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Excellence in Science

European Seminar for Hydrocarbon Processing Industry

GC solutions for Petrochemistry and Refining

May 2022

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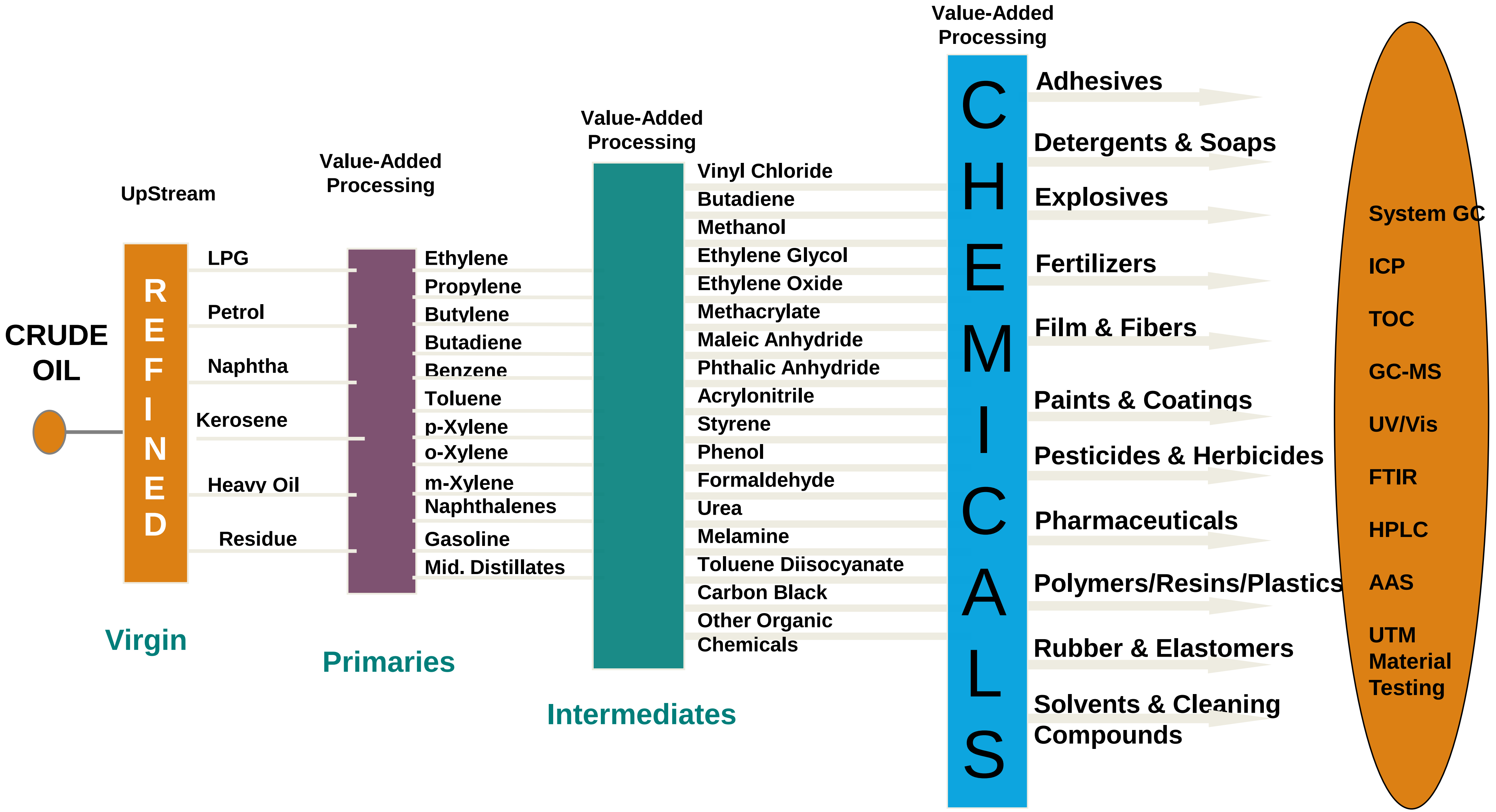
Shimadzu Europa GmbH

Hydrocarbon Processing Industry - HPI



… Shimadzu Solutions to address the HPI Market

Trusted Brand for Quality GC

Shimadzu Corporation, the professional manufacturer of gas chromatograph for more than 60 years

Shimadzu has been developing and manufacturing gas chromatograph products for more than half a century in its development over 140 years. Excellent tradition and outstanding quality has been continued to today, so that Shimadzu has continuously launched a variety of GC application systems to meet the needs of customers.

It is because Shimadzu has always been adhering to the "spirit of craftsmanship", and the combination of solid technical capabilities that "Japanese ingenuity" is more well known.

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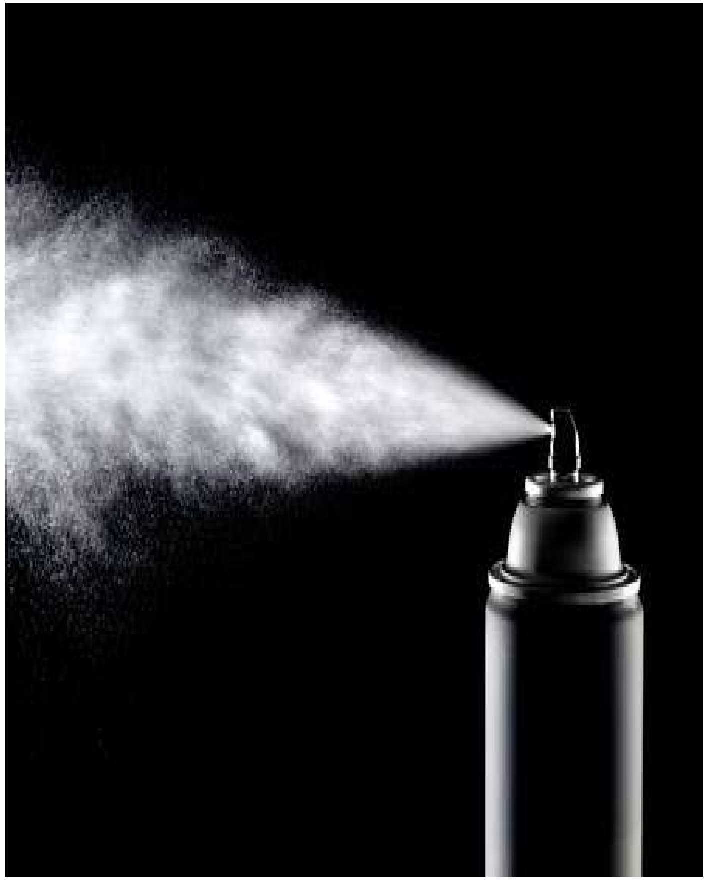
System GC- Types



Gas Phase-
Sampling by using Gas Sampling valve with fixed loop

Stable Liquid Phase-
Injection by using AOC-30i or AOC-20i

Pressurized Liquid Phase-
Injection by using Liquid Sampling Valve

Shimadzu GC solutions for Hydrocarbons Analysis

Natural Gas Analysis	(ASTM D1945/D1946/D3588,ISO 6974-3, ISO 6974-4)
Refinery Gas Analysis	(ASTM D1945/ D1946/ D3588, GPA-2261)
LPG Analysis	
Simulated Distillation Analysis	(ASTM D2887/D3710/D6352/D7213/D7500/D7169, ISO 15199)
Gasoline/Fuel Analysis	(ASTM D3606/D4815/D5580)
Lubricant Analysis	(ASTM D3606/D4815/D5580)
Trace Sulfur Analysis	(ASTM D5504, D5623, D4735, D6228)

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GC Analyzers – Functional classification

Natural Gas Analyzer	Analysis of C1-C15 Hydrocarbons (Saturated) Permanent gases (O2,N2,methane,CO,CO2,H2S,He,H2)
Refinery Gas Analyzer	Analysis of C1-C10 Hydrocarbons (Saturated and Unsaturated) Permanent gases (O2,N2,methane,CO,CO2,H2S,He,H2)
LPG Analyzer	LPG Composition and Trace Hydrocarbons impurities
DHA, SIMDIST	DHA C1-C14 Analysis, SIMDIST C4-C110 HC Boiling point distribution Analysis
Trace Sulfur Impurities	Trace Volatile sulfur impurities in LPG , Natural gases, refinery gases, Naphtha, Gasoline, Aromatics
Trace gases Impurities	Trace Permanent gases CO,CO2,Methane impurities analysis in H2,Ethylene, propylene, N2
Trace Aromatics, Oxygenates Impurities	Trace Oxygenates /Aromatics impurities analysis in C2-C5 Hydrocarbons ,Gasoline Engine Fuel

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Refinery Gases Analyzer (RGA)

Typical Composition of Refinery Gas		
Methane	CH_4	10-12%
C2	C_2H_6 ,C2H4,C2H2	1%-10%
Propane/Propylene	C_3H_8	0-20%
Butanes	C_4H_{10}	0-10%
Pentanes	C_5H_{12}	0-2%
Hexane +, C6+	C6H14+	0-1%
Carbon Monoxide	CO	0-5%
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Hydrogen	H2	0-10%
Rare gases	Ar, He	0-1%

Saturated and Unsaturated Hydrocarbons Gases

Permanent Gases

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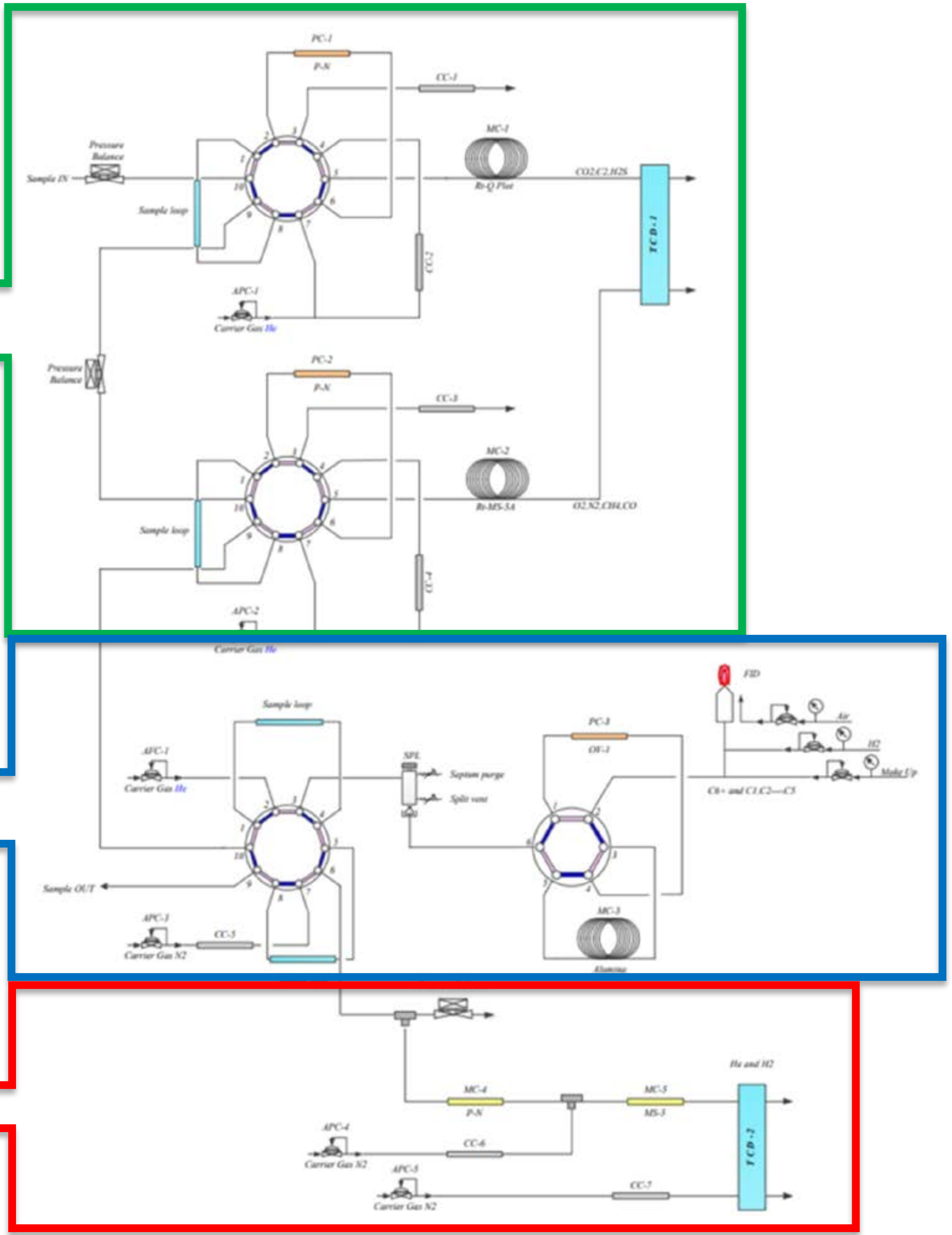
Valve Diagram Refinery Gas Analyzer (RGA)

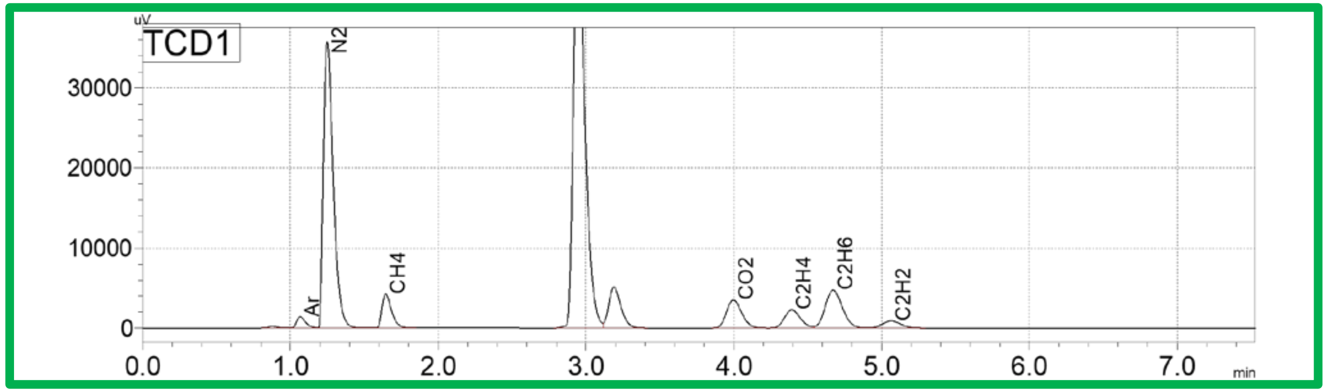
Permanent gases analysis
O2,N2,Methane,CO,
CO2,C2,H2S

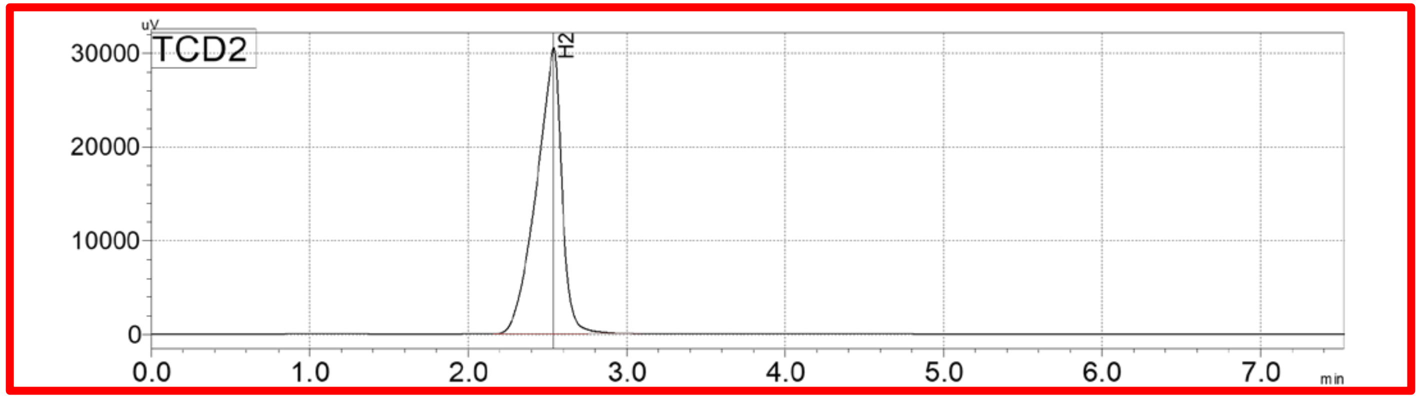
Hydrocarbon gases analysis
C1-C5, C6+, Olefins

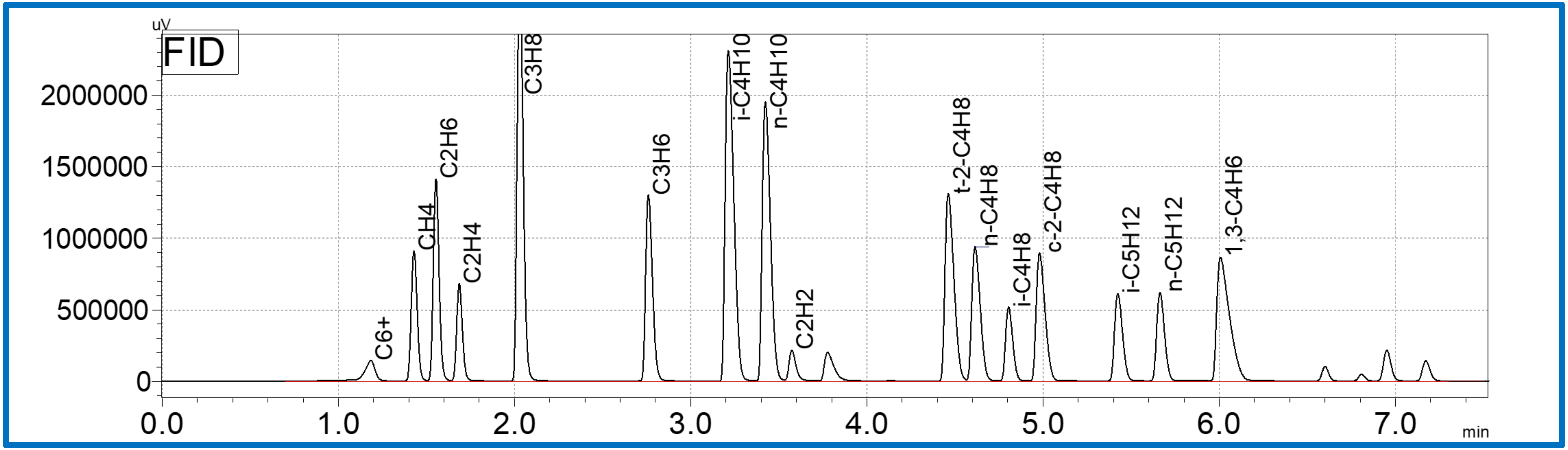
Helium and
Hydrogen
Analysis



RGA Chromatograms







RGA – Results

Detection limits and reproducibility results (n=5) achieved with the Refinery Gas Analyzer

Compound	% RSD	Conc. %	S/N	Calculated LOD (ppm)
Argon (Ar)	0,91	1	500	66,00
Nitrogen (N2)	0,45	37,2	107360	11,43
Methane (CH4)	0,69	5	114366	1,44
Carbon dioxide (CO2)	0,82	3	1029	96,21
Ethene (C2H4)	0,45	2	88364	0,75
Ethane (C2H6)	0,38	4	176954	0,75
Acetylene) C2H2	0,71	1	33059	1,00
C6+	1,3	0,1	18921	0,17
Propane (C3H8)	0,39	6	353829	0,56
Propene (C3H6)	0,43	3	173017	0,57
iso-Butane (i-C4H10)	0,37	5	298353	0,55
n-Butane (n-C4H10)	0,39	4	254157	0,52
trans-2-Butene (t-2-C4H8)	0,47	3	175162	0,57
1-Butene (1-C4H8)	0,43	2	126618	0,52
iso-Buten (i-C4H8)	0,55	1	67512	0,49
cis-2-Butene (t-2-C4H8)	0,51	2	121180	0,54
2-Methylbutane (i-C5H12)	0,53	1	81347	0,41
n-Penatne (n-C5H12)	0,58	1	82436	0,40
1,3-Butadiene (n-C4H10)	0,49	3	119939	0,83
Hydrogen (H2)	0,47	12,5	4485	91,97

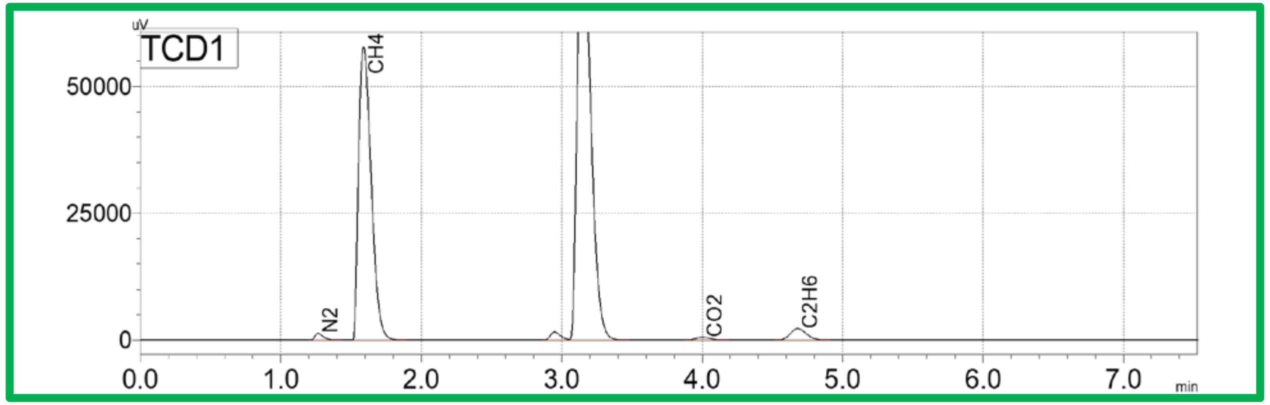
Injection volumes:

Permanent gases (TCD1)
100µl direct injection

Hydrogen/Helium (TCD2)
500µl direct injection

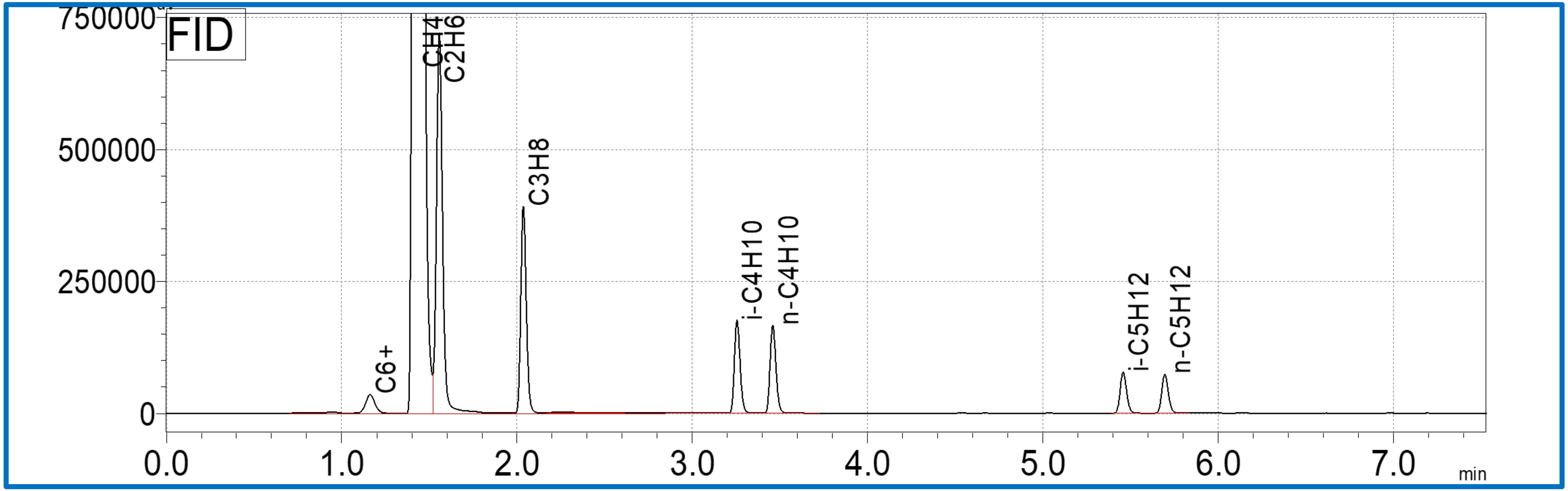
Hydrocarbons (FID)
100µl gas injection with split 1:5

Natural Gas Chromatograms with RGA



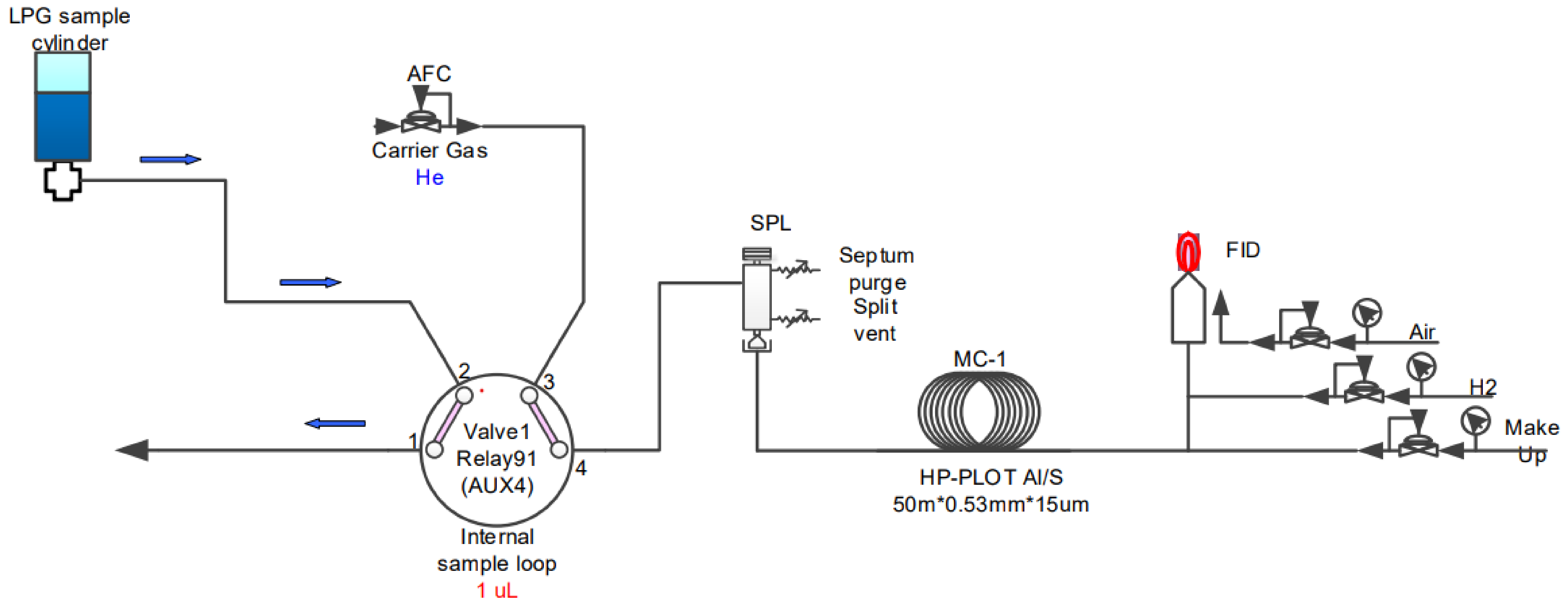
Appropriate also for natural gas measurements:

ASTM D1945
ASTM D1946
ASTM D3588
GPA-2261



Liquified Petroleum Gas (LPG) Analyzer

Injection by Liquid Sampling Valve (LSV) or LPG is evaporated before sampling and injected as gas



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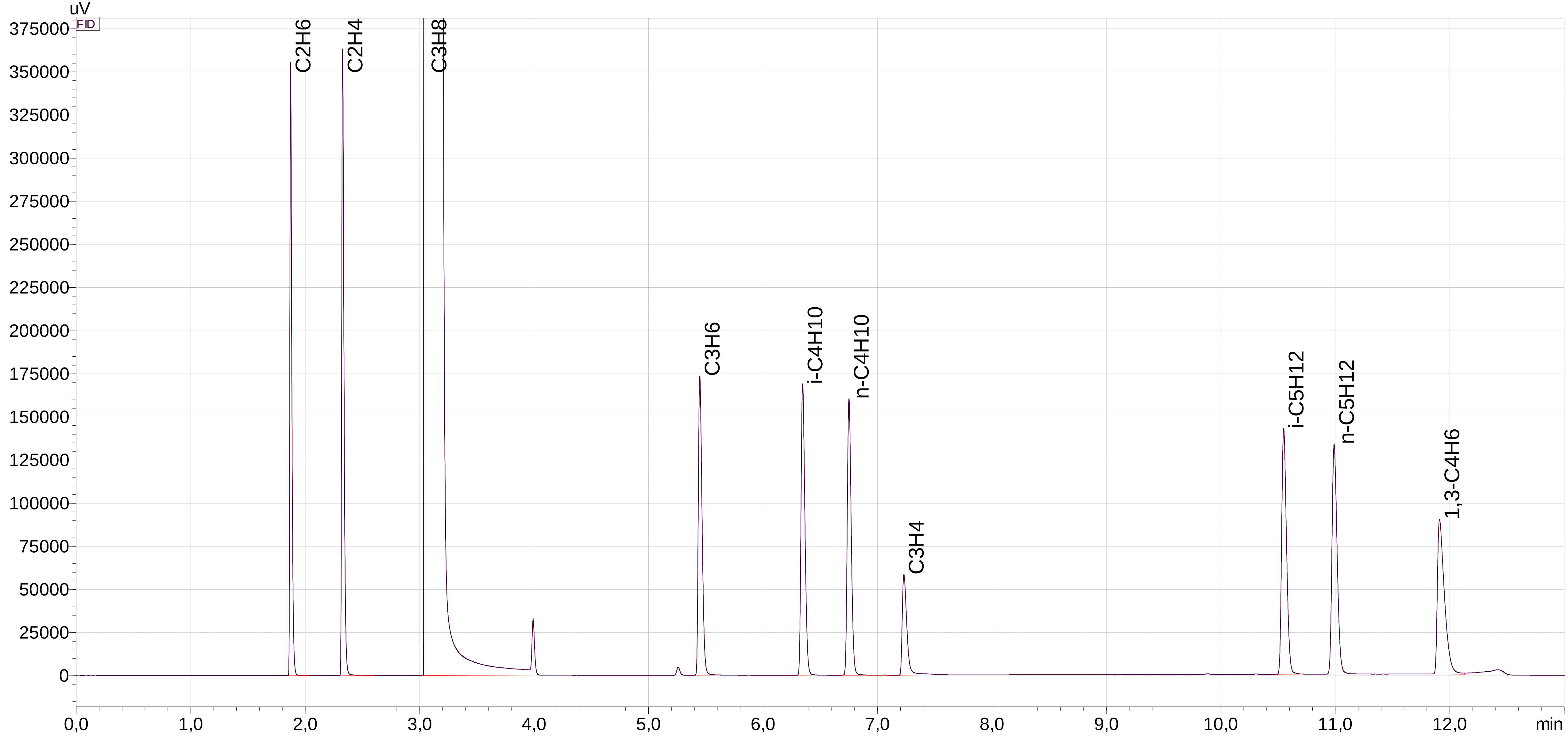
LPG Chromatogram

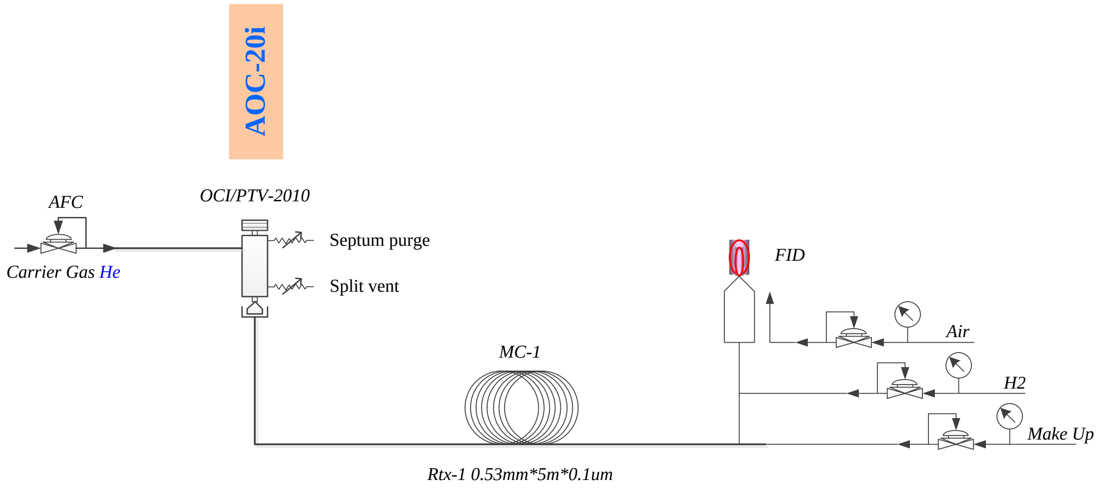


LPG results

Reproducibility results and detection limits achieved by 1µl liquid injection and split ratio 1:15

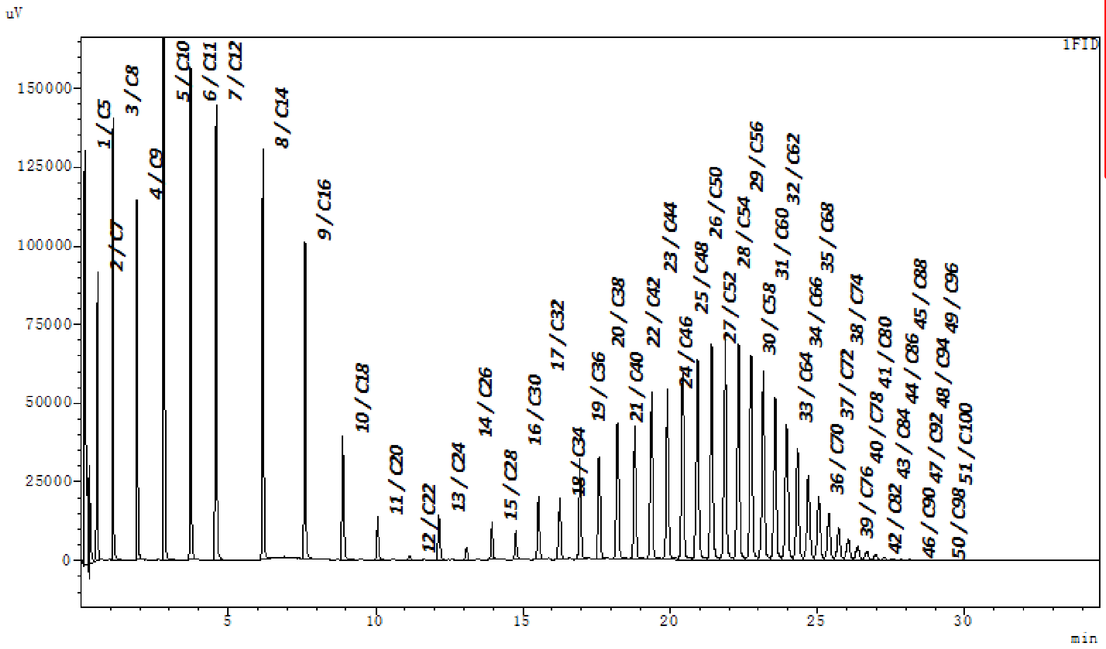
Peak No.	Compound	Conc (%)	LOD(ppb)	Peak area repeatability (N=5; RSD%)
1	Ethane(C2H6)	0.5	210	2,1
2	Ethene (C2H4)	0.5	260	2,8
3	Propane (matrix)	95.5		
4	Propene(C3H6)	0.5	270	1,2
5	Iso-butane (i-C4H10)	0.5	210	1,5
6	n-Butane (n-C4H10)	0.5	210	1,7
7	Propadiene (C3H4)	0.5	470	1
8	2-Methylbutane (n-C5H12)	0.5	230	2,4
9	n-Penatne (n-C5H12)	0.5	240	2,5
10	1,3-Butadiene (n-C4H10)	0.5	410	1,5

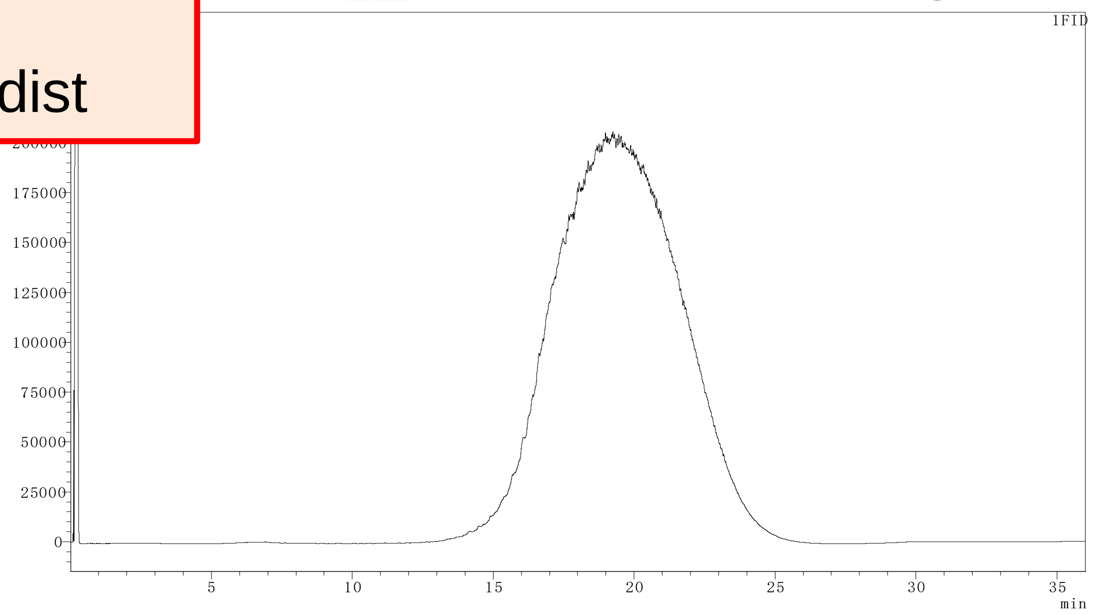
Liquid Injection - Simulated Distillation (SimDist)



System Requirements

GC-2030
OCI Injector
FID
AOC 20i (20S)
LCO2 – Cryo Oven
Simdist Column
LabSolutions - Simdist





Supported Simulated Distillation Standards

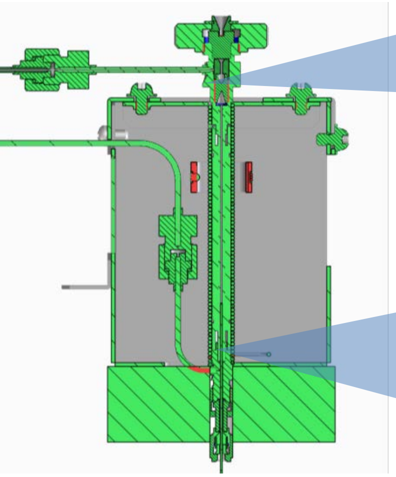
Standards	Carbon Number	Sample
ASTM D 3710□D 7096	n-C_3 to n-C_{15}	Gasoline, naptha
JIS K 2254	-	Kerosene, diesel oil
ASTM D 2887 (ISO3924□ IP406)	n-C_5 to n-C_{44}	Jet oil, diesel oil
ASTM D 6417	n-C_8 to n-C_{60}	Lubricating oil, base stock oil
ASTM D 7213 □Extended D2887□	n-C_7 to n-C_{60}	Lubricating oil, base stock oil
ASTM D 6352	n-C_{10} to n-C_{90}	Lubricating oil, base stock oil
ASTM D 7500	n-C_7 to n-C_{110}	Lubricating oil, base stock oil
EN 15199-1 (IP480□ DIN 51435)	n-C_7 to n-C_{120}	Lubricating oil, base stock oil
ASTM D 5307	n-C_{44} max.	Crude oil (internal standard method)
ASTM D 7169□ EN 15199-2 (IP 507)	n-C_7 to n-C_{100}	Crude oil (external standard method, n-C_{120} max. for EN)

Various standards are available for each analysis sample. The analytical method and functions required differ according to the standard.

Simulated Distillation - On Column Injection

New OCI-2030NX designed for high temperature applications:

Example ASTM D 7500: Lubricating Base Oils-in Boiling Range from 100 °C to 735 °C



Miniaturization of liner

Downsized to fit syringe insertion section

→reduction of heat capacity

Improvement of heat conduction efficiency to column

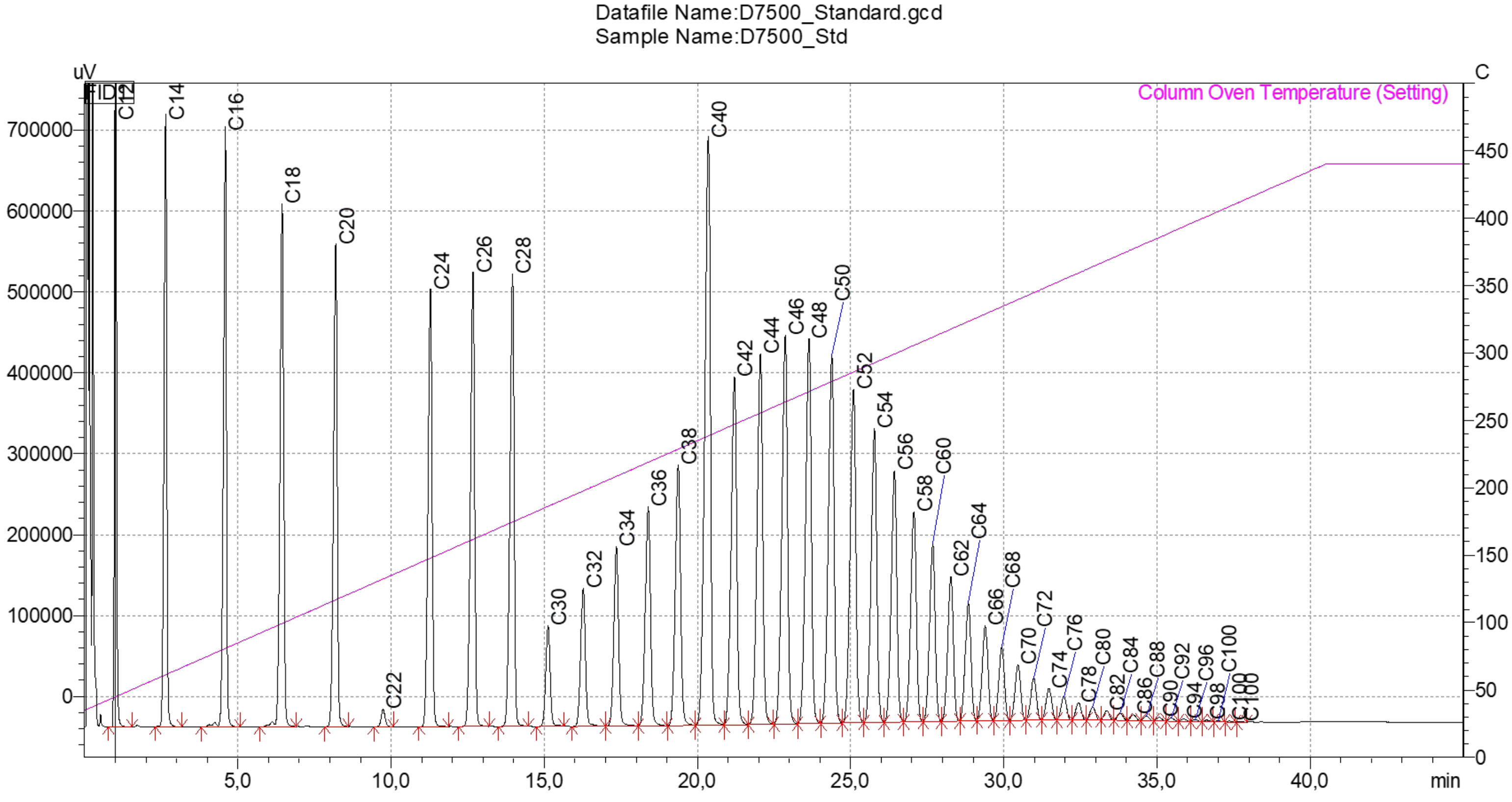
Change base material

- Heat induction material changed from stainless steel to aluminum
- OCI base’s outer diameter downsized from φ6 mm to φ5 mm

→uniform temperature distribution

reduction of heat capacity

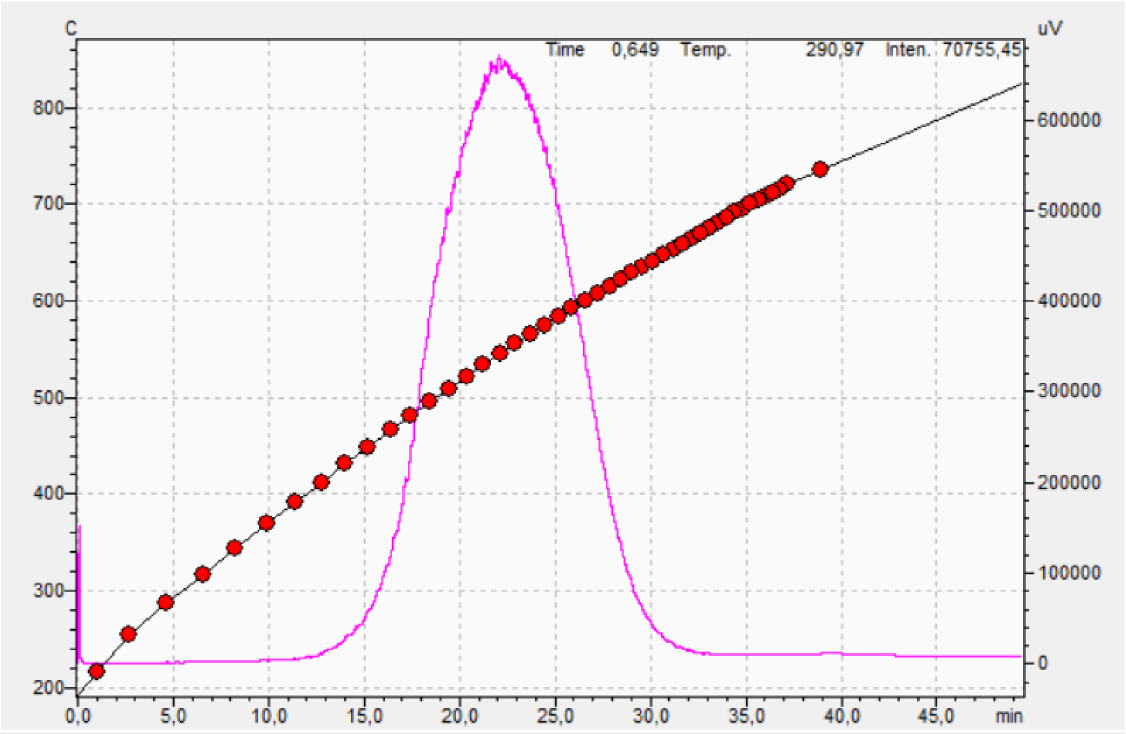
Improvements OCI-2030NX



ASTM D7500: Alkane calibration

Simulated Distillation - ASTM D 7500 results

Boiling Point Retention Time curve with Chromatogram and performance check with Reference material

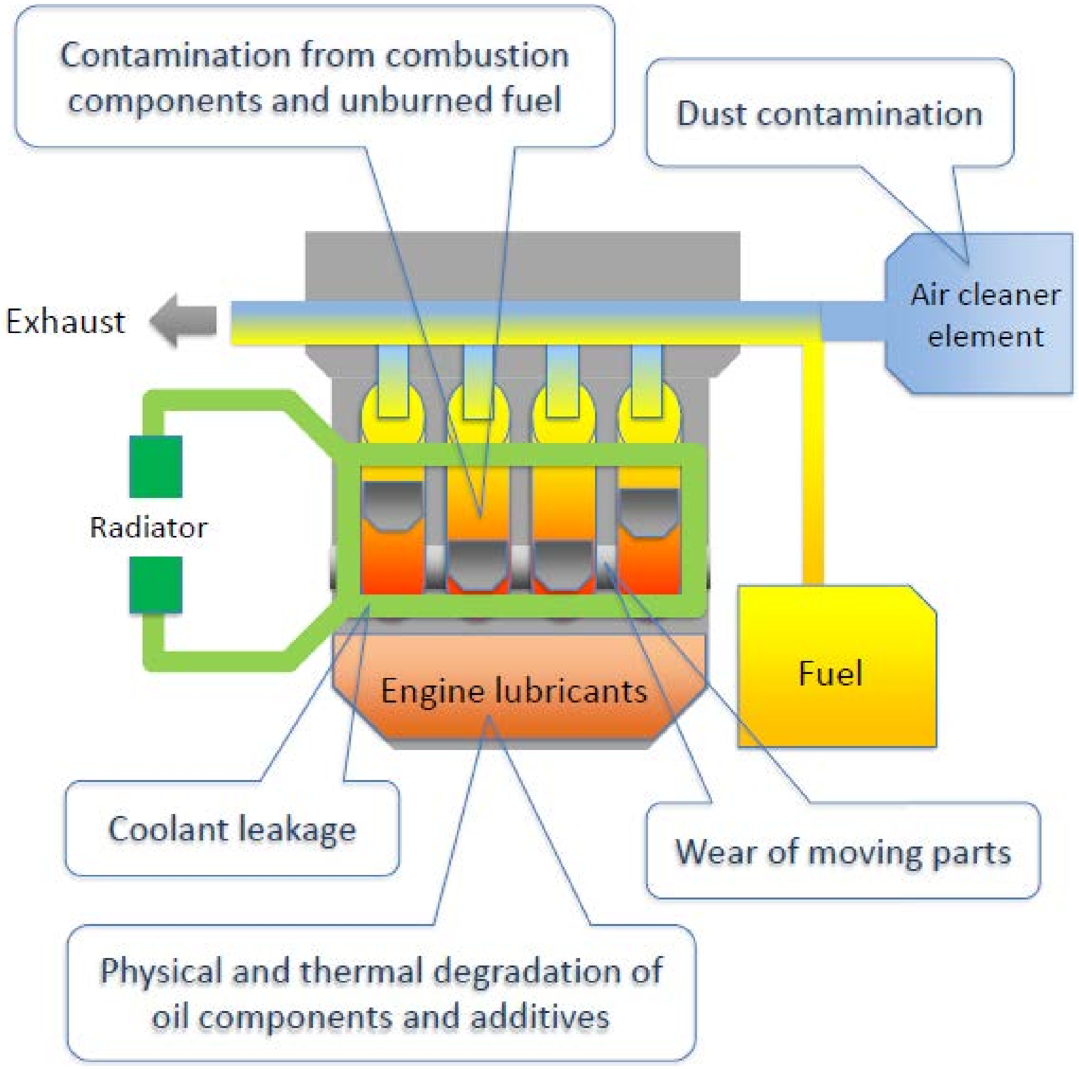


	Item	Value
	Data file name	20210402_ReferenceOil__06uL_ASTM_D7500_008.gcd
	Application	ASTM D7500
	Analysis method	Total Area
	Recovery [w/v]	100,0
	Eluting zone	6,489 - 33,149 [min] (315,2 - 675,5 [C])
	Area	344311922

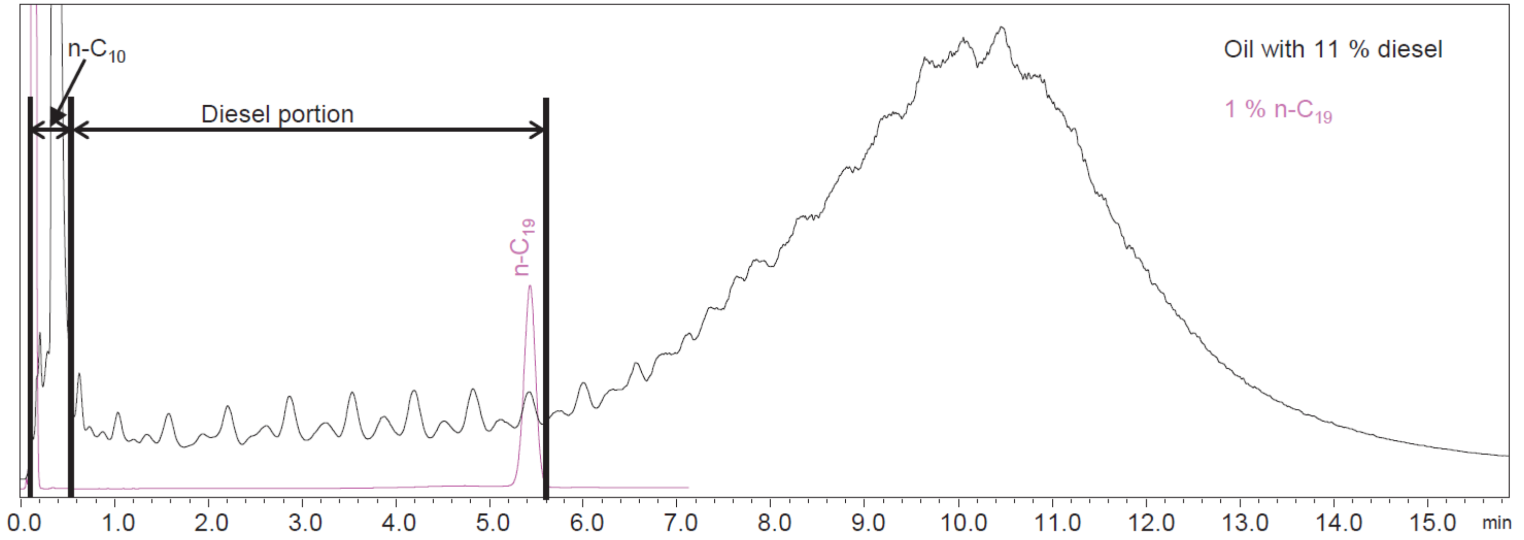
Recovered Mass %	Analysis b.p. (°C)	Analysis b.p. (°C)	Deviation (°C)	Accepted b.p. (Ref. Mat. 5010) (°C)	
IBP	428	429.3	1.3	±9	Pass
5	477	476.5	-0.5	±3	Pass
10	493	492.2	-0.8	±3	Pass
15	502	502.1	0.1	±3	Pass
20	510	510.2	0.2	±3	Pass
25	518	517.7	-0.3	±4	Pass
30	524	524.6	0.6	±4	Pass
35	531	531	0	±4	Pass
40	537	536.9	-0.1	±4	Pass
45	543	542.6	-0.4	±4	Pass
50	548	548.4	0.4	±5	Pass
55	554	554.3	0.3	±4	Pass
60	560	560.1	0.1	±4	Pass
65	566	566	0	±4	Pass
70	572	571.7	-0.3	±4	Pass
75	578	577.8	-0.2	±5	Pass
80	585	584.5	-0.5	±4	Pass
85	593	591.7	-1.3	±4	Pass
90	602	600.7	-1.3	±4	Pass
95	616	613.7	-2.3	±4	Pass
FBP	655	648.7	-6.3	±18	Pass

Liquid Injection - Lubricants

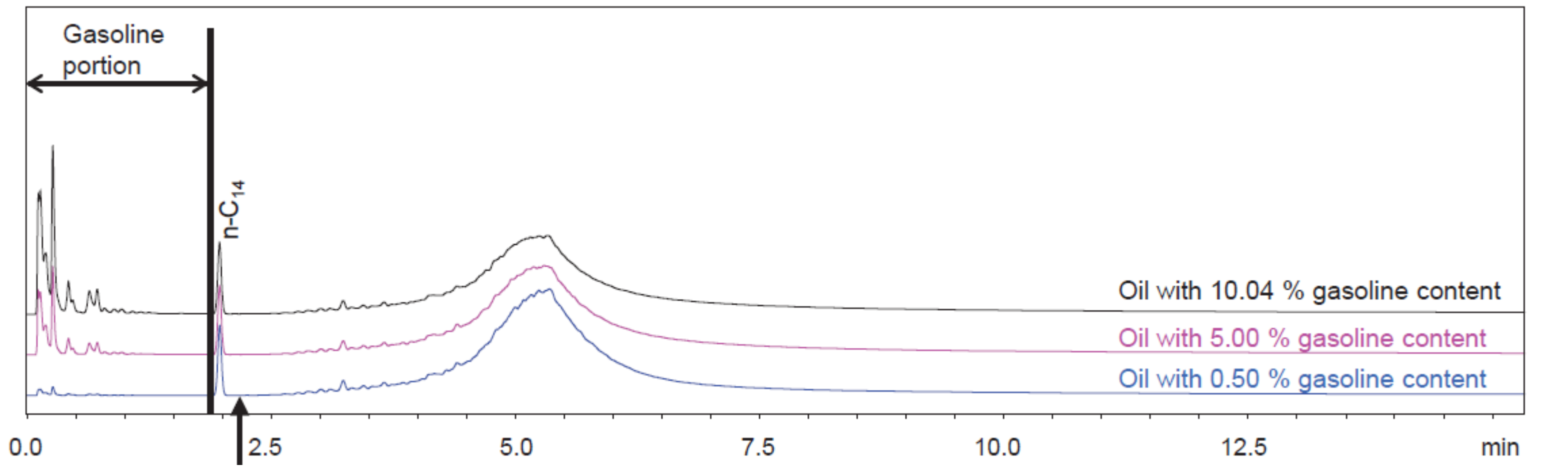
Solutions for Lubricant Monitoring



Dilution Rate of Diesel in Engine Oil in accordance with ASTM D3524



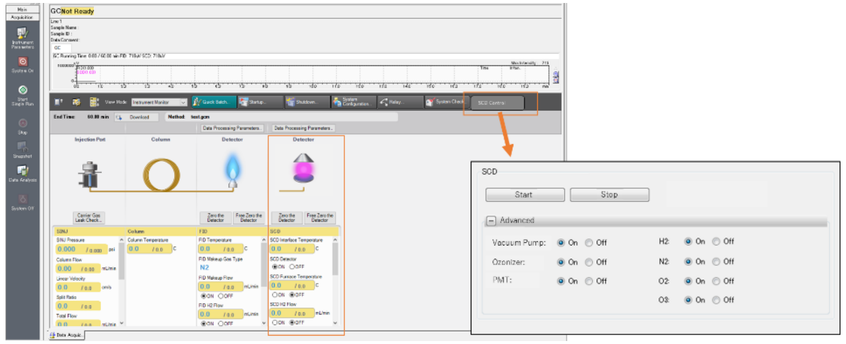
Dilution Rate of gasoline in Engine Oil in accordance with ASTM D3525



Nexis SCD-2030

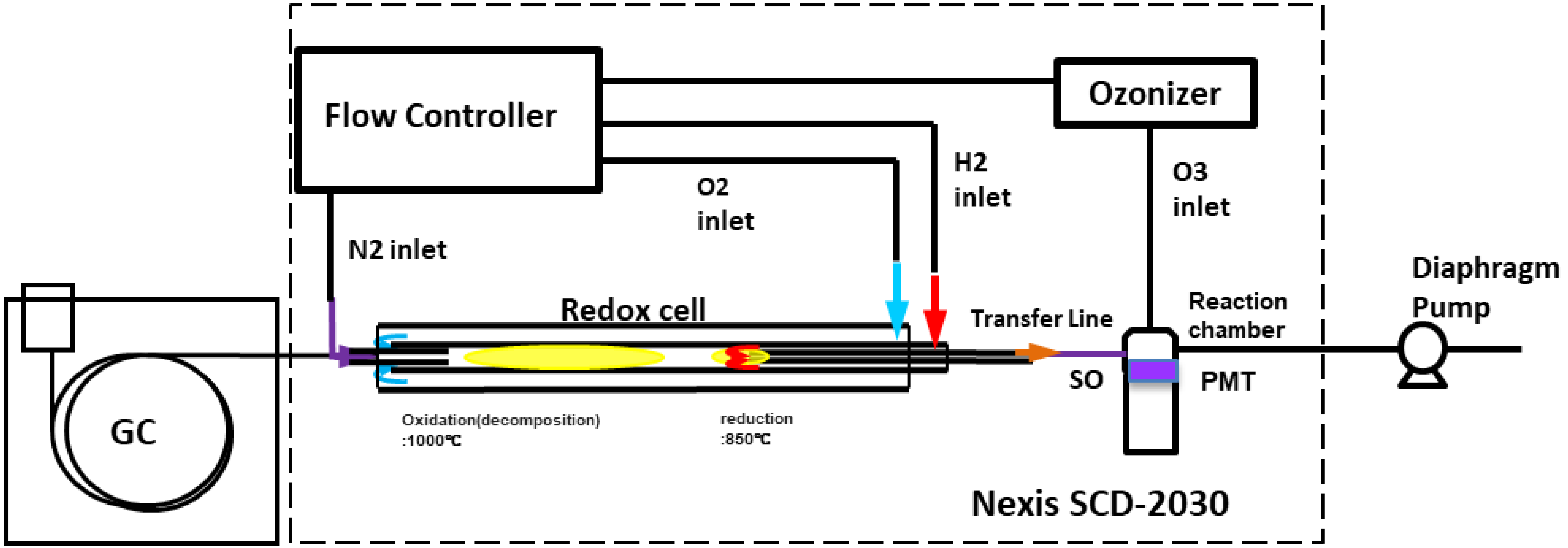
Simplifies complexity

Nexis SCD-2030



New LabSolutions

Nexis SCD-2030



- New horizontally redox cell design allows bigger Redox Cell
- Longer reaction times, higher stability, easier to achieve a quantitative result
- Short way between Redox cell and reaction cell – precision and long-term stability
- Oil free diaphragm pump is sufficient to maintain the vacuum
- Horizontally redox cell easy maintenance due to better access to consumable parts

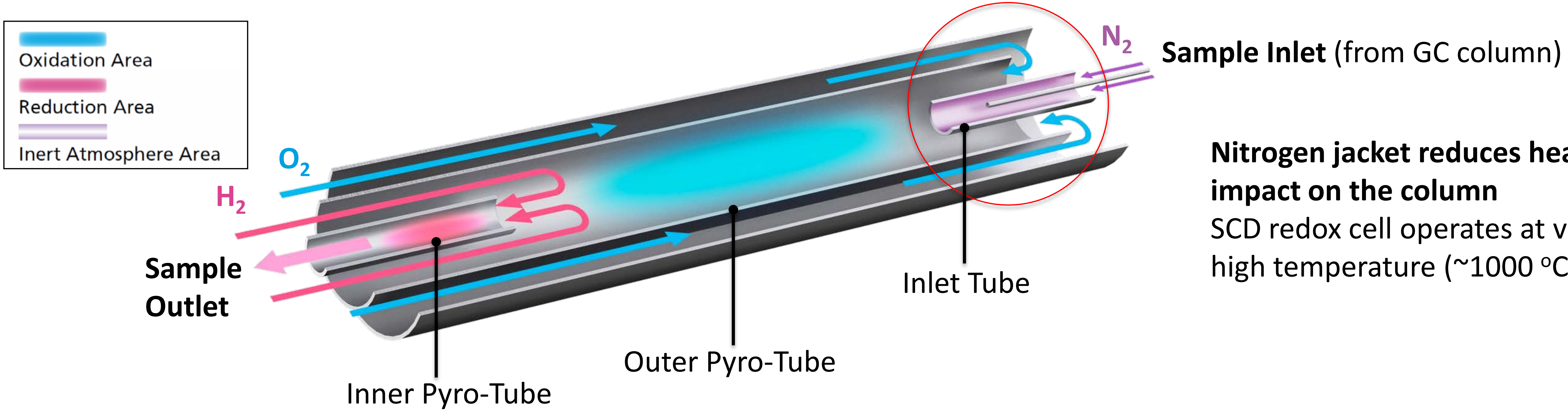
SCD-2030 - Redox Cell

High Efficiency Redox Cell Provides Stable Reactions

- Up to 2 times bigger than current solutions
- Longer reaction time – better efficiency of oxidation and reduction

⇒ less fine tuning of gas flows needed to guaranty selectivity in case of coelution with non sulfur components in high concentrations.

- Design with horizontal redox cell allows ultra short connection to reaction cell
- All this contributes to the high precision and long-term stability of SCD-2030



Nitrogen jacket reduces heat impact on the column
SCD redox cell operates at very high temperature (~1000 ^{o}C)

SCD-2030

Easy maintenance

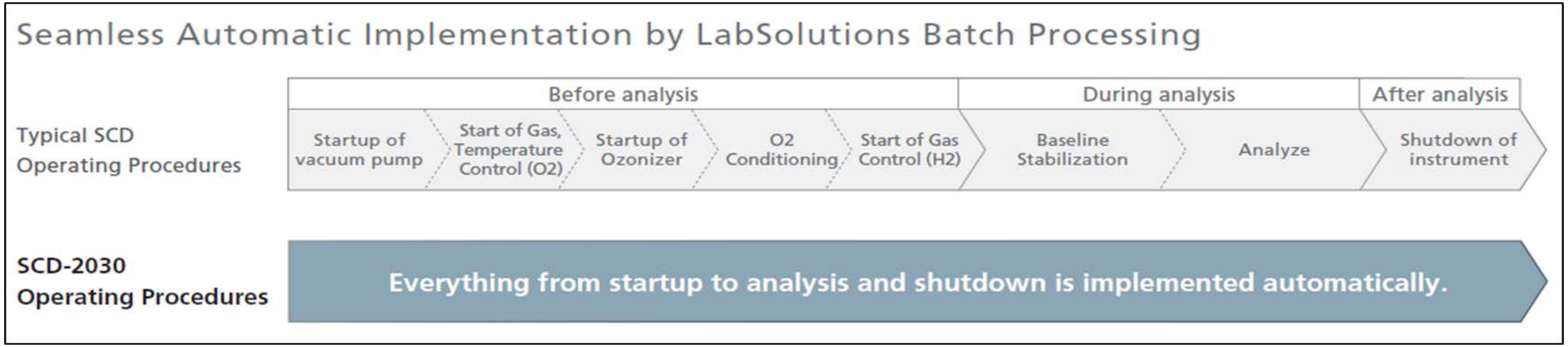
- The inner pyro tube of the redox cell is a consumable. In case of contamination and no improvement by conditioning procedure it must be exchanged.
- Because of the horizontally installation of the redox cell it is easy to access from outside

SCD-2030 – Automated Operation

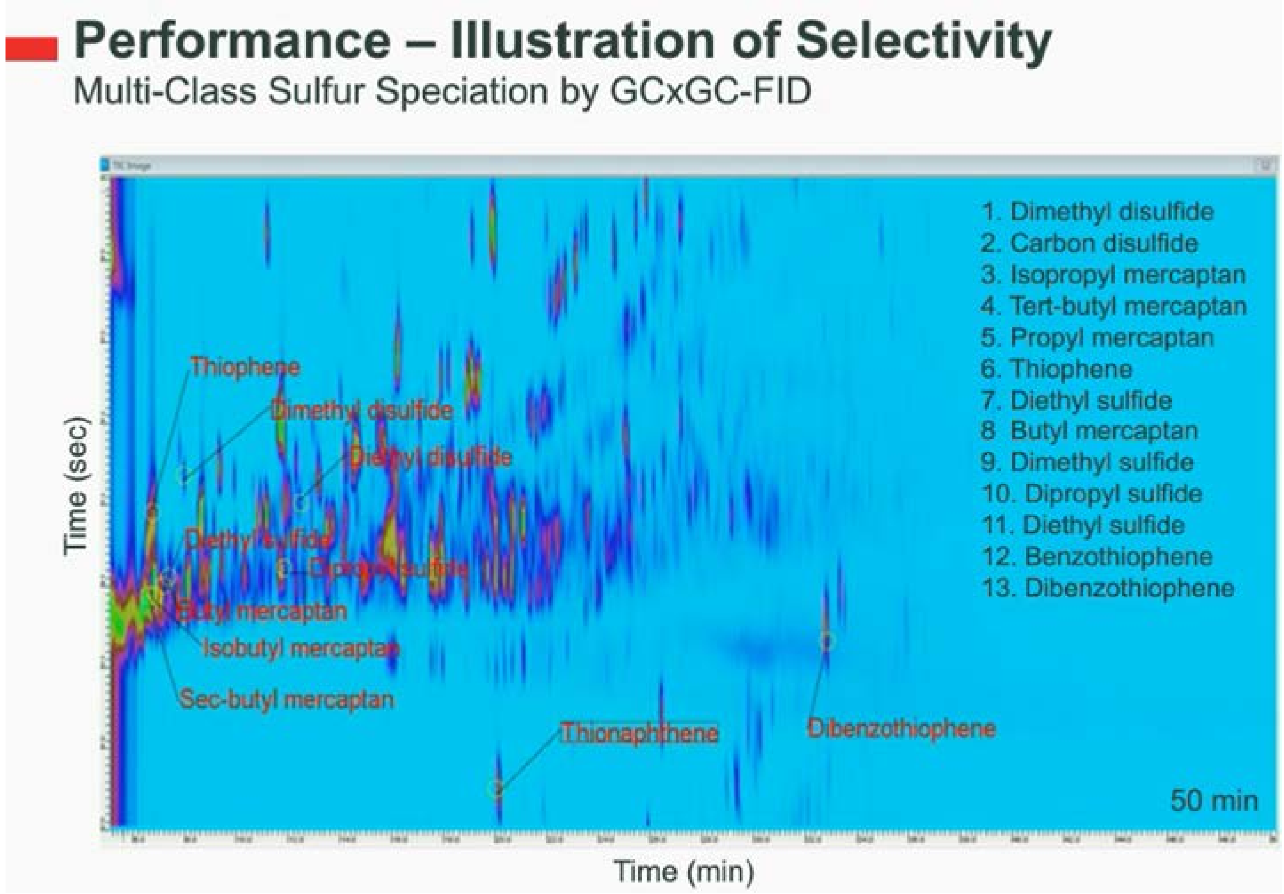
Automation

SCD detectors have several units that must be controlled, and several steps are necessary to prepare them for analysis.

- Startup of an SCD can require more than one hour. SCD-2030 is equipped with a wealth of automation functions doing this **fully** automated. Presence of operator in not needed.
- Defined conditioning procedures can be scheduled within a sequence
- Shutdown of SCD-2030 can be done automatically after last sample of a sequence analysis has been finished. No unnecessary waiting time before starting a scheduled maintenance step.
- Monitoring and diagnostic functions inform before a problem occurs.



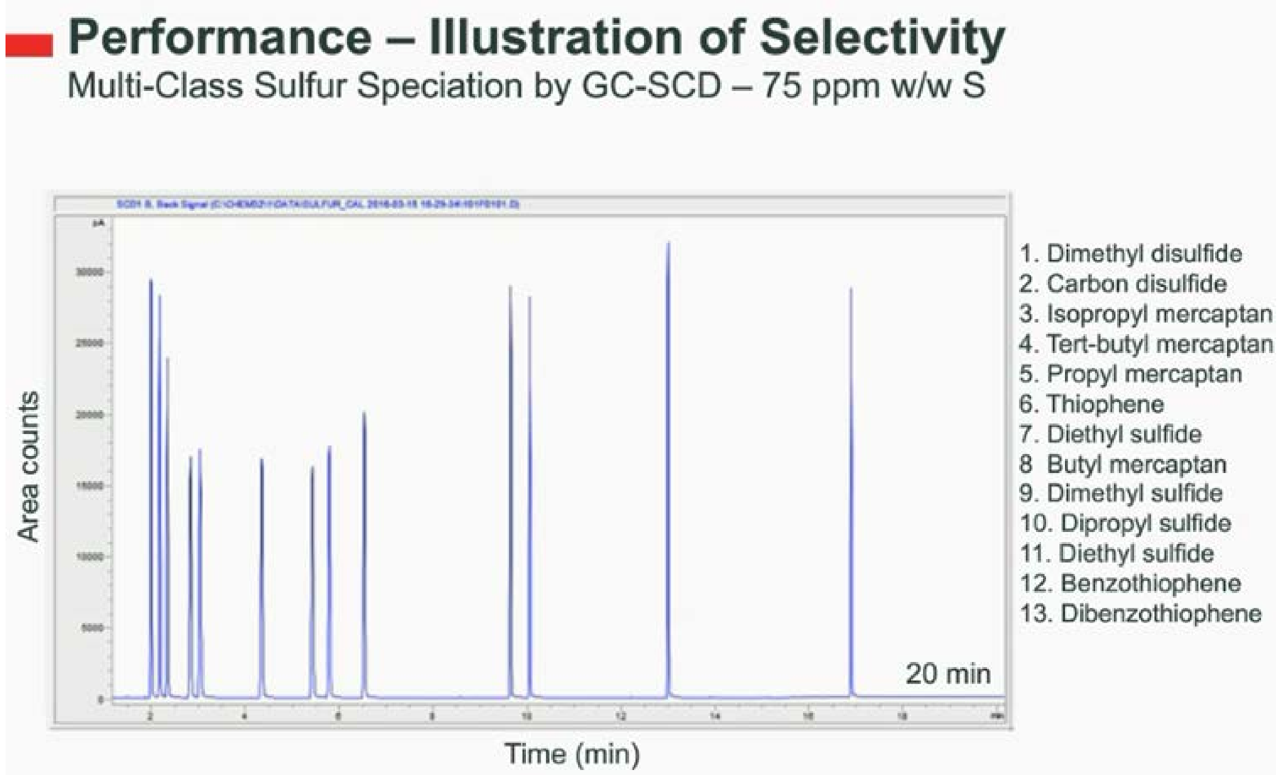
SCD-2030 - Selectivity



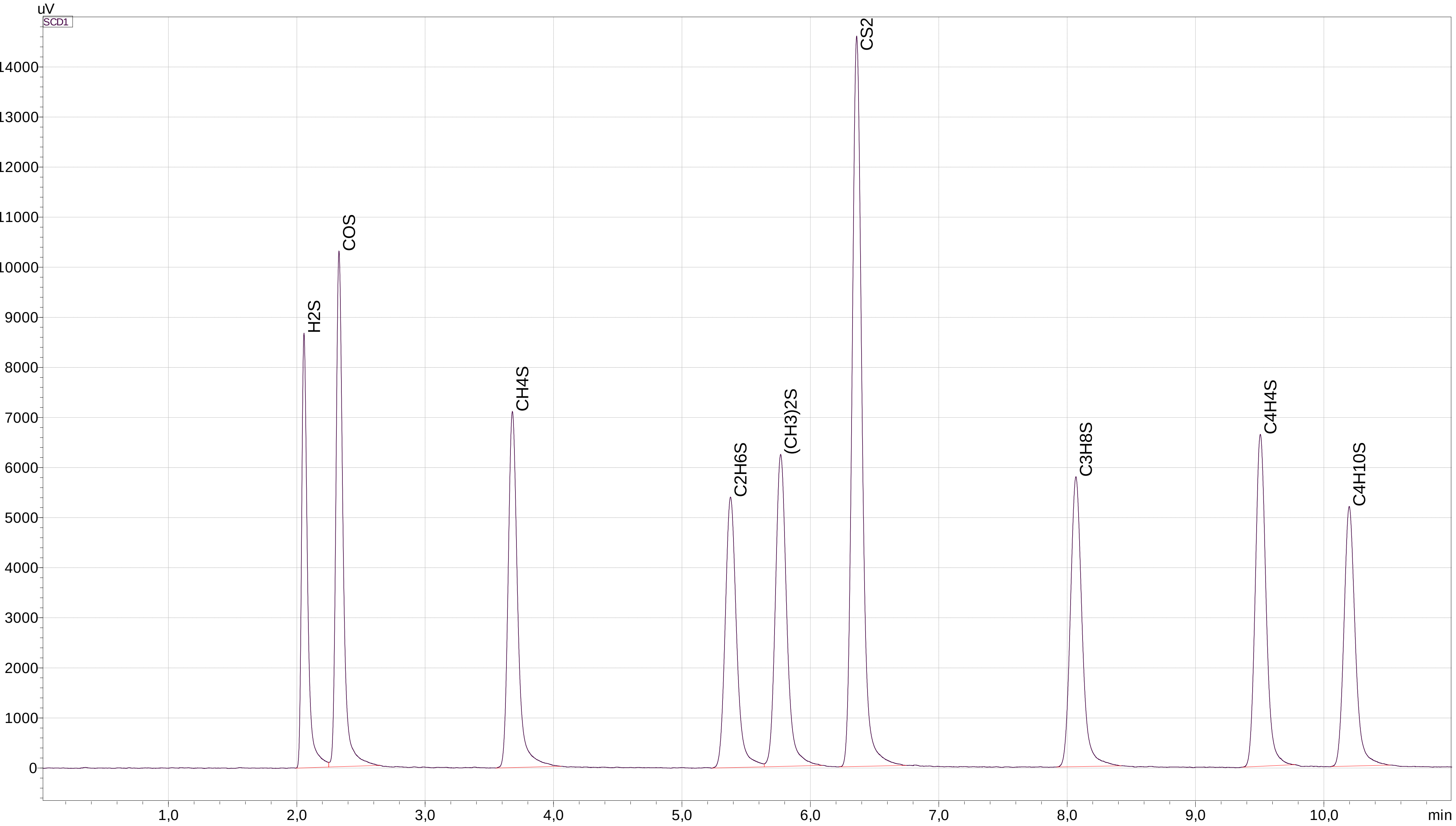
Selectivity Example of SCD-2030:

Left: Comprehensive GCxGC FID chromatogram

Below: SCD-2030 Chromatogram
- only signals from sulfur components



SCD-2030 – Sulfur in gaseous samples



<u>Calibration gas standard</u>

Nine sulfur compounds

concentration 1ppm

each in helium.

RTX-1 column

60m, ID 0.53mm, df 7µm

SCD-2030 – Sulfur in gaseous samples

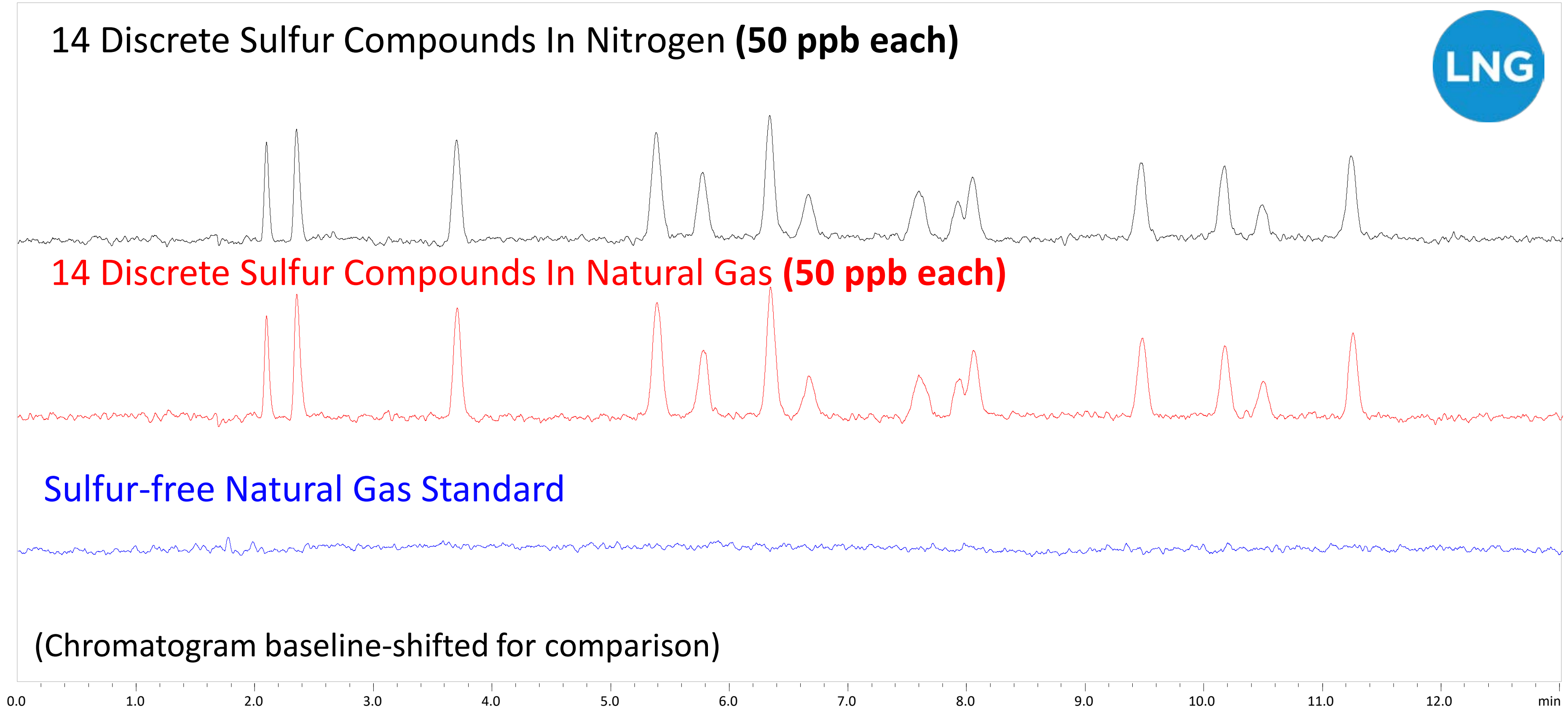
Reproducibility results and detection limits achieved by 1ml gas injection and split ratio 1:9

Peak No.	Compound	S/N	LOD(ppb)	Peak area repeatability (N=8; RSD%)
1	Hydrogen sulphide(H2S)	403	8,2	1,05
2	Carbonyl sulphide(COS)	476	6,9	0,97
3	Methanethiol(CH4S)	330	10	0,48
4	Ethanethiol(C2H6S)	251	13,1	0,94
5	Dimethylsulphide((CH3)2S)	289	11,4	1,33
6	Carbon disulphide(CS2)	676	4,9	0,5
7	Ethyl methyl sulphide(C3H8S)	269	12,3	0,77
8	Thiophene(C4H4S)	308	10,7	0,97
9	Diethyl sulphide(C4H10S)	241	13,7	0,87

SCD-2030 – Sulfur in gaseous samples

Analysis of Sulfur Compounds in Natural Gas (based on ASTM D5504)

Chromatogram Comparison of Standard Sulfur Mixture, Natural Gas Sulfur Mixture, and Sulfur-free Natural Gas Standard

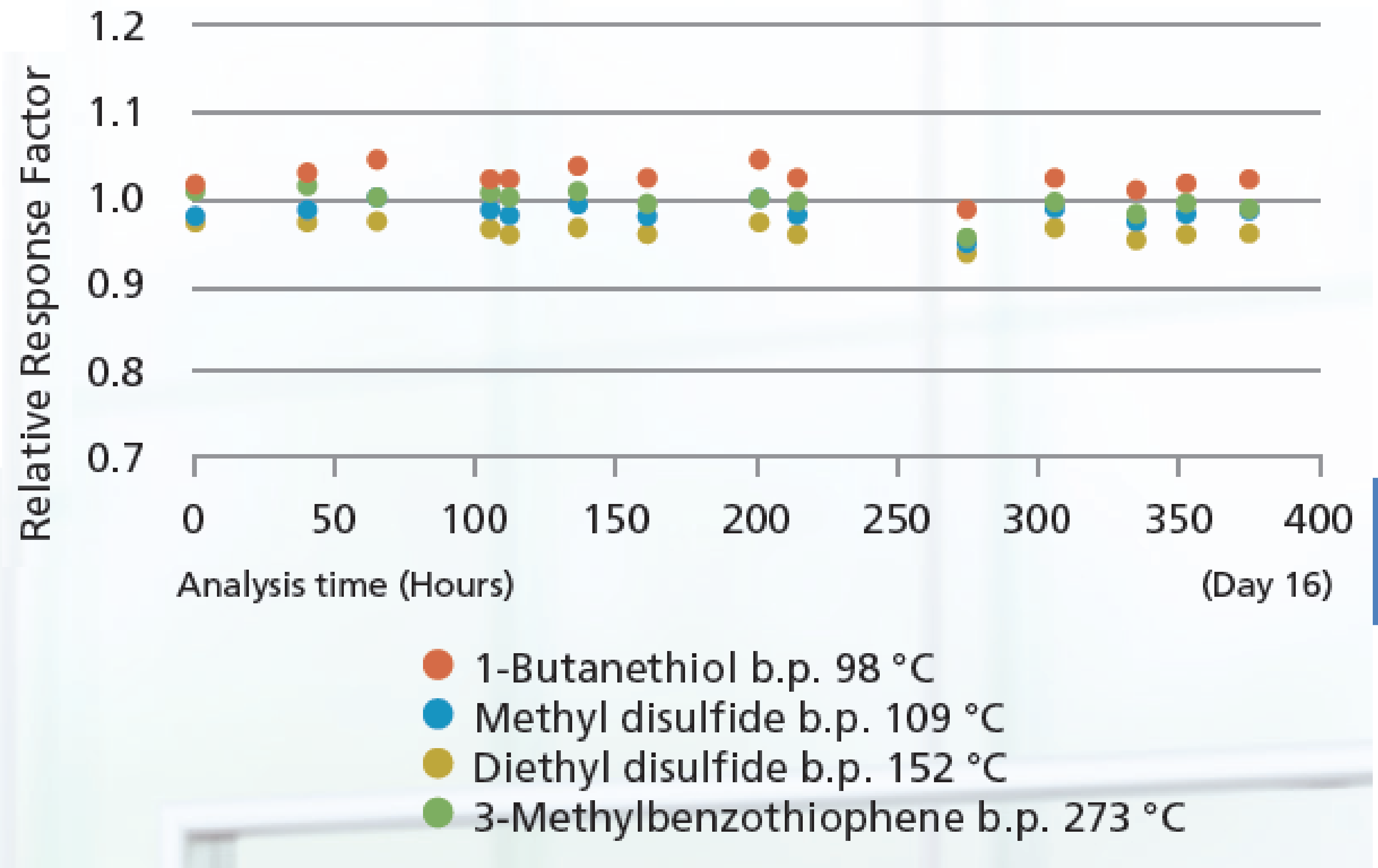


50ppb compounds clearly detected

Excellent selectivity was confirmed

SCD-2030 - Interday Repeatability

Relative repeatability (16 days) 1.2% to 1.9%



Good day-to-day stability for a wide range of boiling points

		Nexis SCD-2030
Stability		< 2% RSD (2 hrs) **< 3% RSD (24 hrs)**

SCD-2030 - High Equimolar Response

Sulfur Compounds	Relative Area Ratio
Thiohene	1.07
2-methyl-1-propanethiol	1.07
diethyl sulfide	1.03
1-butanethiol	1.01
methyl disulfide	0.97
2-methylthiophene	1.08
3-methylthiophene	0.96
diethyl disulfide	0.97
5-methylbenzothiophene	0.94
3-methylbenzothiophene	1.01
diphenyl sulfide (Internal Standard)	1.00

* The relative area ratio for each component was calculated with respect to the area value for diphenyl sulfide (ISTD)

Each compound has a sulfur concentration of 10 ng/uL

All compounds determined accurately in a single calibration

Trace Sulfur Analysis with GC

GC-SCD 2030

Trace PPB level analysis for Natural Gas, LPG sample, trace Sulfur in Benzene, propylene, Permanent gases Matrix. Excellent Sensitivity and Equimolar response.
ASTM D5504, ASTM D5623, ASTM D4735

Features

Long Ceramic Tubes

- Complete Combustion
- High Flows

- Horizontal Redox Cell
  - Easy Maintenance

- Short Transfer Line
  - High Sensitivity

GC-FPD 2030

Trace PPM level Analysis, Quenching issue can be minimized by using proper column separation technique. Applications ,Sulfur in Natural gas, LPG.
ASTM D6228

Any Questions?