



APPLICATION NOTE 204WA0712E

Oxygenates Analysers

EN 13132 ASTM D4815 G.A.S offers custom configured GC analysers for complex separations, data processing and reporting. We have over 35 years of experience in designing and building turnkey analysers for many application fields. Our analysers are designed to meet many accepted standard methods (like GPA, ASTM, UOP, ISO, etc.) in the Oil and Gas industry. The efficient configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.

Automobile emission is reduced nowadays by replacing the usual anti-knock components with oxygenated additives like ethers and alcohols. The type and concentration of these various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. The analysis of these compounds is described in standardised methods ASTM D4815 and EN 13132.

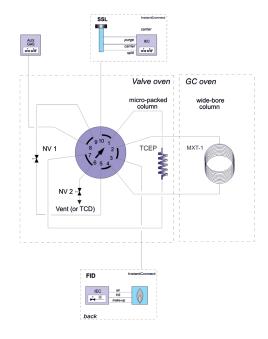


Diagram ASTM D4815 analyser

16 1. methanol 2. ethanol 10 isopropanol 4. tert-butanol 5. n-propanol 6. methyl tert-butyl ether 7. sec-butanol 8. diisopropyl ether (DIPE) 9. isbutanol ethyl-tert-butyl ether (ETBE) 11. tert-amyl ether 12 12. dimethoxyethane (DME) 13. n-butanol benzene 15. tert-amyl methyl ether 16. total heavy hydrocarbons in. 20

Chromatogram ASTM D4815

ASTM D4815

ASTM method D4815 describes the use of 2 separation columns, a 10-port column switching valve, liquid injection using SSL, and FID detection. The first separation column (a highly polar micro-packed TCEP column) retains the oxygenates and the heavy hydrocarbons, while the light hydrocarbons are directed to a vent. The oxygen containing components are subsequently injected onto a non-polar wide-bore column by switching the valve, and separated according to their boiling point order. After eluting TAME (tert-amyl methyl ether), the valve is switched back and the heavy hydrocarbon fraction is backflushed to the detector. Siltek®/Sulfinert® treated tubing is used to prevent adsorption of oxygenates in the sample pathway. The 10-port diaphragm valve is located in an independently heated isothermal valve oven, mounted on top of the GC, avoiding any cold spots and ensuring long valve life time.





G A S diaphragm valve



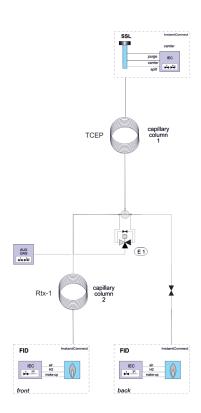
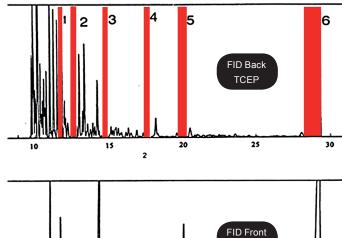
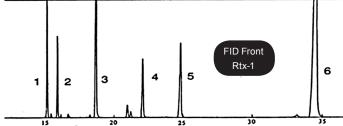


Diagram EN 13132



Trace 1310 GC with optional AS1310 autosampler for liquid samples





Chromatograms EN 13132. Red areas: cutting windows containing oxygenates

EN 13132

Standardised method EN13132 is an alternative to ASTM D4815. Two narrow bore capillary columns are used for enhanced selectivity for oxygenated components. In contrast to D4815, multiple fractions are transferred from the first to the second column using a Deans Heartcut configuration, see the chromatogram (red windows). This results in even higher selectivity, since many hydrocarbon components are excluded from entering the second column, and therefore cannot cause false positive results.

Trace 1300 GC

GAS offers ASTM D4815 and EN 13132 on Thermo Trace 1300 GC series. InstantConnect injector and detector modules guarantee high uptime and easy maintenance.



InstantConnect injector and detector technology



Specifications

ASTM D4815

Sample requirements:

Application: Analysis of oxygenated components (alcohols and ethers) in liquid gasoline samples

Configuration: Single channel instrument based on Thermo Trace 1300 GC series with SSL, valve oven and FID

Optional: Automated liquid sample injector Sample tubing: Sulfinert® tubing for inert sample path

Analytes: see chromatograms

Dynamic range: Alcohols 0,1-12 mass%; ethers 0,1-20 mass%

Analysis Time: 25 minutes Minimum Detectability: > 0.01% for all individual components

Liquid sample

Repeatability: > 2% RSD (n=10)

Data systems Chromeleon, ChromCard, OpenLab, EZChrom, ChromQuest

118486400.00 112398168.00 114292002.00 116390923.00 133795125.00 126432574.00 128557785.00 130986661.00 156237140.00 147946145.00 150113173.00 152816665.00 61566054.00 62799844.00 63886931.00 92020934.00 94106693.00 95792708.00 185972432.00 113729828.00 128163965.00 93924491.00 157716594.00 63415742.00 115583013.00 151832433.00 Max 98073652.00 64983316.00 118486400.00 133795125.00 190598015.00 156237140.00 164676943.00 Mean: Std Dev: 63085248.80 115194362.50 129763822.00 184435484.40 151604026.60 94801531.10 159593332.60

130257330.00

127490613.00

Area

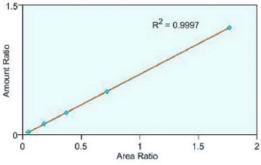
115167155.00 115711239.00

113277238.00

Area

61926993.00

64983316.00



iso-butanol Area	ETBE Area	DME Area	TAA Area	n-butanol Area	benzene Area	TAM Are
187948753.00	104301002.00	213134173.00	77548694.00	172727124.00	196602543.00	196464683.0
183245406.00	101649670.00	207584855.00	75587109.00	168155405.00	192498522.00	191066018.0
183779397.00	101972250.00	208438393.00	75901233.00	168617375.00	193279798.00	191848936.0
180088586.00	100546119.00	201269247.00	74394422.00	165526128.00	189573064.00	188548990.0
188889541.00	106054778.00	216368082.00	78371451.00	173243074.00	199106415.00	199040250.0
178251549.00	100002235.00	200901944.00	73738215.00	164289728.00	187670455.00	186426030.0
181006617.00	101787268.00	205269188.00	75039952.00	166483876.00	191553999.00	190112580.0
183856608.00	103719848.00	208635343.00	76471452.00	169071195.00	195033347.00	193549997.0
180762820.00	101849101.00	204971301.00	74951308.00	166232712.00	190865845.00	190199882.0
183379319.00	102309018.00	206613902.00	75894519.00	168083444.00	193591466.00	192092415.0
178251549.00	100002235.00	200901944.00	73738215.00	164289728.00	187670455.00	186426030.0
188889541.00	106054778.00	216368082.00	78371451.00	173243074.00	199106415.00	199040250.0
183120859.60	102419128.90	207318642.80	75789835.50	168243006.10	192977545.40	191934978.10
3342965.94	1805204.68	4792903.33	1402742.08	2908088.92	3364341.67	3689983.4
1.83	1.76	2.31	1.85	1.73	1.74	1.9

181083453.00

Linearity MTBE (D4815)

Repeatability D4815

EN 13132

Application: Analysis of oxygenated components (alcohols and ethers) in liquid gasoline samples

Configuration: Single channel instrument based on Thermo Trace 1300 GC series with SSL and double FID

Optional: Automated liquid sample injector

Analytes: see chromatograms Sample requirements: Liquid sample **Analysis Time:** 35 minutes

Minimum Detectability: > 0.01% for all individual components

Repeatability: > 2% RSD (n=10)

Chromeleon, ChromCard, Data systems

OpenLab, EZChrom, ChromQuest



Trace 1310 GC with auxiliary oven

Optional:

MTBE

160027158.00

156884630.00

164676943 00

155665435.00 157934608.00

96730492.00 94548119.00 94785798.00 93080557.00

98073652.00

154701553.00 151462471.00

149044444.00

Combining methods like ASTM D4815, D3606, D5580 in a single instrument. Investments are reduced and bench space is saved in this way.



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