





Determination of Oxygenates in Automotive Spark Ignition Engine Fuel according ASTM D7754-11 using AC OXYTRACER

-  **Fast Analysis in <30 Minutes**
-  **Excellent Sensitivity, Repeatability & Linearity**
-  **Robust Solution using AC Deans switch technology**
-  **No Matrix Interference**

Keywords: Oxygenates, ASTM D7754, Dean's switching

INTRODUCTION

International compliance standards dictate strict specifications for ethanol purity and oxygenate content; they also require fuel ethanol to be denatured, rendering it unfit for human consumption. To remain compliant, you must reliably test ethanol for contamination, monitor/report ethanol/methanol concentrations in raw materials, and determine oxygenate levels in finished products. These tests must be performed for bulk fuel ethanol, as well as fuel products blended with ethanol and other oxygenates. Hydro treating and hydro processing are similar processes, which remove impurities such as oxygen that may deactivate process catalysts. Even at ppm levels the presence of oxygen in hydrocarbon feedstocks causes catalyst degradation and reduces the catalyst lifetime. Test method ASTM D7754-11 covers the determination of trace oxygenates in automotive spark-ignition engine fuel. The ethanol blending concentration for which this test method applies ranges from 1 to 15% by volume. The concentration range for the single oxygenates covered by the method is 10 - 2000 ppm.

INSTRUMENTATION

Oxytracer according ASTM D7754 is a multi-dimensional gas chromatographic method, using 1,2-dimethoxy ethane as the internal standard. 14 oxygenates are analyzed: MTBE, ETBE, DIPE, methanol, TAME, n-propanol, i-propanol, n-butanol, i-butanol, tert-butyl alcohol, sec-butyl alcohol, and tert-pentanol. The gas chromatograph is configured with one Split/Splitless (S/SL) Inlet, two capillary columns, one monitor Column, one Flame Ionization Detector (FID) and a Deans switch valve. All flows are EPC controlled. The sample is introduced in the system through the ALS in the S/SL Inlet. A pre separation is made on the pre-column. The oxygenated components are cut from the matrix by applying a pressure switch, directing the effluent from the pre-column either to the monitor column (vent) or to the analysis column (FID detector). The oxygenates are separated on the analysis column in a temperature programmed oven run and detected by the FID

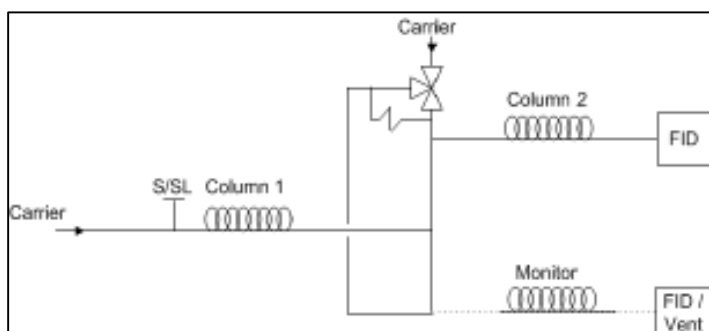


Figure 1. Plumbing diagram for trace oxygenates analyzer according ASTM D7754

PRECOLUMN ANALYSIS

The sample is injected onto a methyl silicone pre-column which elutes lighter hydrocarbons to a monitor column and retains the oxygenated and heavier hydrocarbons. Just before methanol elutes from this column, the valve and thus a PCM pressure is switched and the components coming from the pre-column are directed to the analysis column. After TAME has eluted from the pre-column to the analysis column, the valve is switched back to its original position, switching the pressure again.

All the other components remaining on the pre-column are now directed to the monitor column and the vent. The oxygenated components are now separated from the remaining hydrocarbons on the analysis column and are detected by the Flame Ionization Detector.

According to the ASTM D7754-11 method, a ~ 300 ppm solution without ethanol or internal standard should be injected on the pre-column only (figure 2). From this chromatogram the oxygenate transfer valve time can be determined.

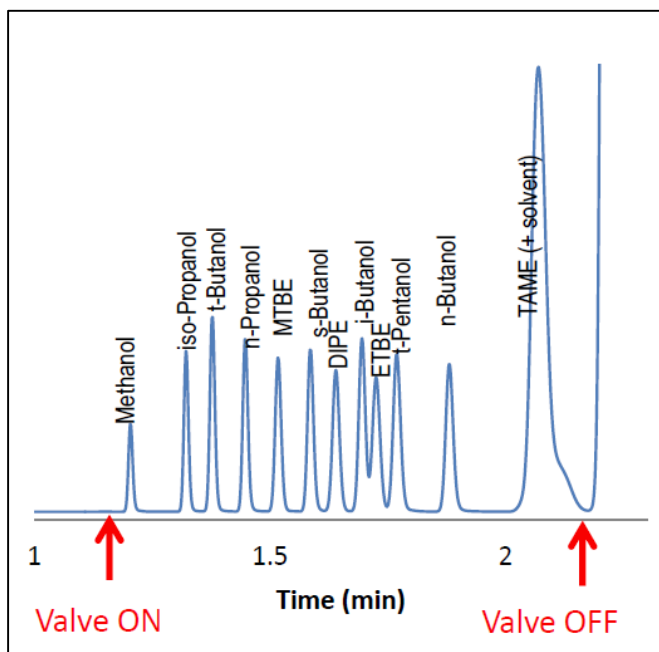


Figure 2. 200 ppm Precolumn mix - Oxygenate Elution Pattern from precolumn only.

VALIDATION

The system and methodology of the Trace Oxygenates analyzer are thoroughly tested for separation efficiency, repeatability, response linearity, recovery and detection levels.

SEPARATION EFFICIENCY

Chromatographic conditions should be optimized to obtain complete separation of the first three eluting peaks (ETBE, MTBE and DIPE). Maximum resolution of these peaks is critical for accurate quantification of each individual component.

REPEATABILITY

Area and retention time are the two primary measurements in gas chromatography. The precision in which they are measured ultimately determines the validity of the generated quantitative data. Retention time and area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exacting tolerances. Furthermore, the inertness of the flow path can considerably affect area precision, especially for active components at low levels.

Area and retention time repeatability for the AC Oxygenates analyzer according ASTM D7754-11 are measured for 10 consecutive runs (table 1) for a standard blend containing approximately 50 ppm per component. Very good repeatability values are obtained.

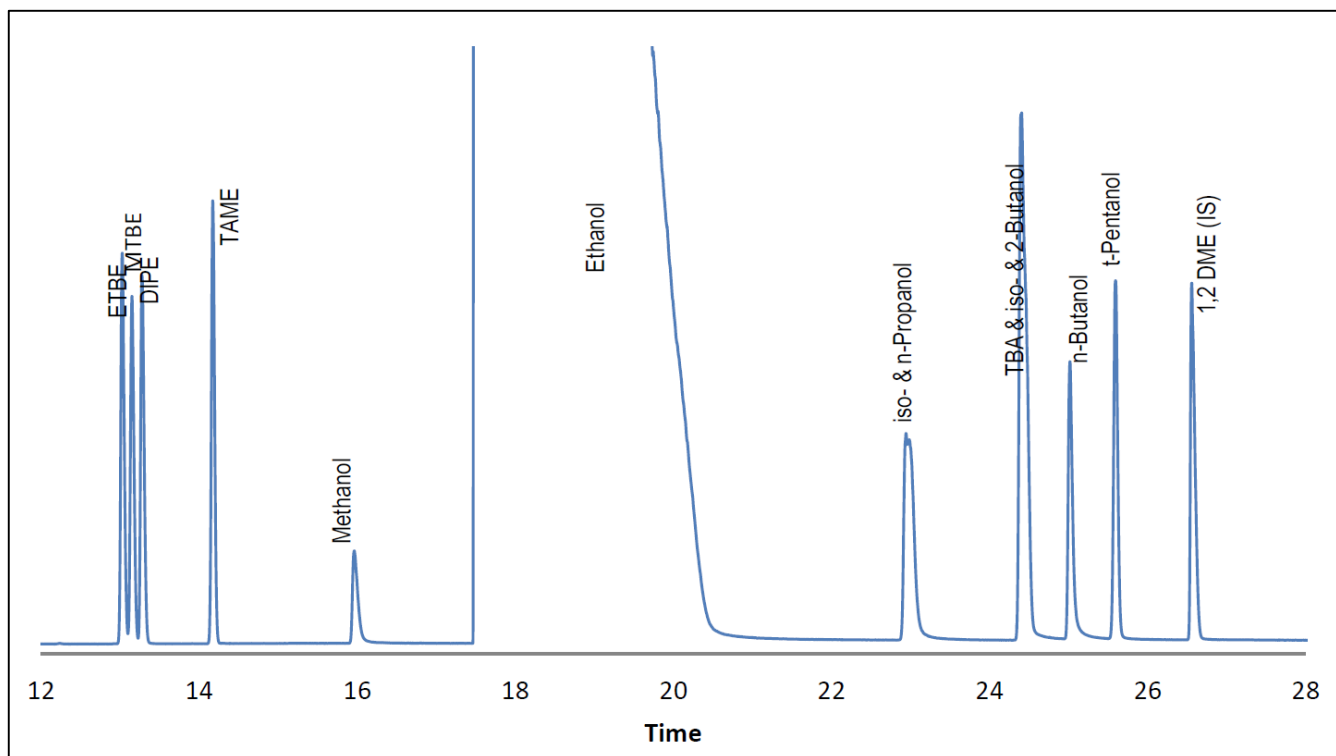


Figure 3. Separation efficiency of 100 ppm standard blend

RUN	ETBE	MTBE	DIPE	TAME	Methanol	N-propanol & i-Propanol	2-Butanol & i-Butanol & t-Butanol	n-Butanol	T-Pentanol
1	43.40	39.62	41.90	46.20	12.41	61.57	118.16	38.16	45.69
2	43.36	39.66	41.94	46.22	12.29	61.63	118.67	38.11	45.63
3	43.39	39.64	41.97	46.28	12.28	61.26	117.92	38.05	45.59
4	43.46	39.71	42.06	46.29	12.19	61.41	118.19	37.90	45.66
5	43.47	39.70	42.07	46.36	12.05	61.26	118.28	38.03	45.67
6	43.54	39.79	42.105	46.41	12.07	61.31	118.51	38.23	45.76
7	43.52	39.76	42.13	46.38	12.26	61.40	118.00	37.79	45.78
8	43.64	39.83	42.19	46.44	12.29	61.69	118.82	38.37	45.82
9	43.58	39.79	42.15	46.46	12.28	61.58	118.71	38.24	45.86
10	43.61	39.80	42.21	46.55	12.20	61.57	118.78	38.25	45.94
Min	43.357	39.619	41.896	46.201	12.052	61.259	117.916	37.792	45.589
Max	43.522	39.830	42.207	46.550	12.415	61.692	118.815	38.368	45.939
Average	43.499	39.729	42.076	46.358	12.233	61.468	118.406	38.113	45.740
Stdev	0.09779	0.07361	0.10882	0.11033	0.10916	0.15899	0.33528	0.17559	0.11078
RSD	0.22%	0.19%	0.26%	0.24%	0.89%	0.26%	0.28%	0.46%	0.24%

Table 1. Area Repeatability for 50 ppm standard blend (n=10), corrected for Internal Standard area

LINEARITY

The linearity of response for the analyzer is verified by analyzing 6 different calibration mixtures in a range of concentration covering the scope of ASTM D7754-11. The set of oxygenate calibration standards consists of 10, 50, 100, 250, 500 and 1000 ppm (m/m). The standards assume ethanol is present in the streams to be analyzed in percent levels, so the calibration for ethanol consists of 1.0, 2.5, 5.0, 7.5, 10 and 15% (m/m). For each component the linearity plots are created (see example figures below). All calibration lines have a linearity correlation > 0.999.

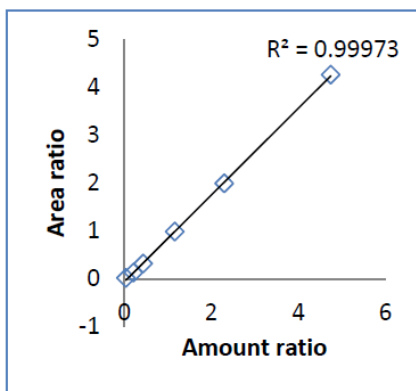


Figure 4: Linearity Plot Methanol

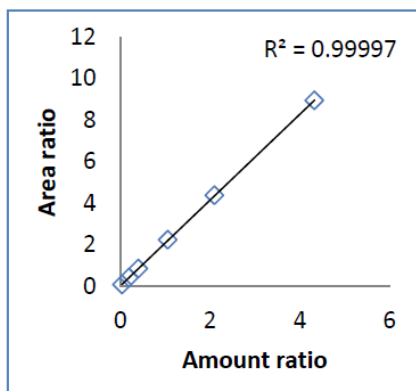


Figure 5: Linearity Plot ETBE

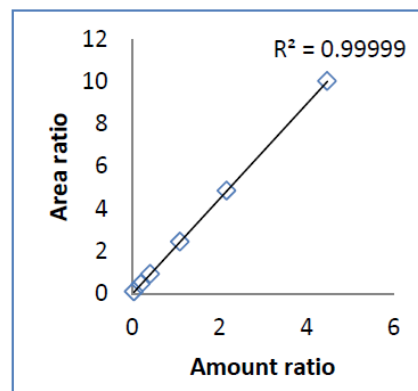


Figure 6: Linearity Plot t-Pentanol

QC REFERENCE MATERIAL

After the calibration has been completed, two quality control check standard reference materials have been analyzed. The two check standards are prepared by diluting an oxygenate stock solution and ethanol in in an oxygenate free automotive spark-ignition fuel sample.

One concentration of the QC reference material is prepared in the lower range (circa 30 ppm) and another in the upper concentration range (500 ppm). The reference material is analyzed as a normal sample. According the method, the oxygenate concentration values obtained should agree within $\pm 15\%$ for the lower range, and $\pm 5\%$ relative for the higher range.

Components	Conc. ppm	Measured ppm	Deviation
ETBE	28.7	27.1	-5.7%
MTBE	28.9	26.1	-9.7%
DIPE	27.9	28.8	3.1%
TAME	29.7	28.4	-4.4%
Methanol	31.5	32.0	1.5%
n-Propanol*	29.8	*	*
i-Propanol*	29.8	*	*
i-Butanol**	30.6	**	**
t-Butanol**	27.7	**	**
n-Butanol	31.0	32.0	3.0%
s-Butanol**	30.5	**	**
tert-Pentanol	29.7	30.1	1.3%
* Coelution SUM	59.7	60.2	0.8%
** Coelution SUM	88.9	90.1	1.3%

Table 2. Recovery Calculation low range QC Sample

Components	Conc. ppm	Measured ppm	Deviation
ETBE	454.8	455.8	0.2%
MTBE	457.6	464.6	1.5%
DIPE	441.4	431.3	-2.3%
TAME	470.2	471.6	0.3%
Methanol	499.1	491.1	-1.6%
n-Propanol*	471.8	*	*
i-Propanol*	472.1	*	*
i-Butanol**	484.1	**	**
t-Butanol**	438.7	**	**
n-Butanol	491.2	483.6	-1.5%
s-Butanol**	483.1	**	**
tert-Pentanol	470.6	468.6	-0.4%
* Coelution SUM	943.9	937.8	-0.6%
** Coelution SUM	1405.9	1396.0	-0.7%

Table 3. Recovery calculation high range QC Sample

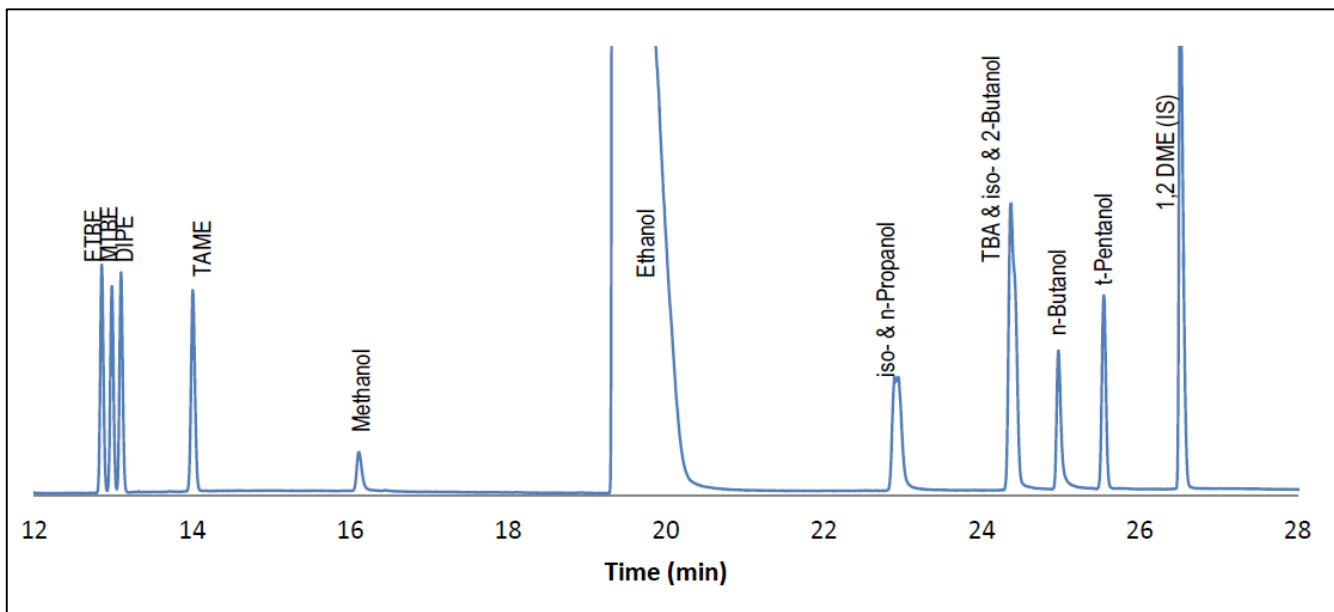


Figure 7: Chromatogram of 30 ppm QC reference material.

VERIFICATION OF DETECTABILITY

To verify the detectability of the system, a 5 ppm (m/m) calibration solution should be injected, and ensured that a signal/noise level of at least 5 is observed.

DETECTABILITY

Figure 8 shows the signal to Noise verification of the 5 ppm Oxygenates / 1.0 % Ethanol check standard. It clearly show the signal to noise ratio is > 5 for all oxygenates.

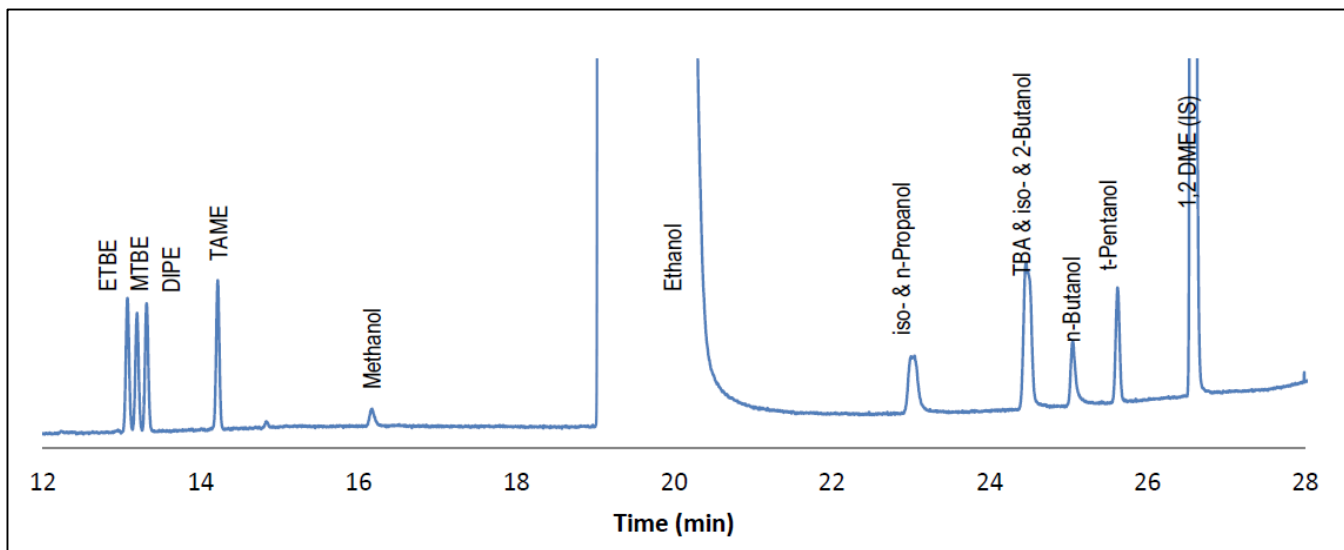


Figure 8: Chromatogram of 5 ppm QC check sample to calculate detectivity.

CONCLUSION

The AC Trace oxygenates analyzer is a dedicated solution for determination of traces Oxygenates in Automotive Spark Ignition Engine Fuel by Deans Switch Gas Chromatography. Its performance not only meets but exceeds ASTM D7754-11, ensuring the best quality data that can be used to estimate oxygenates in downstream processes or car engine management.

The application of a FID detector, well known for its stability and ruggedness, in combination with the proprietary AC Deans Switch Technology makes AC Oxytracer very robust and easy to use in routine environments. Because the analysis column is free of interfering components, AC Oxytracer provides unambiguous identification and accurate quantitation every time. The hydrocarbon matrix is vented for the fastest run to run cycle time of under 30 minutes to guarantee the highest possible sample throughput.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer®, DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.