Blind Validation of Lonestar vs GC on Methanol in Crude Oil

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A team from Owlstone performed blind testing on methanol samples for a major global oil producer to show that results from the Lonestar Analyzer were equivalent to those obtained using gas chromatography.

Introduction: Methanol in Crude Oil

Methanol may be deliberately introduced into crudes to prevent the formation of hydrates in cold weather when wells are shut in, or production slowed. Its presence in the crude is problematic further down the line, because it is carried with water in the crude into refinery wastewater treatment systems. Bacteria in the system preferentially break down the methanol, which can have the effect of leaving other contaminants untreated, leading to EPA permit excursions[1]. For this reason, refineries require a method of testing the methanol content of incoming crude.

Methanol Analysis Methods

The most widely-used current method, ASTM D7059, is a direct injection, multidimensional gas chromatography (GC) method, which typically takes around 45 minutes to perform, and must be carried out by specialist personnel in a laboratory environment. Owlstone have developed a significantly faster test for methanol, which uses the Lonestar Analyzer to produce a result in less than 15 minutes. The Lonestar can be operated at-line, by non-specialist personnel. However, these advantages count for nothing if Lonestar does not deliver performance equivalent to GC. That is why a team from Owlstone performed a blind validation experiment to compare Lonestar performance to that of GC.

Test Format

The test consisted of two stages. In the first stage, known concentrations of methanol were used to align Lonestar results with those of the GC system. Each sample was run three times, to establish that Lonestar results were repeatable. In the second stage, ten samples of unknown methanol concentration were tested with both Lonestar and GC, in order to show that GC results could be reproduced with Lonestar. Table **1** below shows the key acceptance criteria agreed with the client, which define what constitutes a successful test in phase 2: in summary, Lonestar results could vary by up to ±20% for each known sample, and needed to be within ±30% of the GC reading.

Gulf of Mexico Crude Oil with Methanol spike (ppm)	Repeatability* (+/- ppm)	Reproducibility** (+/- ppm)
30	Not required	Not Required
50	10	15
75	15	23
100	20	30
200	40	60

Table 1 - Key acceptance criteria

* Repeatability: Allowable range of Lonestar readings

** Reproducibility: Allowable difference between GC and Lonestar results

Results: Phase 1

Table 2 shows the methanol results for the standards provided for both the GC ASTM method and Lonestar ion count with respective %RSD. In Figure 1, example Lonestar CV spectra for each of the MeOH oil standards are presented (more information on the meaning of these spectra can be found here). Using this data and that in Table 1 the Lonestar MeOH calibration was created as shown in Figure 2.

GoM Oil with Methanol spike (ppm)	GC concentration (ppm)	Lonestar Ion Count (A.U.)	Average GC concentration (ppm)	Average Lonestar Ion count (A.U)	Lonestar RSD (%)
35	27	0.14	27	0.13	3.23
35	27	0.13			
35	-	-			
50	34	0.19	33.5	0.20	7.55
50	33	0.22			
50	-	0.20			
75	56	0.30	56.5	0.30	5.15
75	57	0.29			
75	-	0.29			
75	-	0.32			
100	70	0.37	71.5	0.36	4.53
100	73	0.37			
100	-	0.37			
100	-	0.37			
100	-	0.33			
202	160	0.66	157	0.63	4.70
202	154	0.60			
202	-	0.65			
202	-	0.61			

Table 2 - GC / Lonestar calibration alignment

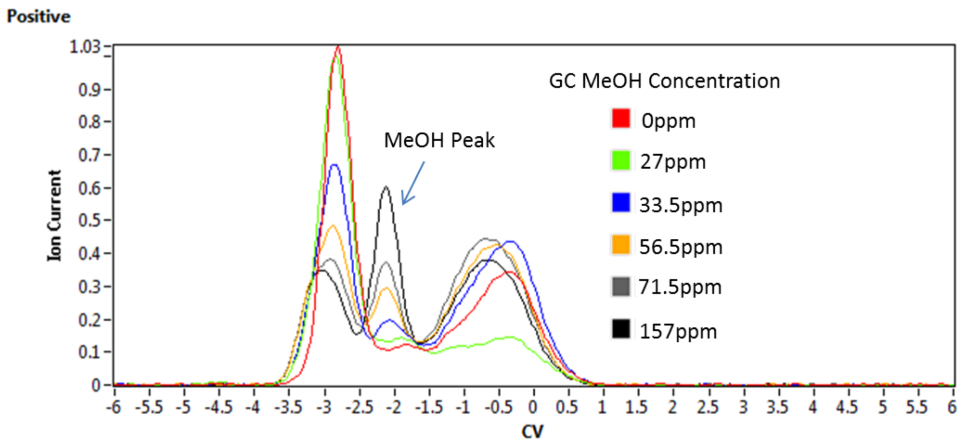

Figure 1 - Example Lonestar CV spectra for each of the MeOH oil standards

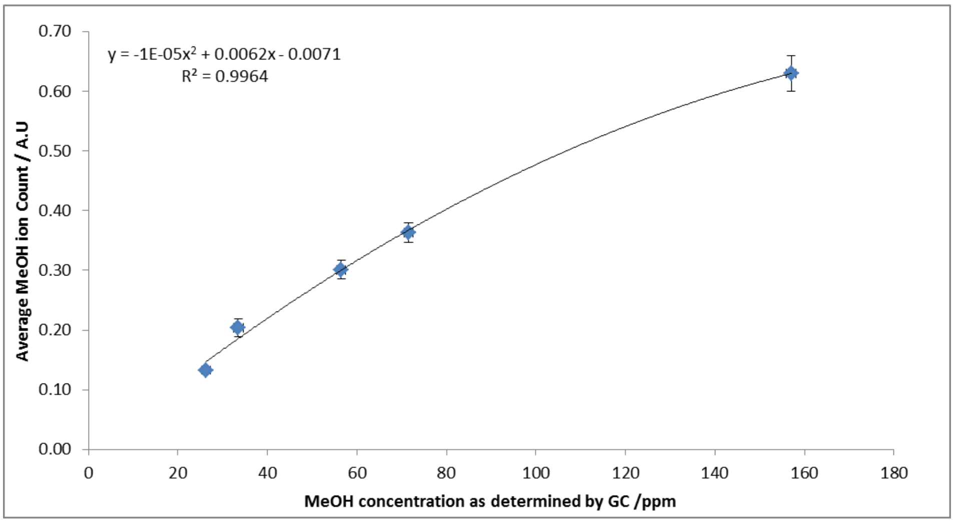

Figure 2 - Lonestar MeOH Calibration using the reported GC MeOH concentrations

Results: Phase 2

Figure 3 shows example CV spectra for 2 of the unknown samples and Table 3 details all of the GC and Lonestar MeOH determinations for all unknown samples. From this table it can be observed that the Lonestar has passed the repeatability as well as the reproducibility requirement of the validation test.

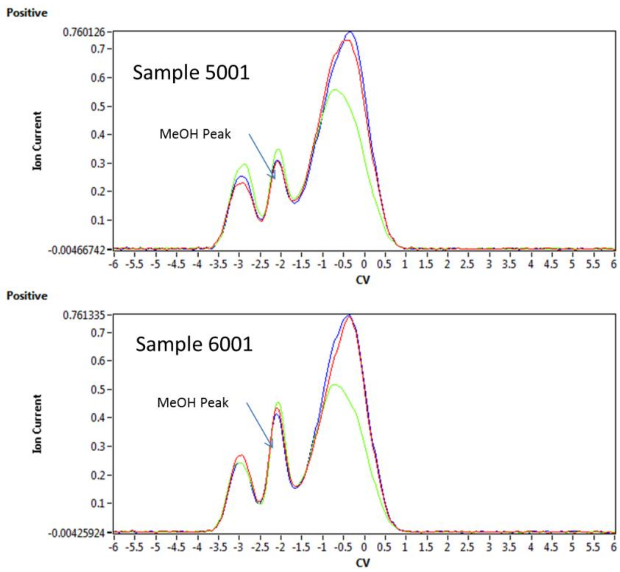

Figure 3 - Example CV spectra of unknown oil sample repeats

Sample Name	GC concentration (ppm)	Lonestar Concentration (ppm)	Average GC concentration (ppm)	Average Lonestar Concentration (ppm)	Lonestar RSD (%)	Pass / Fail (Repeatability / Reproducibility)
A	52	55	53	60	12	Pass /Pass
	53	67				
	-	56				
B	88	82	89	88	7	Pass /Pass
	90	94				
	-	88				
C	53	54	53	58	12	Pass /Pass
	52	55				
	-	66				
D	<20	24	<20	20	23	N/A
	<20	17				
	-					
E	75	77	73	71	11	Pass /Pass
	71	65				
	-					
F	168	160	164	156	3	Pass /Pass
	160	153				
	-					
G	35	34	35	36	7	Pass /Pass
	34	37				
	-					
H	25	30	25	31	6	Pass/Pass
	24	33				
	-					
I	13	24	12	24	0	N/A
	11	23				
	-					
J	55	54	56	52	5	Pass /Pass
	56	50				
	-					

Table 3 - Equivalency Testing Results

Conclusion

Lonestar passed both the repeatability and reproducibility requirements in all required cases (i.e. those with concentrations >30ppm), showing that it can be used with confidence in place of the current ASTM GC method for methanol measurement.