GLOBAL™ ANALYSER SOLUTIONS

G·A·S

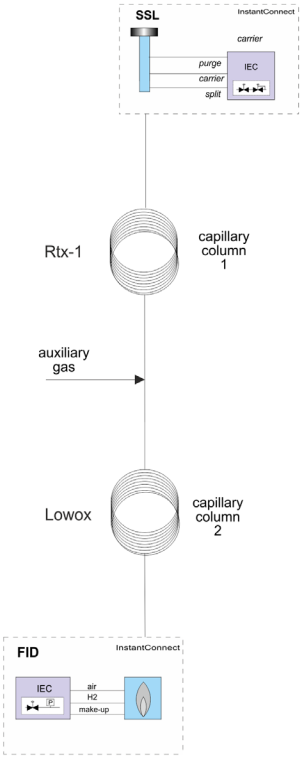
APPLICATION NOTE 218WA1113A

Low Level Oxygenates Analyser

UOP 960
ASTM D7423

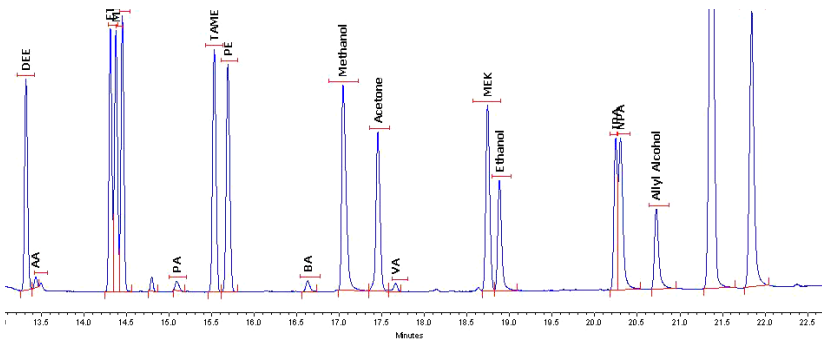
G·A·S offers custom configured GC analysers for complex separations, data processing and reporting. We have over 35 years of experience in designing and building turnkey analysers for many application fields. Our analysers are designed to meet many accepted standard methods (like GPA, ASTM, UOP, ISO, 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.

The low level oxygenates analyser from G·A·S analyses oxygen containing components like alcohols and ethers at (sub) ppm level. The presence of of these components in hydrocarbon feedstock reduces catalyst lifetime, even at low ppm level. From environmental requirements low level oxygenated component also need to be analysed at low levels. The analyser complies with ASTM D7423 and UOP 960.



ASTM D7423

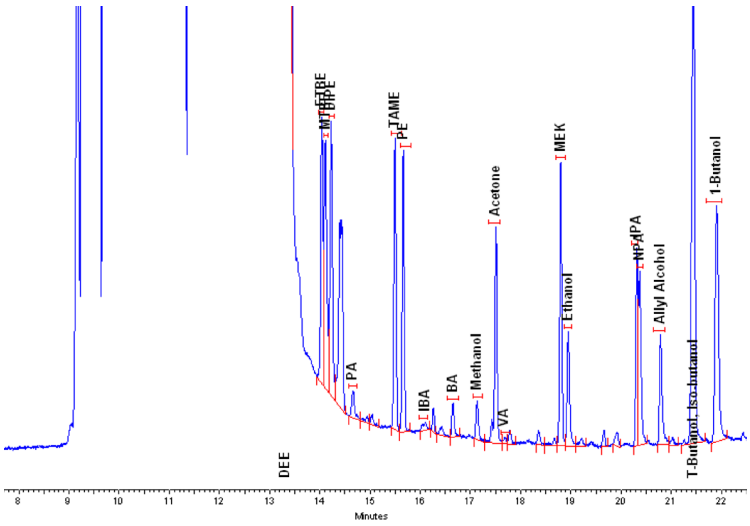
Methods ASTM D4815 and EN 13132 cover the analysis of oxygenates components in finished products at (sub) % level, while the described method covers the 0.1-1000 ppm range. A highly selective capillary column (Lowox) separates the components of interest from the hydrocarbon matrix. Heavier components are backflushed using a Deans column switch configuration. Oxygen containing compounds with boiling points up to 100 °C are analysed in hydrocarbon streams with final boiling point below 250 °C. In the diagram an injector for liquid samples is shown. GSV (Gas Sampling Valve) and LSV (Liquid Sampling Valve) with pressure facility are available as well.



Chromatogram: Lowox calibration standard 100 ppm

LOWOX CALIBRATION STANDARD
(100 ppm for each component)

Dimethylether
Acetaldehyde
Methanol
Ethanol
Propylether
Propionaldehyde
iso-propanol
T-Butanol
Propanol
Methyl Ethyl Ketone
Diethylether
Iso-Butanol
N-Butanol
Iso-Butanal
Buteraldehyde
Ethyl Tert Butyl Ether
Di-Isopropylether
Methyl Tert Butyl Ether
Tert Amyl Methyl Ether TAME
Acetone
Valeraldehyde
Allyl Alcohol



Chromatogram: oxygenates free gasoline spiked with 100 pmm calibration standard

Trace 1310 GC with InstantConnect injector and detector technology

Lowox analysis using GC-MS: The next step

The latest high yield catalyst are extremely prone to poisoning by feedstock impurities like oxyenated components. Therefore a solution based on GC-MS was developed for substantial increase in identification and sensitivity compared to GC-FID analyses. The table below shows sensitivity gains of the individual oxygenated components in naphta. The gain is particulary significant when SIM mode is used. The ISQ mass spectrometer conveniently combines full scan and SIM in a single run for both increased sensitivity and reliable identification.

Name	MS (FS), *S/N*	MS (EIC), *S/N*	MS (SIM), *S/N*	%RSD
Diethyl ether	1.2	2.6	81	9.27
Acetaldehyde	0.2	4.1	10	18.9
ETBE	0.6	9.9	66	7.56
MTBE	0.6	3.1	53	6.84
Diisopropylether	0.7	6.5	70	10.1
Propanal	0.3	6.6	27	11.9
t-Amyl ether	1.1	4.4	64	4.60
Propyl ether	1.3	17	70	6.56
iso-Butanal	0.4	5.0	38	5.35
Butyraldehyde	0.8	4.4	23	2.31
Methanol	1.5	1.8	6.5	12.2
Acetone	0.8	18	100	7.21
Valeraldehyde	1.5	8.4	177	5.09
MEK	1.3	2.0	4.4	10.9
Ethanol	0.3	1.2	3.7	13.4
iso-Propanol	0.6	2.9	5.6	18.7
Propanol	0.5	1.6	5.5	12.4
Allyl alcohol	0.3	1.1	14	11.0
iso-Butanol	1.1	8.1	45	11.7
t-Butanol	0.9	2.1	49	9.34
n-Butanol	0.7	1.9	25	11.7

Average sensitivity gains in different MS detection modes. FS=full scan; EIC=extracted ion chromatogram; SIM= selected ion monitoring. %RSD at 10 ppm level (n=6).

Trace 1310 GC with ISQ Mass Spectrometer and RSH autosampler

Specifications

Standardised method:	ASTM D7423, UOP 960
Application:	Analysis of oxygenated components (alcohols, ethers, ketones) in liquids, liquefied gases and gases
Configuration:	Single channel instrument based on Thermo Trace 1300 GC series with FID detection.
Injection:	SSL (Liquid Injection), GSV (Gas Sampling Valve) or LSV (Liquid Sampling Valve); all three injection techniques can be combined
Optional:	Automated liquid sample injector Pressure Facility for highly quantitative injection of liquefied gas samples using LSV Mass Spectrometer for enhanced identification and sensitivity gain factor up to 177 (see page 3)
Tubing:	Sulfinert® tubing for inert sample path
Analytes:	see table (page 2).
Calibration standards:	1, 10, 100 and 100 ppm each individual component in n-Hexane
Dynamic range:	0.1-1000ppm

	ETBE Area	MTBE Area	DIPE Area	TAME Area	PE Area	MEK Area	T-Butanol, Iso... Area	1-Butanol Area
	217590.00	219186.00	225544.00	234268.00	221104.00	197462.00	668182.00	352884.00
	218929.00	223651.00	228403.00	238190.00	225201.00	199992.00	674969.00	364892.00
	216047.00	220135.00	223283.00	232977.00	220184.00	195684.00	661960.00	356955.00
	223290.00	227834.00	233581.00	243023.00	229025.00	201593.00	684831.00	353251.00
	215944.00	218017.00	224411.00	233341.00	219821.00	194399.00	658748.00	339042.00
	216799.00	220695.00	227555.00	235189.00	221814.00	194438.00	661578.00	348803.00
	218518.00	220454.00	227493.00	236573.00	223679.00	193629.00	661017.00	351983.00
	223242.00	224438.00	232150.00	241893.00	228986.00	197467.00	675404.00	353714.00
	215976.00	215619.00	222285.00	232897.00	219837.00	190374.00	646960.00	347844.00
	222034.00	224530.00	232040.00	241757.00	227848.00	195446.00	664451.00	354400.00
Min:	215944.00	215619.00	222285.00	232897.00	219821.00	190374.00	646960.00	339042.00
Max:	223290.00	227834.00	233581.00	243023.00	229025.00	201593.00	684831.00	364892.00
Mean:	218836.90	221455.90	227674.50	237010.80	223749.90	196048.40	665810.00	352376.80
Std Dev:	2974.18	3624.26	3916.83	3966.46	3776.53	3234.66	10573.04	6631.43
%RSD:	1.36	1.64	1.72	1.67	1.69	1.65	1.59	1.88

Repeatability Lowox analysis (GC-FID, 100pmm calibration standard)

Trace 1310 GC with optional Pressure Facility for injection of Liquefied Gas
(using Liquid Sampling Valve)

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