

Determination of Oxygenates in C2, C3, C4 and C5 hydrocarbon Matrices according ASTM D7423-09 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 D7423, Dean's switching

INTRODUCTION

The determination of oxygenates is important in the manufacture of ethene, propene, 1,3-butadiene, C4 hydrocarbons and C5 hydrocarbons. Alcohols, ethers, aldehydes and ketones are known trace impurities in these hydrocarbons. Even at ppm levels the presence of oxygen in hydrocarbon feedstocks decrease catalyst activity in downstream polymerization processes.

Test method ASTM D7423-09 covers the gas chromatographic procedure for the quantitative determination of organic oxygenates in C2, C3, C4, and C5 matrices. The test method is applicable when the hydrocarbon matrices have final boiling point not greater than 200 °C. The linear working range for oxygenates is 0,50 mg/kg to 100 mg/kg.

INSTRUMENTATION

The test method is intended to determine the mass concentration of each oxygenate in the hydrocarbon matrix. The detector response and retention times for each oxygenate peak in a calibration standard is measured and used to externally calibrate the flame ionization detector response. The concentration of each oxygenate is calculated by the external standard technique. Calibration materials are listed in table 1. The gas chromatograph is configured with one Split / Splitless Inlet (S/SL), two capillary columns, one monitor column, one or two Flame Ionization Detectors (FID), two automated valves (one Gas Sampling Valve (GSV) and one Liquid Sampling Valve (LSV)), one sample shut off valve, a back pressure regulator and a Deans switch valve. All flows are EPC controlled. The sample is introduced in the system through the Automatic Liquid Sampler, LSV or GSV in the Split / Splitless Inlet (S/SL). 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 or to the analysis column. The oxygenates are separated on the analysis column in a temperature programmed oven run and detected by the Flame Ionization Detector.

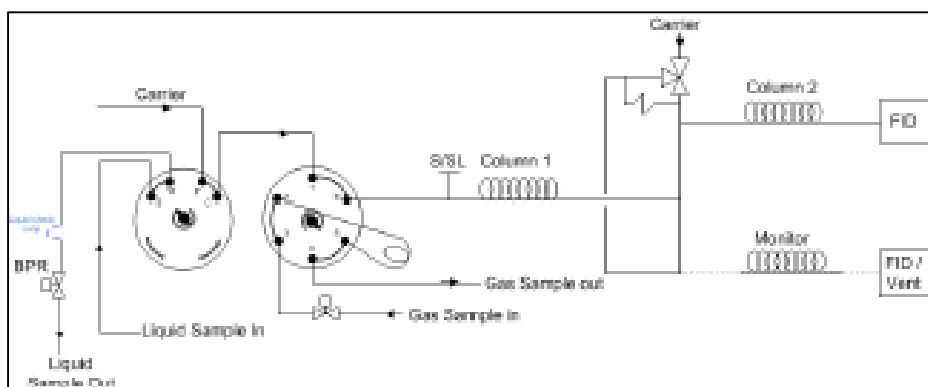


Figure 1. Plumbing diagram for trace oxygenates analyzer according ASTM D7423

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

SAMPLES

Analytical Controls delivers two dedicated liquid samples to completely validate and calibrate the Trace Oxygenates analyzer according ASTM D7423-09. The composition of the samples are mentioned in table 1. An overlay of the elution profile is pictured in Figure 2 (samples diluted to approx. 25 ppm).

Sample #	Components
2	Dimethyl ether
2	Diethylether
2	Acetaldehyde
1	Ethyl tert-butyl ether (ETBE)
1	Methyl tert-butyl ether (MTBE)
1	Diisopropyl ether (DIPE)
2	Propionaldehyde (propanal)
1	Tertiary amyl methyl ether (TAME)
2	Propylether
2	Isobutylaldehyde
2	Butylaldehyde
1	Methanol
1	Aceton
2	Isovaleraldehyde
2	Valeraldehyde
1	2-Butanone (MEK)
1	Ethanol
1	n-Propanol* (co-elution)
1	i-Propanol* (co-elution)
2	Allylalcohol
1	2-Butanol** (co-elution)
1	i-Butanol** (co-elution)
1	t-Butanol** (co-elution)
1	n-Butanol

Table 1. Calibration components ASTM D7423

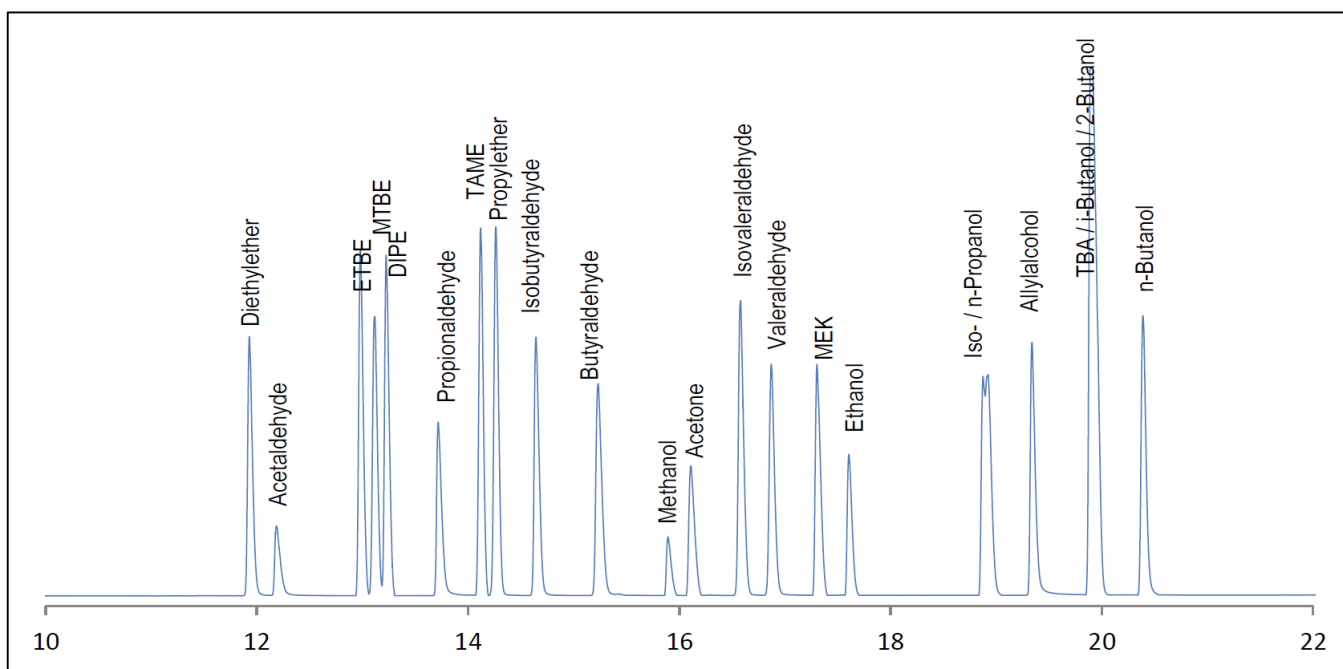


Figure 2. Overlay of AC calibration samples by LSV injection @25 ppm each component

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.

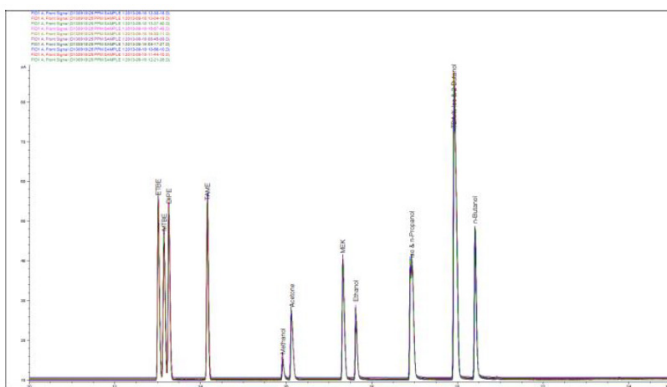


Figure 3: Repeatability overlay of 10 consecutive runs in ASTM D7423-09 - LSV injection.

Area and retention time repeatability for the AC Oxygenates analyzer according ASTM D7423-09 are measured for 10 consecutive runs for a standard blend containing approximately 25 ppm per component by LSV (figure 3). Retention time repeatability of some key components is calculated in table 2.

Area and retention time repeatability results for GSV injection are measured by analyzing a calibration gas for 10 consecutive runs, injected by the gas sampling valve (figure 4). Very good repeatability values are obtained (table 3 and 4).

RUN	RETENTION TIME (minutes)					
	ETBE	MTBE	DIPE	TAME	MEK	N-Butanol
1	13.02	13.15	13.27	14.17	17.31	20.40
2	13.01	13.15	13.26	14.16	17.32	20.40
3	13.02	13.15	13.26	14.17	17.31	20.40
4	13.01	13.15	13.26	14.16	17.32	20.41
5	13.02	13.15	13.27	14.17	17.32	20.41
6	13.01	13.15	13.26	14.17	17.32	20.40
7	13.02	13.15	13.27	14.17	17.32	20.41
8	13.02	13.16	13.27	14.17	17.33	20.41
9	13.02	13.16	13.27	14.17	17.33	20.42
10	13.01	13.14	13.25	14.16	17.33	20.42
MIN	13.01	13.14	13.25	14.16	17.31	20.40
MAX	13.02	13.16	13.27	14.17	17.33	20.42
Average	13.02	13.15	13.26	14.17	17.32	20.41
Stdev	0.005	0.004	0.005	0.005	0.006	0.006
RSD	0.04%	0.03%	0.03%	0.03%	0.03%	0.03%

Table 2: Retention time repeatability of a standard blend in ASTM D7423-09 by LSV introduction

Run	RETENTION TIME (Minutes)		
	MTBE	Methanol	Aceton
1	13.132	15.886	16.101
2	13.133	15.889	16.102
3	13.133	15.890	16.103
4	13.136	15.894	16.113
5	13.137	15.895	16.113
6	13.139	15.894	16.113
7	13.138	15.898	16.116
8	13.139	15.896	16.114
9	13.140	15.895	16.116
10	13.141	15.899	16.118
MIN	13.132	15.886	16.101
MAX	13.141	15.899	16.118
AVERAGE	13.137	15.894	16.111
Stdev	0.003	0.004	0.006
RSD	0.02%	0.03%	0.04%

Table 3: Retention time repeatability of a standard blend by GSV introduction

Run	AREA (pA*s)		
	MTBE	Methanol	Aceton
1	296.05	26.15	73.32
2	296.18	26.13	73.52
3	295.45	25.96	73.40
4	295.27	25.96	73.31
5	295.23	25.99	73.21
6	294.61	25.96	73.16
7	294.67	26.03	73.14
8	294.43	25.84	72.90
9	294.36	24.76	73.40
10	293.75	25.06	73.54
MIN	293.75	24.76	72.90
MAX	296.18	26.15	73.54
AVERAGE	295.00	25.78	73.29
Stdev	0.77	0.47	0.19
RSD	0.26%	1.84%	0.27%

Table 4: Area repeatability of a standard blend by GSV introduction

LINEARITY

The linearity of response for the analyzer is verified by analyzing 5 different calibration mixtures by LSV in a range of concentration covering the scope of ASTM D7423-09.

The set of oxygenate calibration standards consists of 5, 10, 25, 50 and 100 ppm (m/m). For each component the linearity plots are created (see example figures below). All calibration lines have a linearity correlation > 0.999.

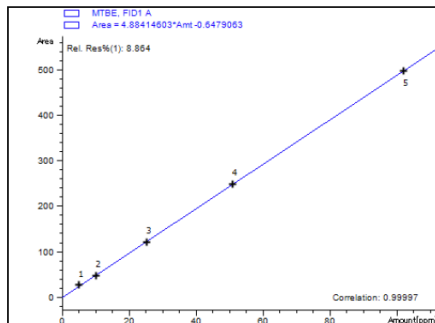


Figure 4: Linearity Plot MTBE

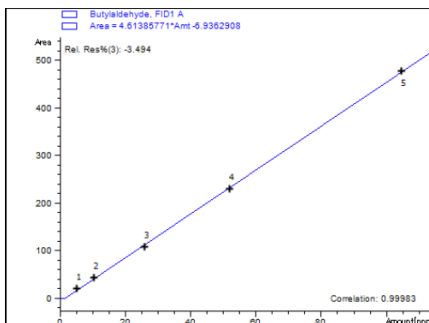


Figure 5: Linearity Plot Butyraldehyde

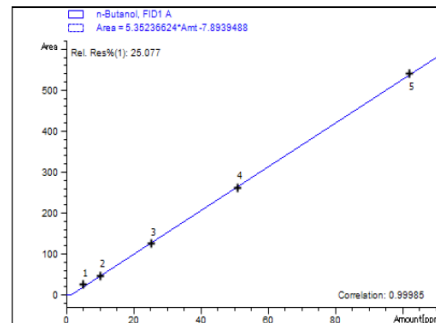


Figure 6: Linearity Plot n-Butanol

DETECTABILITY

To verify the detectability of the system, a 5 ppm (m/m) calibration solution is injected by LSV and GSV, as mandated by the method. Detection limit is calculated according to the below formula. Results are listed in Tables 5 and 6, the chromatogram is figure 7.

$$LDL = \frac{3 * c * N}{A} * W * 60$$

LDL = Lower detection limit (ppm weight)
C = Concentration of component of interest (ppm weight)
N = Noise (peak to peak) (pA)
A = Area of peak of interest (pA * s)
W = Width of peak at half height (minutes)

Component	Noise (pA)	Area (Pa*s)	Conc. (ppm)	Width (min)	LDL (ppm)
Diethylether	0.0138	20.14	5.20	0.0456	0.03
Acetaldehyde	0.0138	5.13	5.12	0.0456	0.11
Ethyl tert-butyl ether (ETBE)	0.0138	28.40	5.13	0.0450	0.02
Methyl tert-butyl ether (MTBE)	0.0138	24.70	5.13	0.0456	0.02
Diisopropyl ether (DIPE)	0.0138	27.94	5.13	0.0446	0.02
Propionaldehyde (propanal)	0.0138	13.85	5.26	0.0444	0.04
Tertiary amyl methyl ether (TAME)	0.0138	29.72	5.13	0.0439	0.02
Propylether	0.0138	28.74	5.09	0.0483	0.02
Isobutylaldehyde	0.0138	20.76	5.11	0.0461	0.03
Butylaldehyde	0.0138	20.28	5.18	0.0544	0.03
Methanol	0.0138	2.30	5.13	0.0461	0.26
Aceton	0.0138	12.16	5.13	0.0489	0.05
Isovaleraldehyde	0.0138	26.04	5.18	0.0517	0.03
Valeraldehyde	0.0138	19.91	5.14	0.0522	0.03
2-Butanone (MEK)	0.0138	21.30	5.13	0.0494	0.03
Ethanol	0.0138	9.88	5.13	0.0437	0.06
n-Propanol & i-propanol	0.0138	32.96	10.26	0.0908	0.07
Allylcohol	0.0138	18.50	5.16	0.0456	0.03
TBA&Iso-&2-Butanol	0.0138	71.17	15.39	0.0692	0.04
n-Butanol	0.0138	22.77	5.13	0.0467	0.03
Methyl tert-butyl ether (MTBE)	0.0146	309.95	10.07	0.0561	0.01
Methanol	0.0146	26.65	5.34	0.0528	0.03
Aceton	0.0146	76.71	5.10	0.0622	0.01

Table 5: Lower Detection Levels for individual oxygenates using LSV injection

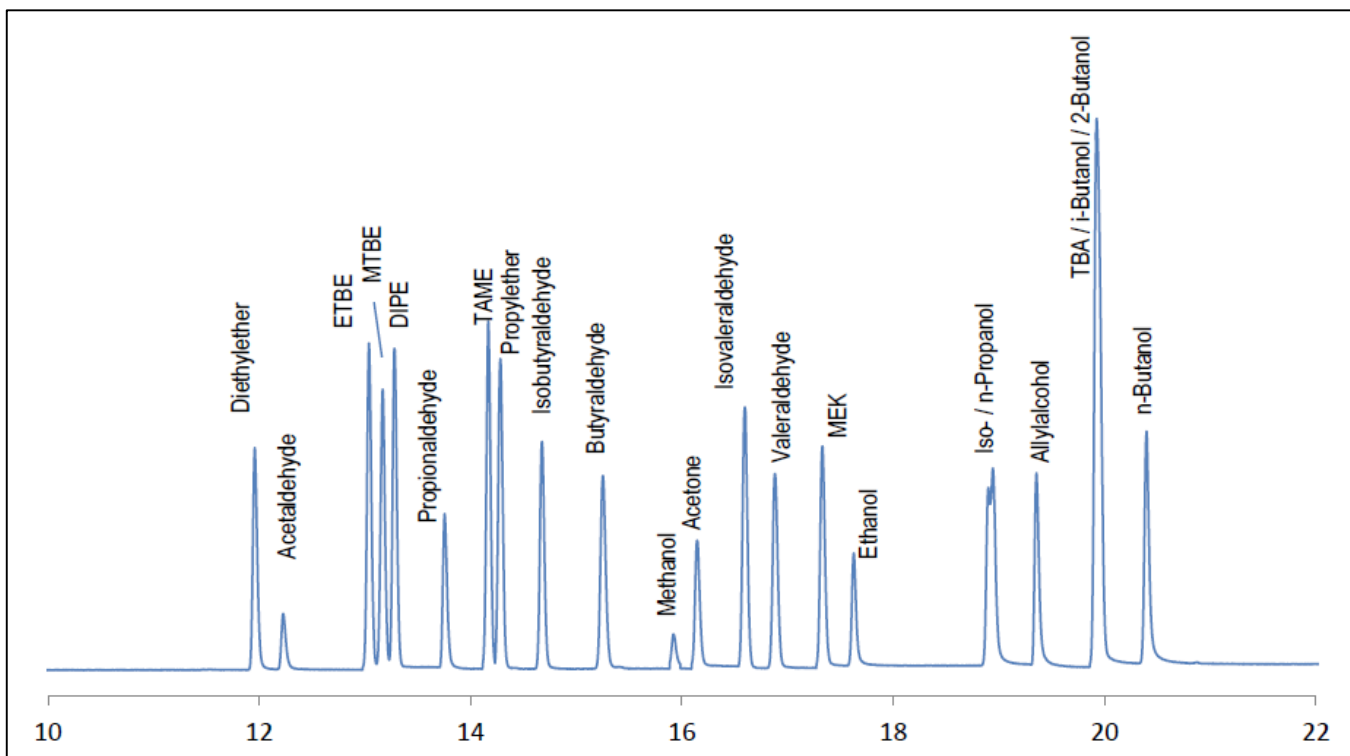


Figure 7: 5 ppm QC sample injected by LSV to calculate detectability

CONCLUSION

The AC Trace oxygenates analyzer (Oxytracer) is a dedicated solution for accurate determination of traces Oxygenates in Automotive Spark Ignition Engine Fuel by Deans Switch Gas Chromatography. Its performance not only meets but exceeds ASTM D7423-09 requirements, ensuring the best quality data that can be used to estimate effects of oxygenates in downstream fuel blends and blend processes.

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.