	0.8758	1.76	10.3	3.2
	T2B	0.06946	0.00064				
	T2C	0.19461	0.00147				
WG13	T2A	0.09123	0.02497	0.8218	0.32	2.7	1.1
	T2B	0.43143	0.10619				
	T2C	1.29217	0.15257				
WG14	T2A	0.14738	0.00438	0.8429	0.00	2.6	1.1
	T2B	0.52805	0.01079				
	T2C	1.21620	0.02019				
WG15	T2A	0.19481	0.00321	0.7858	0.19	1.6	0.8
	T2B	0.73061	0.00207				
	T2C	1.73552	0.00298				
WG16	T2A	0.08611	0.02252	0.8204	0.03	3.2	1.2
	T2B	0.40263	0.09429				
	T2C	1.24248	0.16123				
WG17	T2A	0.01578	0.00020	0.9041	0.27	23.5	5.6
	T2B	0.06638	0.00015				
	T2C	0.19047	0.00017				
WG18	T2A	0.14777	0.00022	0.8086	0.02	2.3	1.0
	T2B	0.55267	0.00334				
	T2C	1.35459	0.01099				
WG19	T2A	0.02168	0.00037	0.8917	0.69	14.5	4.2
	T2B	0.10626	0.00184				
	T2C	0.33654	0.00453				
WG20	T2A	0.00305	0.00014	0.9366	6.68	79.6	15.6
	T2B	0.01099	0.00038				
	T2C	0.02987	0.00037				
WG21	T2A	0.02501	0.00036	0.8430	2.18	4.7	1.9
	T2B	0.13147	0.00264				
	T2C	0.36188	0.00882				
WG22	T2A	0.05508	0.00087	0.8369	0.34	4.0	1.5
	T2B	0.26660	0.00334				
	T2C	0.72746	0.00661				
WG23	T2A	0.02660	0.00081		3.33	5.2	1.7
	T2B	0.13700	0.00511				
	T2C	0.34780	0.00835				
WG24	T2A	0.02373	0.00045	0.8531	1.81	5.6	2.1
	T2B	0.11127	0.00163				
	T2C	0.28565	0.00265				
WG25	T2A	0.00344	0.00069	0.9309	7.87	88.1	19.2
	T2B	0.01375	0.00429				
	T2C	0.03879	0.01298				
WG26	T2A	0.00959	0.00009	0.8730	2.76	14.5	4.0
	T2B	0.04478	0.00050				
	T2C	0.11213	0.00085				
WG27	T2A	0.00394	0.00009	0.9311	4.96	67.9	14.5
	T2B	0.01628	0.00021				
	T2C	0.05418	0.00029				
WG28	T2A	0.03141	0.00031	0.8572	1.65	6.4	2.3
	T2B	0.16715	0.00247				
	T2C	0.47840	0.00721				
WG29	T2A	0.00353	0.00004	0.9354	8.13	125.2	23.1
	T2B	0.01422	0.00018				
	T2C	0.03594	0.00020				
WG30	T2A	0.00380	0.00003	0.9334	7.05	71.0	17.7
	T2B	0.03647	0.02724				
	T2C	0.03598	0.02597				
WG31	T2A	0.02940	0.00011	0.8597	1.74	5.7	2.4
	T2B	0.15356	0.00203				
	T2C	0.45768	0.00848				

Results wt% Asphaltene: Differentiation was effectively achieved between wt% asphaltene using T2A as a marker in groups of high, medium and low concentration (correlation coefficient of 0.59) (see Graph 4 & Table 3). Here, T2A refers to the smaller T2 value from the set of values resulting from a tri-exponential estimate of the measured T2 decay signal. In Table 3, for each sample there are three rows of T2 results, where the rows correspond to the three T2 values from the tri-exponential estimate listed in increasing T2 order. Samples WG25, WG29, and WG30 had wt% high asphaltene concentrations. Samples WG4, WG13, and WG15 have close to zero asphaltene concentration and have a longer T2A.

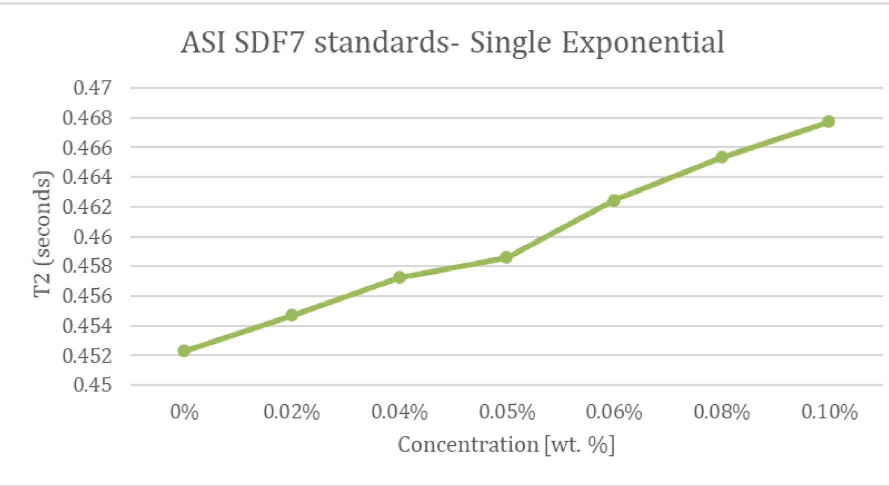


Graph 5: T2 of Crude Oil vs. Kinematic Viscosity

Results Viscosity: Comparing 1/T2 vs kinematic viscosity (the time it takes for a specific volume of oil to flow through a capillary tube) one can see a linear-like slope exists (correlation coefficient of 0.94) with the more viscous oil samples displaying a fast T2A, and with less viscous materials yielding a longer T, (seen in Graph 5). Comparing 1/T2 vs absolute viscosity (the force needed by a fluid to overcome its own internal molecular friction so that it can flow) one can see a linear-like slope exists (correlation coefficient of 0.95) with the more viscous oil samples displaying a fast T2, and the less viscous materials yielding a longer T2 (seen in Graph 6).

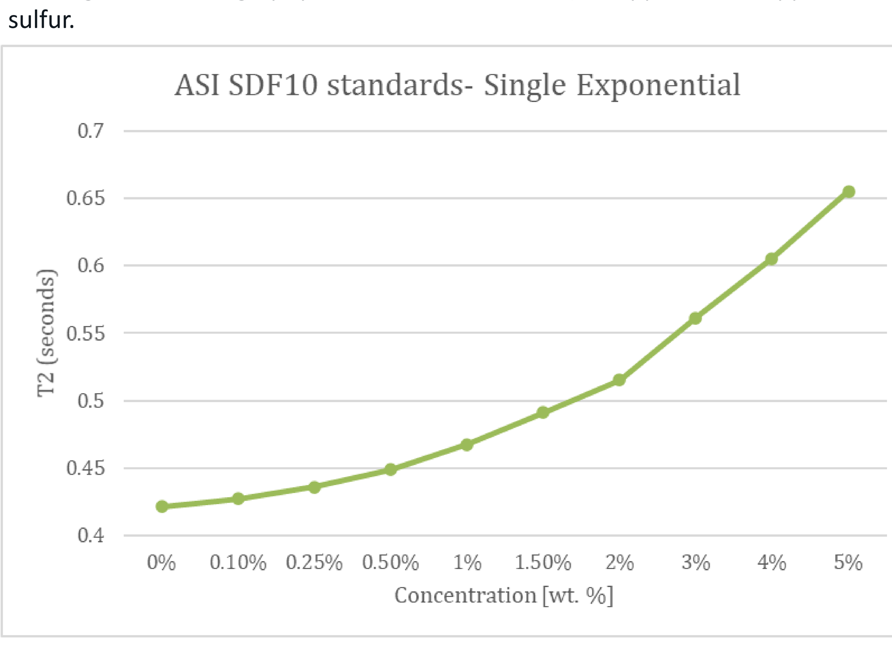


Graph 6: T2 of Crude Oil vs. Absolute Viscosity

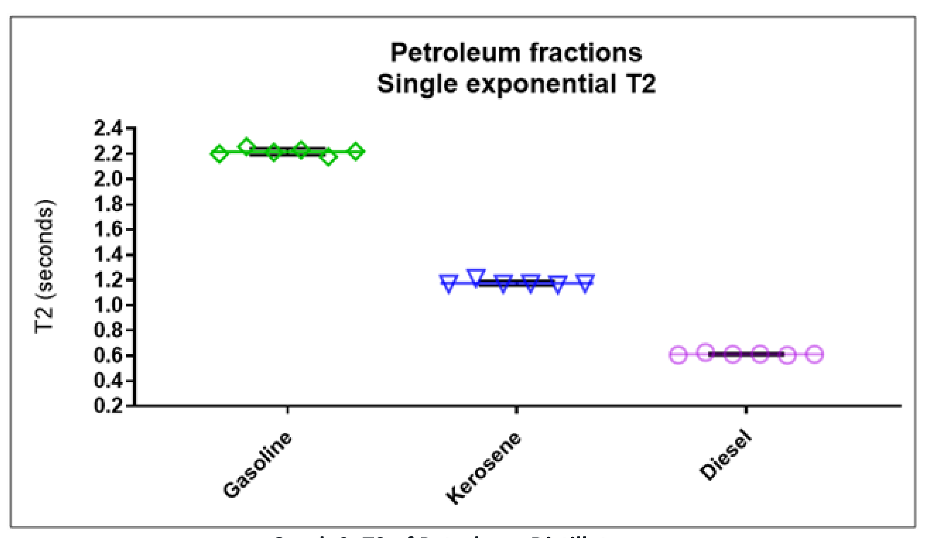


Graph 7: T2 of ASI Diesel Oil vs. Concentration

Results ASI Diesel Oil: Data was analyzed and plotted using the average T2 measurements of samples collected in triplicate with a single, and a bi-exponential fit for the ASI standards. The WaveGuide Formμla™ was able to effectively detect in a linear fashion the known set of sulfur standards with only a single exponential fit shown (Graphs 7-8). The dynamic limit of detection using the small molecule sulfur gas chromatography ASI standard was 500,000 ppm to 200 ppm of total sulfur.



Graph 8: T2 of ASI Diesel Oil vs. Concentration



Graph 9: T2 of Petroleum Distillates

Results ONTA Petroleum Distillate Standards: The data was analyzed using average T2 measurements of samples tested in triplicate with single, and bi-exponential fits for the ONTA standards. The WaveGuide Formμla™ was able to effectively detect the difference in the distillates standards with a single exponential shown (Graph 9). Gasoline has the longest T2 and the crude diesel sample had the shortest T2.