Oxygenates analyser

- ASTM D4815, EN 13132
- optional D5580 / D3606 integration
- highest uptime

AN 204WA0625G

GAS offers custom configured GC analysers for many application fields for over 40 years. GAS analysers are designed to meet many standardised methods from GPA, ASTM, UOP, ISO, EN and others. The efficient configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.

Oxygenated components like ethers and alcohols are used as additives to reduce engine knocking and increase fuel's octane rating. Anti-knock agents 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.

ASTM D4815

ASTM method D4815 describes the use of 2 separation columns, 10-port switching valve, liquid sample injection and FID detection (figure 1). The first separation column (a highly polar micro-packed TCEP column) retains oxygenates and heavy hydrocarbons, while light hydrocarbons are vented. Then the oxygen containing components are 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 (see figure 2). 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, avoiding any cold spots and ensuring long valve life time.

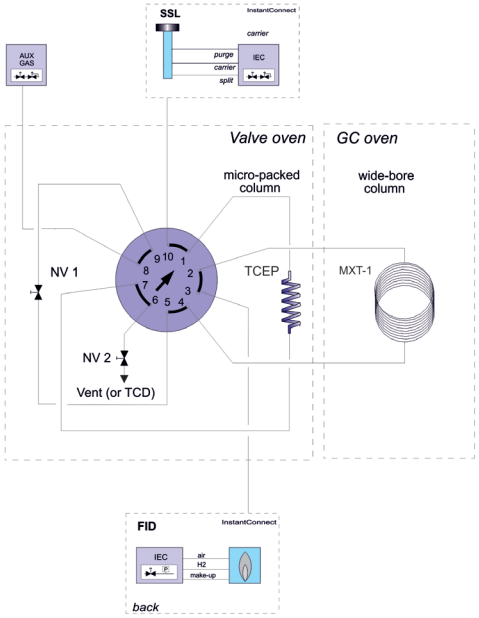

Figure 1. Diagram ASTM D4815 analyser

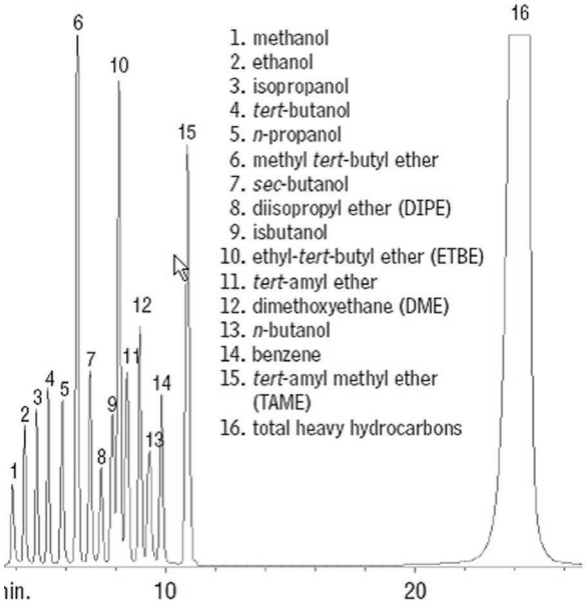

Figure 2. Chromatogram ASTM D4815

Figure 3. Trace GC1600 with autosampler for liquid samples

EN 13132

Standardised method EN13132 is an alternative to ASTM D4815. Two narrow bore capillary columns are used for enhanced selectivity for oxygenated components (figure 5). In contrast to D4815, multiple heartcut fractions are transferred from the first column (TCEP) to the second column (Rtx-1) using a Deans Heartcut switch configuration (see figure 4; each green windows represents a heartcut). The result is a highly selective separation, since many hydrocarbon components are excluded from entering the second column, offering reliable component identification.

Trace 1600 GC

GAS offers ASTM D4815 and EN 13132 on Thermo Trace 1600 GC series. InstantConnect injector and detector modules guarantee high uptime and easy maintenance (figure 3, 6).

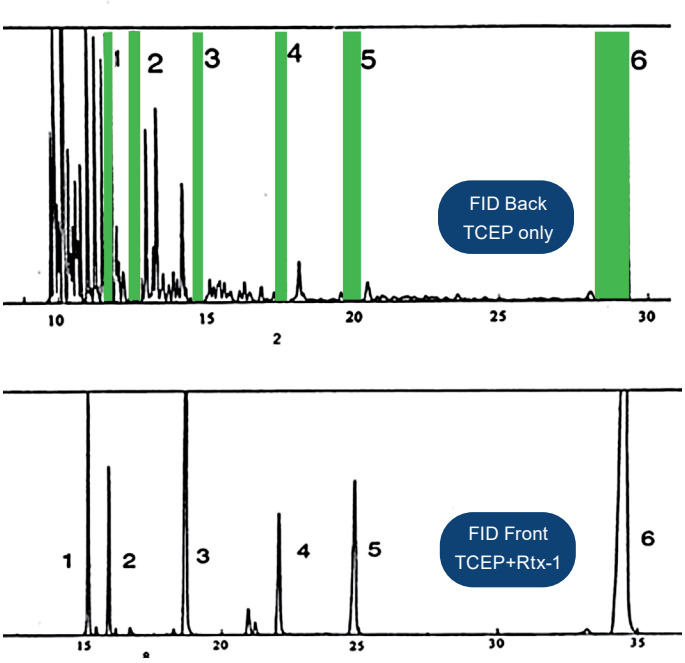

Figure 4. Chromatograms EN 13132. Green windows: multiple heartcut fractions containing oxygenated components.

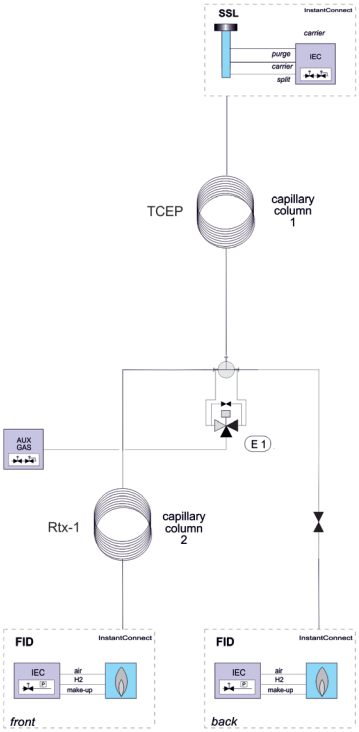

Figure 5. Diagram EN 13132

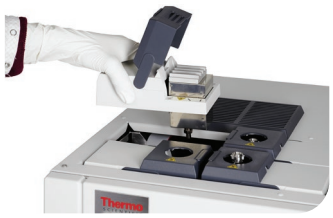

Figure 6. InstantConnect injector and detector technology

Combine methods: highly efficient!

Standardised methods can efficiently be combined in a single instrument, taking full advantage of GC1600's potential (figure 7). Integrating for instance ASTM D4815, D3606 and D5580 offers small footprint and low purchase costs, providing small bench space requirement and short return on investment.

Figure 7. Trace GC1600 with XXL valve oven and 4 detectors

Specification

ASTM D4815

Application:	Analysis of oxygenated components (alcohols and ethers) in liquid gasoline samples
Configuration:	Single channel instrument based on Thermo Trace 1600 GC series with SSL, valve oven and FID
Optional:	Automated liquid sample injector
	Integrate 1-4 standardised methods in a single instrument (like ASTM D4815, D3606 and D5580)
Sample tubing:	Sulfinert® tubing for inert sample path
Analytes:	see figure 2
Dynamic range:	Alcohols 0,1-12 mass%; ethers 0,1-20 mass%
Sample requirements:	Liquid sample
Analysis Time:	25 minutes
Minimum Detectability:	> 0.01% for all individual components
Repeatability:	> 2% RSD (n=10)
Data systems	Chromeleon, OpenLab

FID Back	methanol Area	ethanol Area	iso-propanol Area	tert-butanol Area	n-propanol Area	MTBE Area	sec-butanol Area	DIPE Area
	63270608.00	116907659.00	132222037.00	188493863.00	154701553.00	96730492.00	163275989.00	103948218....
	63107282.00	115167155.00	129645627.00	184103697.00	151462471.00	94548119.00	159355677.00	101323061....
	63488695.00	115711239.00	130257330.00	184986922.00	152205250.00	94785798.00	160027158.00	101459211....
	61926993.00	113277238.00	127490613.00	181083453.00	149044444.00	93080557.00	156884630.00	99751325.00
	64983316.00	118486400.00	133795125.00	190598015.00	156237140.00	98073652.00	164676943.00	105471776....
	61566054.00	112398168.00	126432574.00	179676025.00	147946145.00	92020934.00	155665435.00	98601285.00
	62799844.00	114292002.00	128557785.00	182513989.00	150113173.00	94106693.00	157934608.00	100944516....
	63886931.00	116390923.00	130986661.00	185972432.00	152816665.00	95792708.00	160705901.00	102649199....
	62407023.00	113729828.00	128163965.00	182257677.00	149680992.00	93924491.00	157716594.00	100864102....
	63415742.00	115583013.00	130086503.00	184668771.00	151832433.00	94951867.00	159690391.00	101682148....
Min:	61566054.00	112398168.00	126432574.00	179676025.00	147946145.00	92020934.00	155665435.00	98601285.00
Max:	64983316.00	118486400.00	133795125.00	190598015.00	156237140.00	98073652.00	164676943.00	105471776....
Mean:	63085248.80	115194362.50	129763822.00	184435484.40	151604026.60	94801531.10	159593332.60	101669484....
Std Dev:	985627.10	1828076.99	2221860.17	3326686.29	2556404.72	1746190.60	2787590.17	1973200.34
%RSD:	1.56	1.59	1.71	1.80	1.69	1.84	1.75	1.94

iso-butanol Area	ETBE Area	DME Area	TAA Area	n-butanol Area	benzene Area	TAME Area
187948753.00	104301002.00	213134173.00	77548694.00	172727124.00	196602543.00	196464683.00
183245406.00	101649670.00	207584855.00	75587109.00	168155405.00	192498522.00	191066018.00
183779397.00	101972250.00	208438393.00	75901233.00	168617375.00	193279798.00	191848936.00
180088586.00	100546119.00	201269247.00	74394422.00	165526128.00	189573064.00	188548990.00
188889541.00	106054778.00	216368082.00	78371451.00	173243074.00	199106415.00	199040250.00
178251549.00	100002235.00	200901944.00	73738215.00	164289728.00	187670455.00	186426030.00
181006617.00	101787268.00	205269188.00	75039952.00	166483876.00	191553999.00	190112580.00
183856608.00	103719848.00	208635343.00	76471452.00	169071195.00	195033347.00	193549997.00
180762820.00	101849101.00	204971301.00	74951308.00	166232712.00	190865845.00	190199882.00
183379319.00	102309018.00	206613902.00	75894519.00	168083444.00	193591466.00	192092415.00
178251549.00	100002235.00	200901944.00	73738215.00	164289728.00	187670455.00	186426030.00
188889541.00	106054778.00	216368082.00	78371451.00	173243074.00	199106415.00	199040250.00
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	3689983.45
1.83	1.76	2.31	1.85	1.73	1.74	1.92

Figure 8. Repeatability D4815

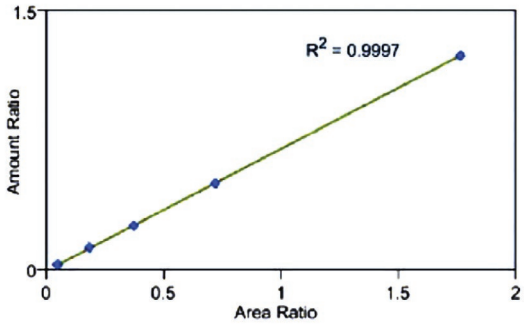

Figure 9. Linearity MTBE (D4815)

EN 13132

Application:	Analysis of oxygenated components (alcohols and ethers) in liquid gasoline samples
Configuration:	Single channel instrument based on Thermo Trace 1600 GC series with SSL and double FID
Optional:	Automated liquid sample injector
Analytes:	Organic oxygenates components, see EN 13132
Sample requirements:	Liquid sample
Analysis Time:	35 minutes
Minimum Detectability:	> 0.01% for all individual components
Repeatability:	> 2% RSD (n=10)
Data systems	Chromeleon

Global Analyser Solutions

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