



ASTM D2163 and D5501 Analysis Comparison with Polyarc/FID

Application Note

Hydrocarbons and Oxygenates

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Introduction

ASTM D2163 (Standard test Method for Determination of Hydrocarbons in Liquefied Petroleum Gases and Propane/Propene Mixtures by Gas Chromatography) and ASTM D5501 (Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20% Ethanol by Gas Chromatography) are routinely used in refinery laboratories. Both test methods require the use of response factors and were chosen to evaluate the effectiveness of the Polyarc system. As written test method ASTM D2163 gives users the option of using theoretical FID response factors or calculating response factors from the use of certified calibration standards. ASTM 5501 suggests typical mass response factors that are validated using multilevel calibration standards. Reported results for D2163 analysis are calculated using the theoretical response factors stated in the method relative to n-butane.

Additionally, a demo "cryo sleeve" and updated "cryo block" were evaluated with the Polyarc reactor to allow the reactor to operate when cryogenic oven cooling is needed.

The evaluation of ASTM D2163 was accomplished using a 150 meter column and cryogenic oven cooling. The GC conditions are listed below.

Experimental

GC conditions D2163 with Polyarc

Front inlet Split/Splitless

Split Ratio 25:1
Inlet temperature 250°C
Inlet pressure 30.85 psi
Septum purge flow 3 sccm
Oven 10°C to 180°C at 10°C/min
Column 150 m x 250µm x 1 µm DB1
Sample Injection Liquid Sample Valve
Injection volume 0.2 µL

FID conditions D2163 with Polyarc

Temperature 300°C
H₂ 1.5 sccm
Air 350 sccm
Makeup 20 sccm
Sampling rate 20 Hz

Polyarc reactor conditions

Setpoint 293 °C
H₂ 35 sccm
Air 2.5 sccm

Average analysis of seven runs of D2163 certified standard run with and without the Polyarc compare well (Table 1).

Table 1. ASTM D2163 Liquid Volume %.

Component (Liquid vol %)	With Polyarc	Without Polyarc
Propylene	0.56	0.53
Propane	1.10	1.10
i-Butane	88.48	88.66
n-Butane	5.69	5.61
i-Pentane	2.41	2.35
n-Pentane	1.22	1.19
Benzene	0.50	0.57

Three propylene samples were analyzed with and without the Polyarc, two of the three samples compared well, the discrepancy in results on the third sample can be attributed to an insufficient amount of sample in the cylinder.

Table 2. ASTM D2163 Sample Comparison.

Sample ID	Sample 1		Sample 2		Sample 3	
Component (Liquid vol %)	ARC RRF	TRRF	ARC RRF	TRRF	ARC RRF	TRRF
Ethane	0.01	<0.01	1.51	1.84	4.02	3.88
Propylene	72.11	76.11	0.58	0.58	0.55	0.53
Propane	27.41	23.43	97.61	97.32	94.95	95.11
i-Butane	0.45	0.41	0.29	0.25	0.46	0.45
n-Butane	<0.01	<0.01	0.02	<0.01	0.02	0.02
i-Pentane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
n-Pentane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzene	0.01	<0.01	<0.01	<0.01	<0.01	<0.01

*This discrepancy could not be investigated due to lack of sample in the cylinder analyzed.

Test method ASTM D5501 was also included in the Polyarc evaluation.

These conditions are listed below:

GC conditions D5501 with Polyarc

Front inlet Split/Splitless
 Split Ratio 50:1
 Inlet temperature 250°C
 Inlet pressure 29.29 psi
 Septum purge flow 3 sccm
 Oven 35°C to 45°C at 17°C/min for 8.8 min; 1.7°C/min to 60°C for 8.8 min; 3.39°C to 220°C for 2.92 min

Column 100 m x 250µm x 0.5µm
 J&W
 Syringe 5 µL
 Injection volume 0.1 µL

FID conditions D5501 with Polyarc

Temperature 250°C
 H₂ 1.5 sccm
 Air 350 sccm
 Makeup 20 sccm
 Sampling rate 20 Hz

Polyarc reactor conditions

Setpoint 293 °C
 H₂ 35 sccm
 Air 2.5 sccm

Results between the Polyarc/FID without calibration and the FID with multilevel calibration (RMFR) compare well.

Table 3. ASTM D5501

Sample ID	Sample A		Sample B		Sample C		Sample D	
Wt % Component	RMRF	MRF (ARC)	RMRF	MRF (ARC)	RMRF	MRF (ARC)	RMRF	MRF (ARC)
Ethanol	99.27	99.22	98.21	98.06	98.08	97.99	99.22	99.14
Methanol	0.04	0.05	0.11	0.15	0.15	0.20	0.10	0.13
Other Hydrocarbons	0.69	0.73	1.68	1.79	1.77	1.81	0.69	0.73

compare well and eliminate the need for a multilevel calibration.

Conclusions

As written D 5501 analysis requires the use of a multilevel set of calibration standards to determine the relative molar response factors for methanol, ethanol and the other hydrocarbons. Results using the Polyarc

ASTM D2163 uses theoretical response factors relative to i-butane or n butane. These factors are listed in the ASTM test method. Using the Polyarc and its calculation using molar response factors relative to methane did not save any time and the cost associated with the bi-yearly replacement of the unit (catalyst) did not add benefit.

Contact Us

For more information or to purchase a Polyarc® system, please contact Activated Research Company at 612-787-2721 or contact@activatedresearch.com. Please visit their website for details and additional technical literature, www.activatedresearch.com.

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