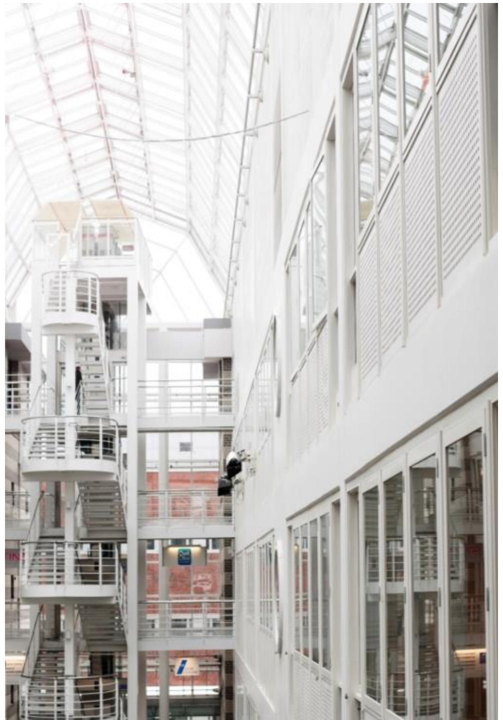
16ENG05 – METROLOGY FOR BIOMETHANE

MEASUREMENT TECHNIQUES AND TEST METHODS FOR THE DETERMINATION OF **COMPRESSOR OIL** CARRYOVER

Oliver Büker RISE, Karine Arrhenius RISE, Francois Lestremau INERIS, Ahmad El Masri INERIS, Tim Robinson WAVERTON Analytics

Workshop on conformity assessment of biomethane, 23th of January 2019, Delft, the Netherlands






Problem with oil in the biomethane

- Lube oil from gas refuelling stations can be entrained in the gas streams during refuelling
- This oil can deposit in the gas vehicle tanks and fueling systems

Potential negative effects:

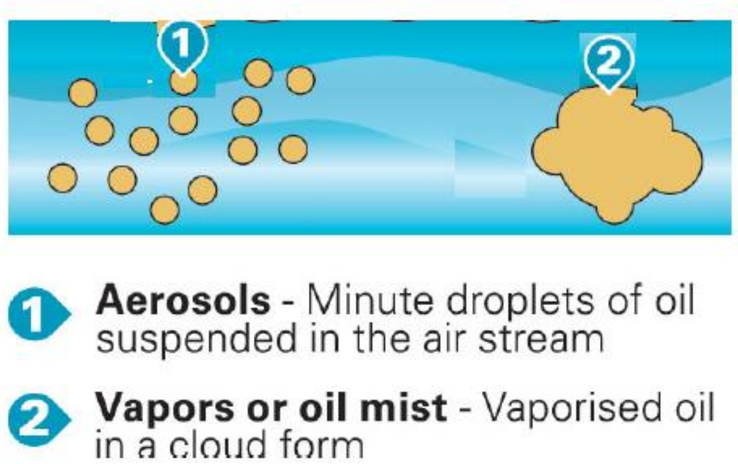
- ❑ Station: Oil aerosol affects the compressor heat exchanger surfaces (reduce storage capacity and consume more compressor power)
- ❑ Station: Increase of refueling station´s maintenance costs (maintenance and replacement of oils separators, filters…)
- ❑ CNG (compressed natural gas) vehicles: Oil carryover increases the vehicle emissions during combustion
- ❑ CNG vehicles: risk of oil soaking of the pressure regulator diaphragm affecting its accuracy
- ❑ CNG vehicles: Sensors of the engine system are extremely sensitive to any contamination

Challenges when analyzing oil carryover

- Oil is carried by the compressed gas in two forms:

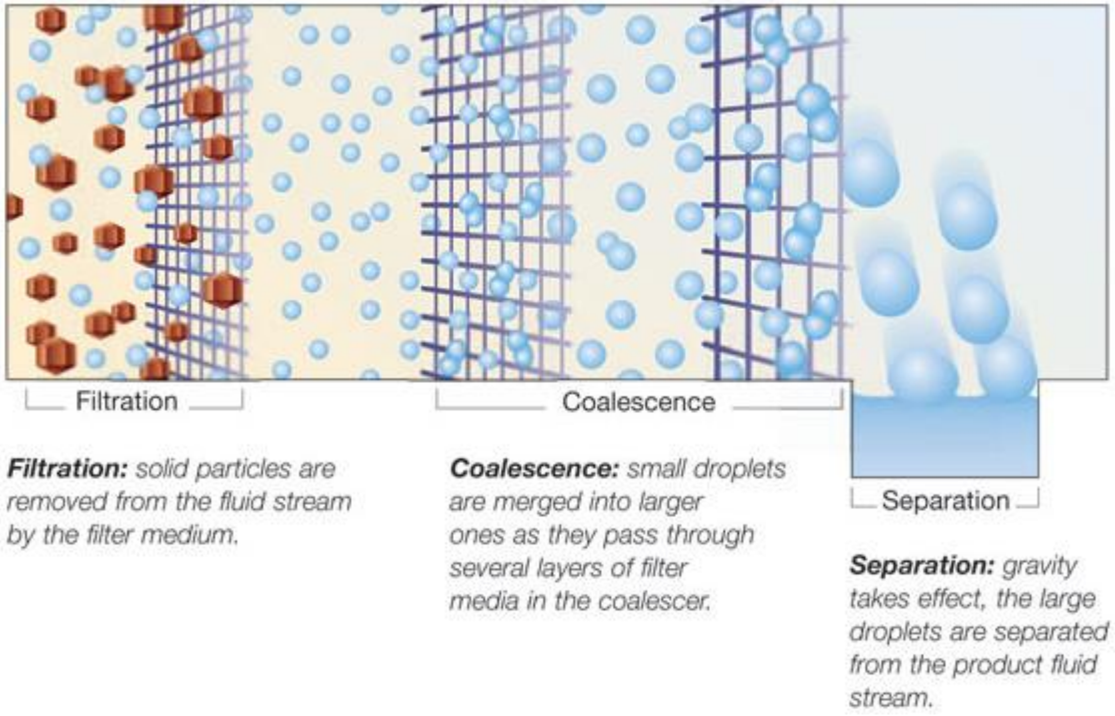
- As an aerosol which is formed by the mechanical shearing in the compressor

- As a vapour which is formed during the oil vaporization and absorption in the gas: depending on their compositions, oils are more or less susceptible to being partly absorbed/dissolved in the gas mostly when the gas is at supercritical (acting like a solvent)



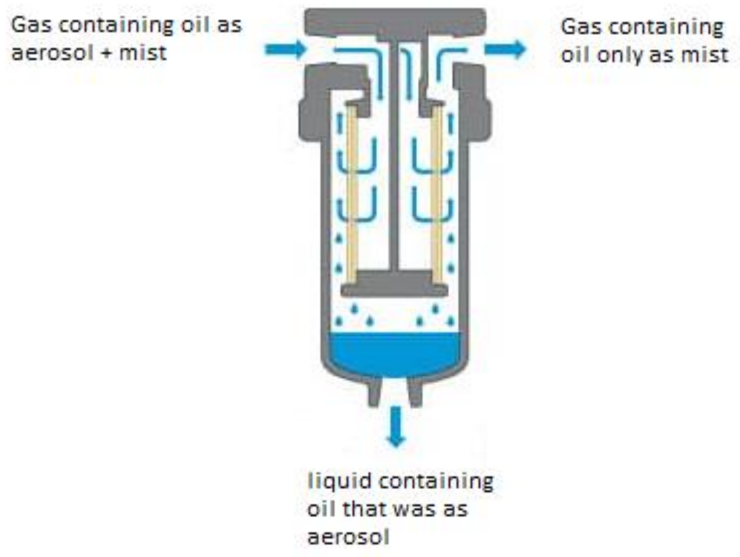
Principle of coalescence

- Coalescence is a steady-state process in which larger droplets are created from smaller droplets and aerosols. The gas passes through a fiber media cartridge. Aerosol droplets are forced through the coalescing media from the inside of the cartridge tube to the outside walls. The increased mass of the droplets cause them to fall by gravity from the cartridge into a low velocity area in the bottom of the coalescer housing where oil accumulates until purged



Principle of coalescence

- While aerosol can be trapped on coalescing filters (widely used in compressor stations), vapour oil cannot be filtered by them unless pressure and/or temperature decreases causing the evapourized oil to condense.
- Oil vapours can however be removed by adsorption on activated carbon, alumina or similar adsorbents



Standard EN16723-2:2017: Automotive fuels specification

Table 1 — Requirements, limit values and related test methods for natural gas and biomethane as automotive fuels

Parameter	Unit	Limit values[a]		Test method (informative)
		Min	Max	
Compressor oil			[e]	ISO 8573-2

[e] The fuel shall be free from impurities other than “de minimis” levels of compressor oil and dust impurities. In the context of this European Standard, “de minimis” means an amount that does not render the fuel unacceptable for use in end user applications.

Annex D
(informative)

Voluntary dedicated grades

Table D.1 — Requirements, limit values and related test methods for natural gas and biomethane as automotive fuels with dedicated grade

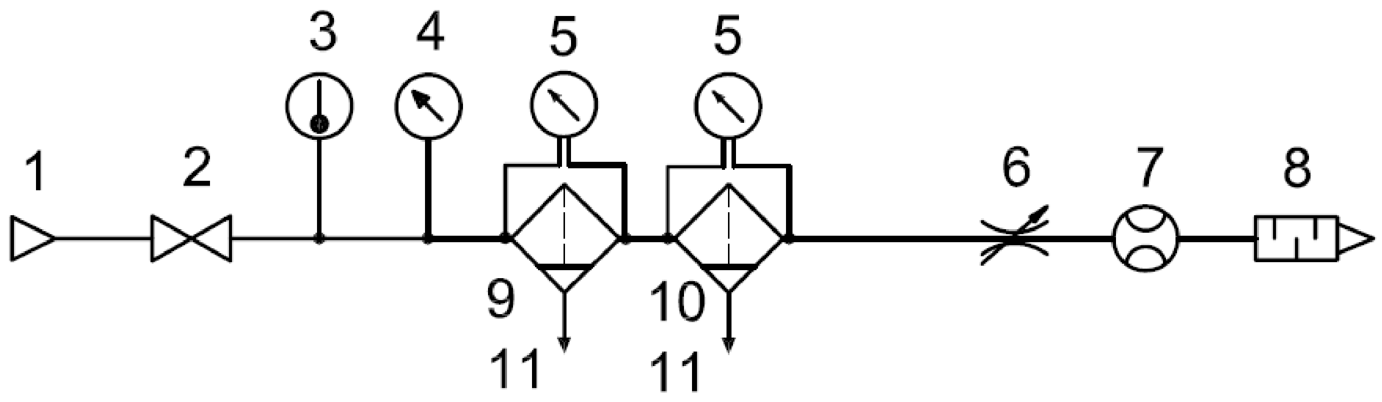
Parameter	Unit	Limit values [a]		Test method
		Min	Max	
Compressor oil [e,g]	mg/m³	-	15	ISO 8573-2

[e] The test method is “SP 5184 Oil: Biomethane/CNG – Oil carryover sampling and determination”

[g] The fuel shall be free from impurities other than “de minimis” levels of solid particulates. In the context of this European Standard, “de minimis” means an amount that does not render the fuel unacceptable for use in end user applications.

ISO8573-2:2007: compressed air: test methods for oil aerosol content

Method A



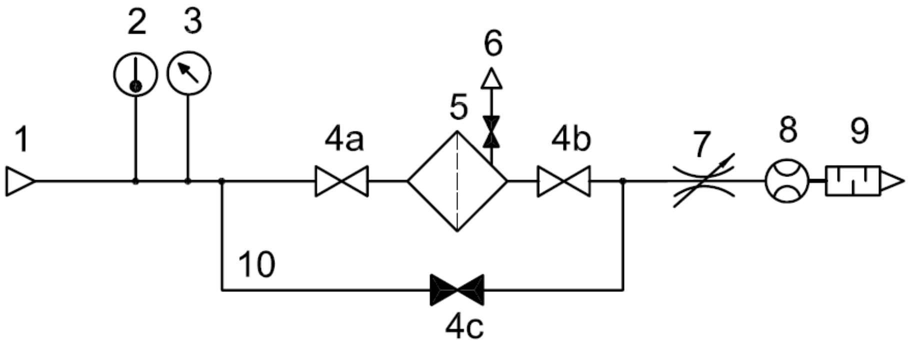
Key

1 compressed air sampling point
2 full-flow ball valve
3 temperature sensing/measuring
4 pressure sensing/measuring
5 differential pressure gauge
6 multi-turn flow control valve
7 flow sensing/measuring
8 silencer
9 sampling filter
10 back-up filter
11 liquid collection

The sampling filter is a high-efficiency, coalescing filter capable of removing the oil whose concentration is being measured from the upstream concentration and of reducing the downstream concentration to 0,01 mg/m^3 or less as determined by ISO 12500-1.

ISO8573-2:2007: compressed air: test methods for oil aerosol content

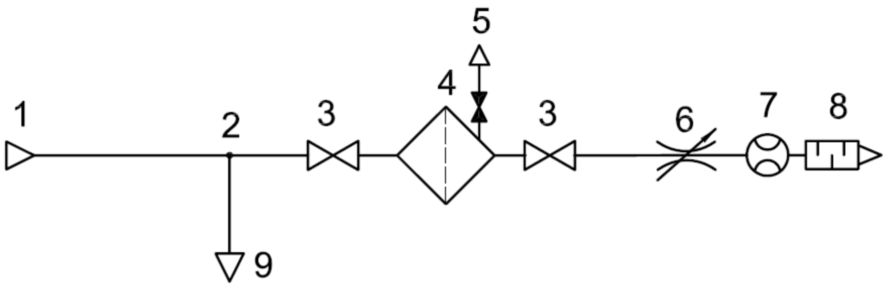
Method B1



Key

1	compressed-air sampling point
2	temperature sensing/measuring
3	pressure sensing/measuring
4a to 4c	full-flow ball valves
5	membrane holder
6	membrane holder depressurising valve
7	multi-turn flow control valve
8	flow sensing/measuring
9	silencer
10	bypass pipe

Method B2



Key

1	compressed air supply (upstream)
2	isokinetic probe insertion point
3	full-flow ball valve
4	membrane holder
5	membrane holder depressurising valve
6	multi-turn flow control valve
7	flow sensing/measuring
8	silencer
9	compressed air supply (downstream)

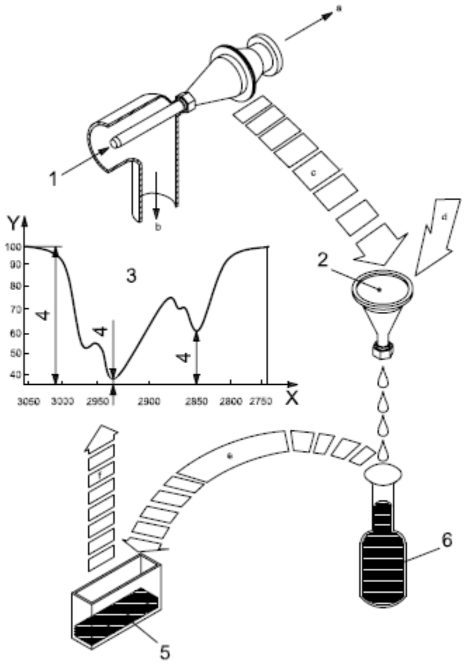
In order to obtain good measuring accuracy, a high-efficiency micro-fibreglass membrane should be used.

ISO8573-2:2007: compressed air: test methods for oil aerosol content

Analytical procedures

- Method 1: volume or weight measurement

- Method B1 and B2: the oil collected on the membrane or membrane holder is dissolved in a suitable solvent and the amount determined by infrared spectrometry or by gas chromatography/FID



SP5184 Oil: biomethane/CNG – Oil caryover sampling and determination

Background

Method has been developed through two projects financed by
The Swedish Energy Research Centre

2013: Development and validation of methods for test of CNG quality inclusive of oil carryover

2015: Optimal range oil CNG-biomethane

RISE has developed and tested a sampler. Due to the safety tests performed at a refuelling station, the gas must first be sampled in a buffer tank before it can pass onto coalescing filters.

Improvement of method SP5184 within the project 16ENG05

- We are working on:

- ❑ Improving methods to extract oil from the coalescing filters

- ❑ Improving analytical procedures

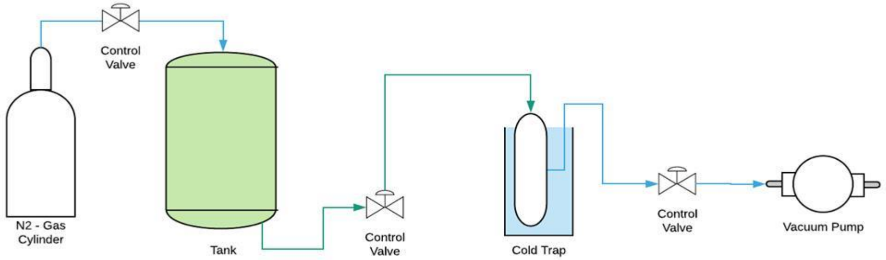
- ❑ Improving methods to recover deposits in the buffer tank

Methods to recover oil deposits in the buffer tank

	Method 1	Method 2	Method 3
	Propane	Pentane	Vacuum
Description of the steps	Sample of propane is taken as blank Sampler is set upside down and is connected to a propane bottle. The propane bottle is opened (15 – 30 s) to fill the buffer tank Three different fractions are then recovered	The methane left after sampling is removed with nitrogen. The buffer tank is disconnected and rinced 3 times with pentane. The buffer tank is flushed with nitrogen and the sampler is reassembled.	The tank is filled with pure nitrogen. The nitrogen is extracted and the tank put under vacuum using a pump connected at the exit. This process is repeated until the tank is cleaned.
Time consuming	Yes – method takes at least 1 hour	No – the method is straight forward	Yes – method will take at least 1 hour
Safety´s aspects			
Need to dissemble the sampler	no	Yes	No
Use of toxic substances (see below)	yes	No	No
Comments	Must be handled outside	A bit difficult to recover all the pentane due to some loss by evaporation	Method has not been tested

Propane

Pentane



Vacuum

Improvement of the analytical methods

- Survey sent to gas grid operators on the type of oil used
- Collection of at least 10 samples of oil
- Analytical method development using the collected oils:
  - Gas Chromatography /Mass Spectrometry - GC/MS (RISE)
  - Gas Chromatography / Flame ionization Detector – GC/FID (INERIS)
  - Thermal desorption tube (TDT)-Fourier Transform Infrared spectroscopy - TDT-FTIR (WAVERTON Analytics)

- Methods validation: performances evaluation (limit of detection, trueness, precision…)
- Methods uncertainty calculations (objective: < 10% rel.)
- Intercomparabilities of methods developed

Survey gas grid and biogas upgrading plant owners on the types of oils used

Survey type of oils used at compressor stations

Please take a moment to complete this brief survey. This survey is performed as part of the European research project 16ENG05 "Metrology for biomethane", from the European Metrology Program for Innovation and Research (EMPIR) (June 2017 – May 2020).
If you are operating several compressor stations, please select 1-4 preferably using different oils. In that case, please fill one survey per compressor station.
Provided information will be used to further develop an analytical method to measure oil carryover in compressed gas.

Compressor system (compressor types and brand):

Pressure before/after:

Which oil/oils are used in this site? (name + available characteristics)

Relevant information about the site (for cars, busses, how much gas is used…):

Which gas is delivered (biogas, natural gas, mixtures):

Are you measuring the oil consumption (if yes, how and what is the consumption?):

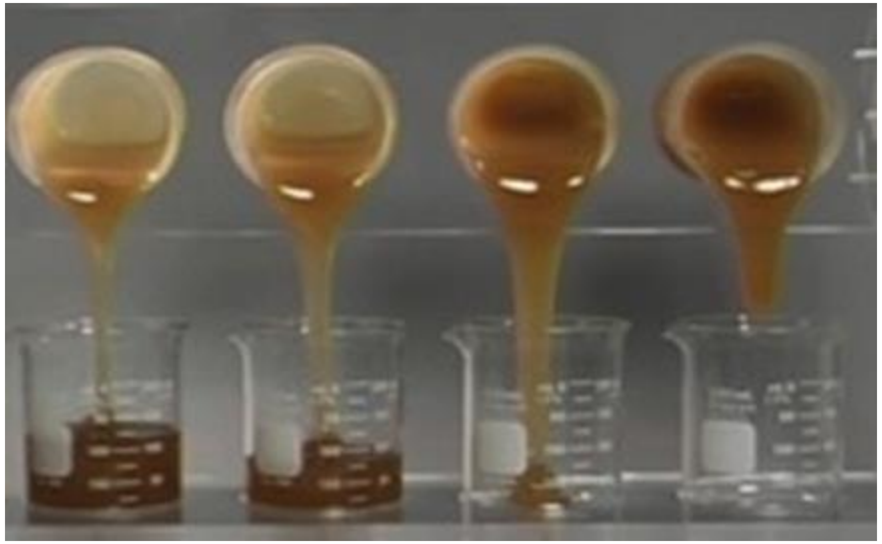
If any, describe the system to remove oils at the site (coalescing filters…):

Have drift problems being observed and are they related to oil?

Any observations in the vehicles using the site?

At least 10 samples of compressed oil collected

Oil name	Formulation	ISO viscosity grade	cST @40°C	cST @100°C	Density @15°C
Mobil Rarus SHC 1025		46	44	7.2	0.849
Mobil Rarus TM 427	high quality mineral base-oils and high performance additive system	100	104.6	11.6	0.879
Mobil SHC 629		150	150	21.1	0.86
Shell Tellus 32	Mineral oil		32	6.1	0.872
Mobil Univis TM N 32	hydraulic oils	32	32	6.39	0.876
Fuchs Titan Ganymet Ultra	Synthetic zinc-free oil				
Mobil SHC 527	synthetic hydraulic oils	100	100	15.94	0.8576
Mobil Pegasus 1			94	13	
Q8 Schumann 32	Synthetic oil based on poly-alpha-olefins	32	32	5.95	0.83
Q8 Schumann 68	Synthetic oil based on poly-alpha-olefins	68	68	10.3	0.837



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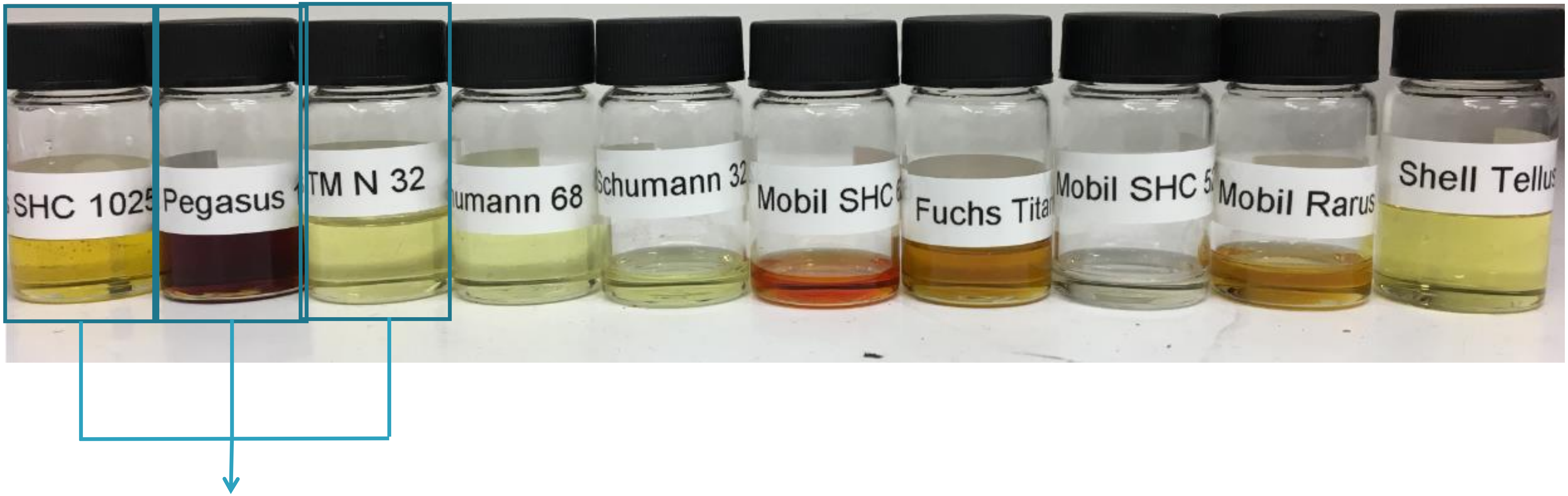
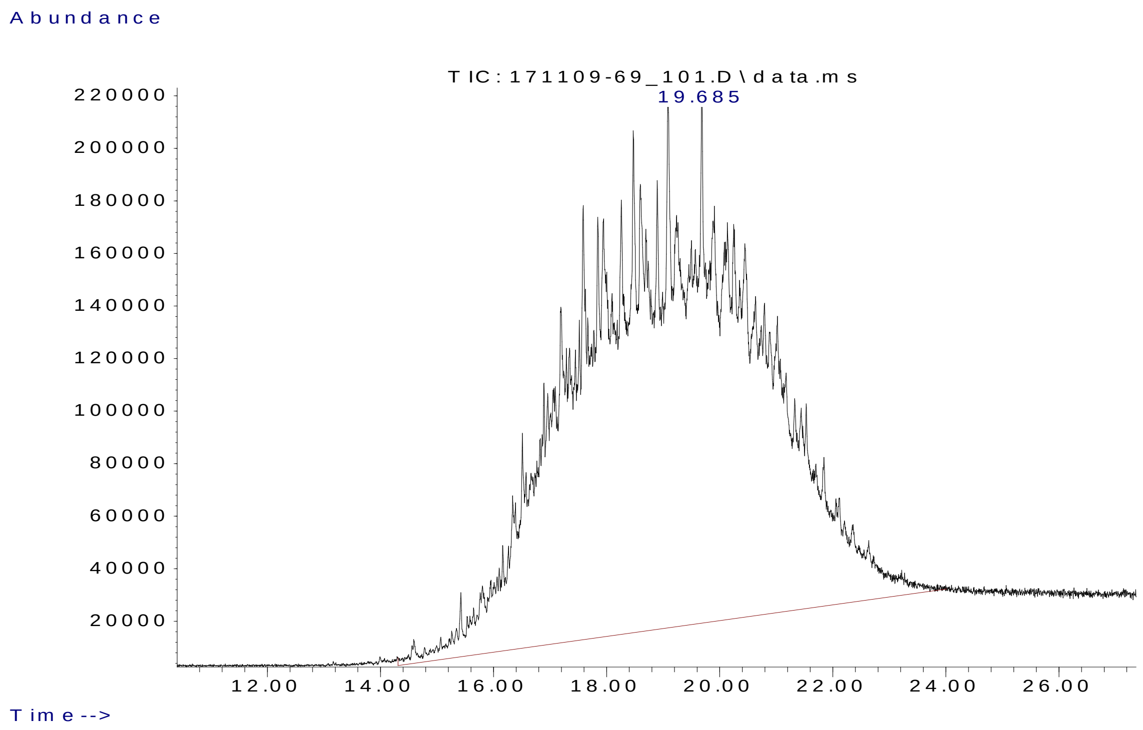
At least 10 samples of compressed oil collected

10 Oils sent to WAL and INERIS in September 2017 for methods development



3 oils selected for methods validation

GC profile of oils

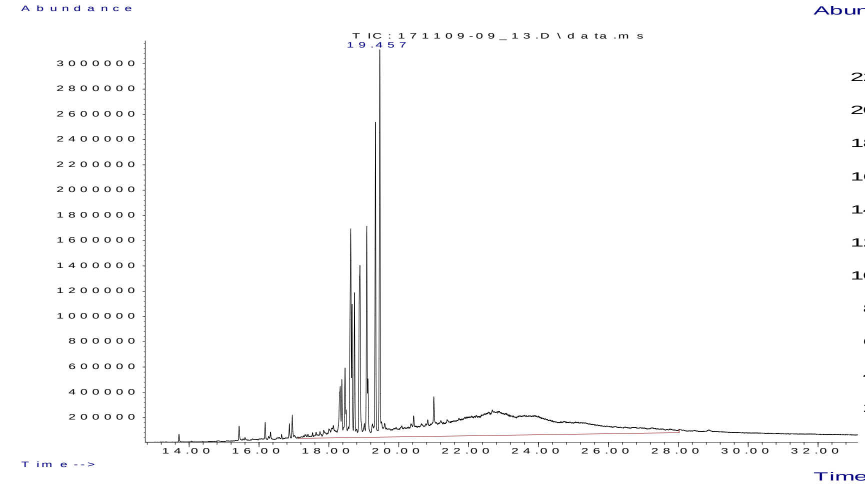


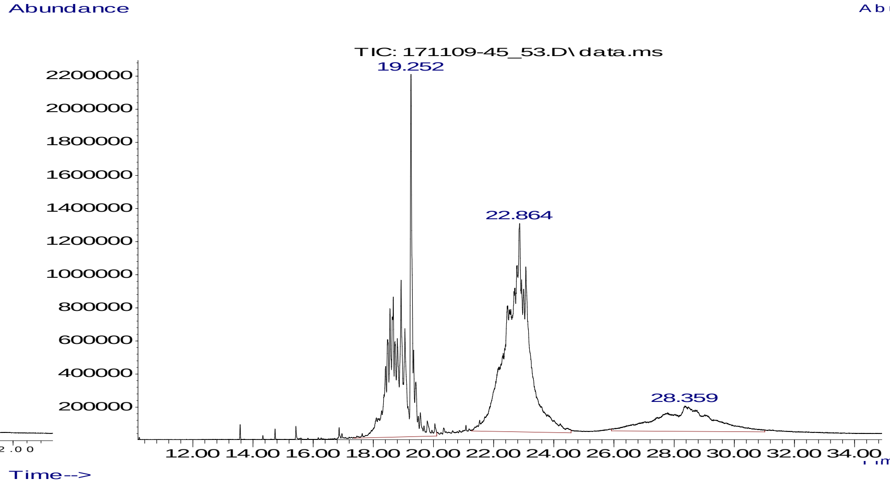
Mobil Univis TM N32

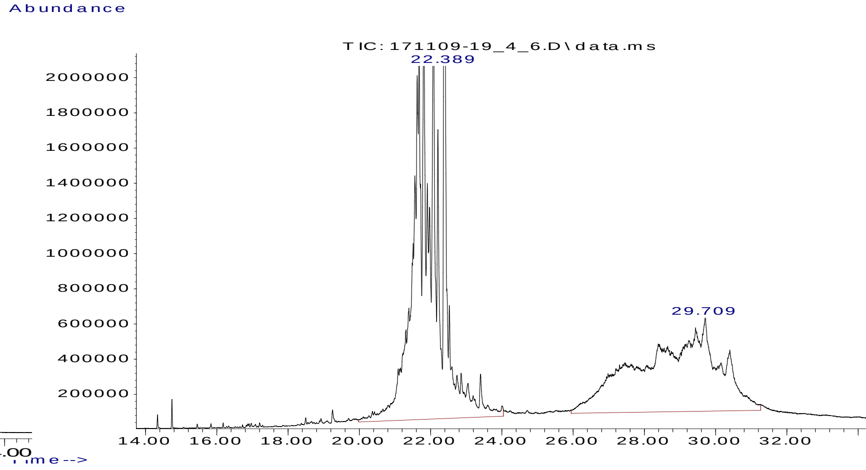
Oil itself is an astonishingly complex mixture comprising many individual compounds often including hydrocarbons and additives.

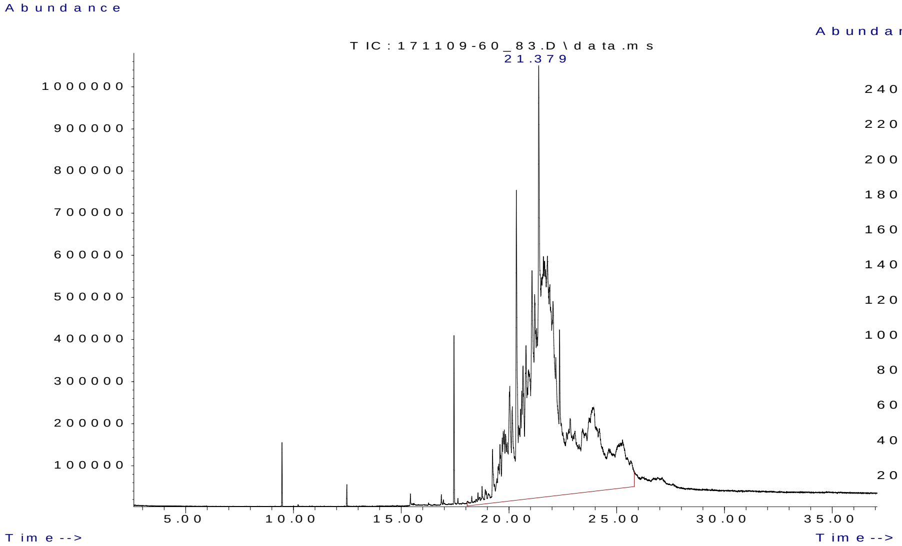
Compounds are unresolvable using conventional gas chromatography.

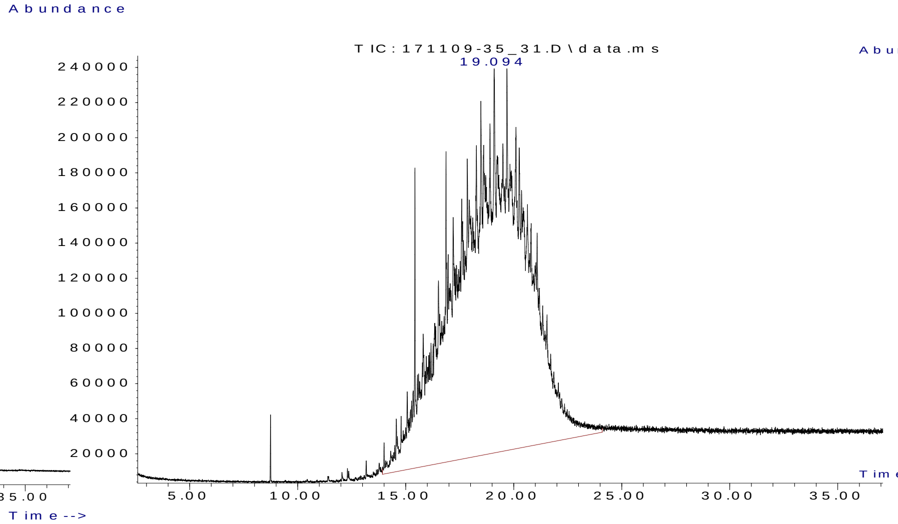
GC/MS profiles: however different profiles from oil to oil

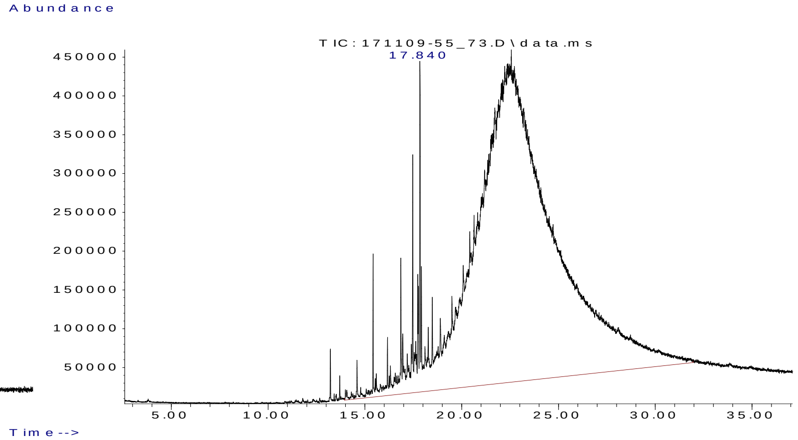




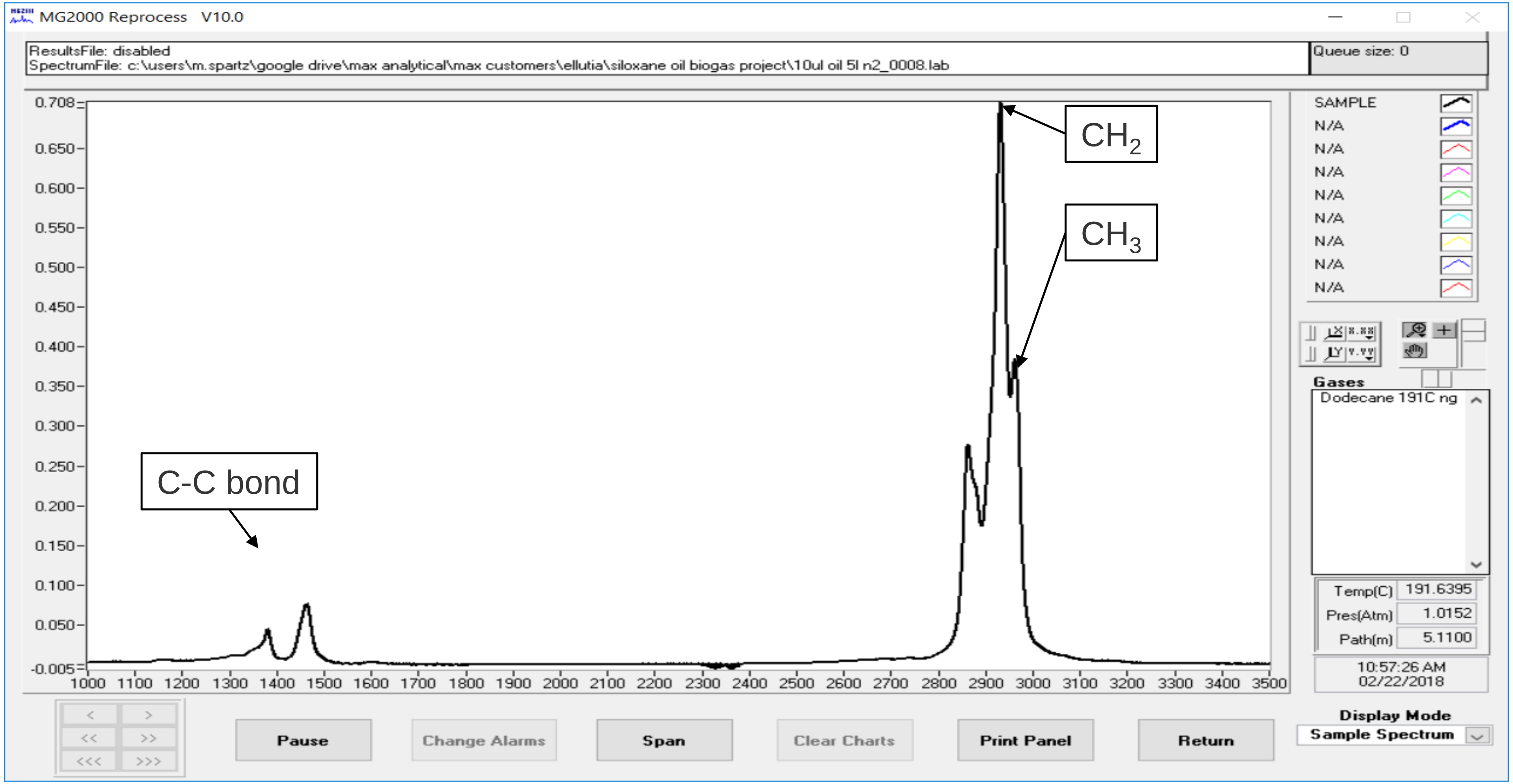








IR Spectrum of oil



Mobil Univis TM N32

Direct vaporisation of oil into N_2 stream

MDL of ~ 29 ng

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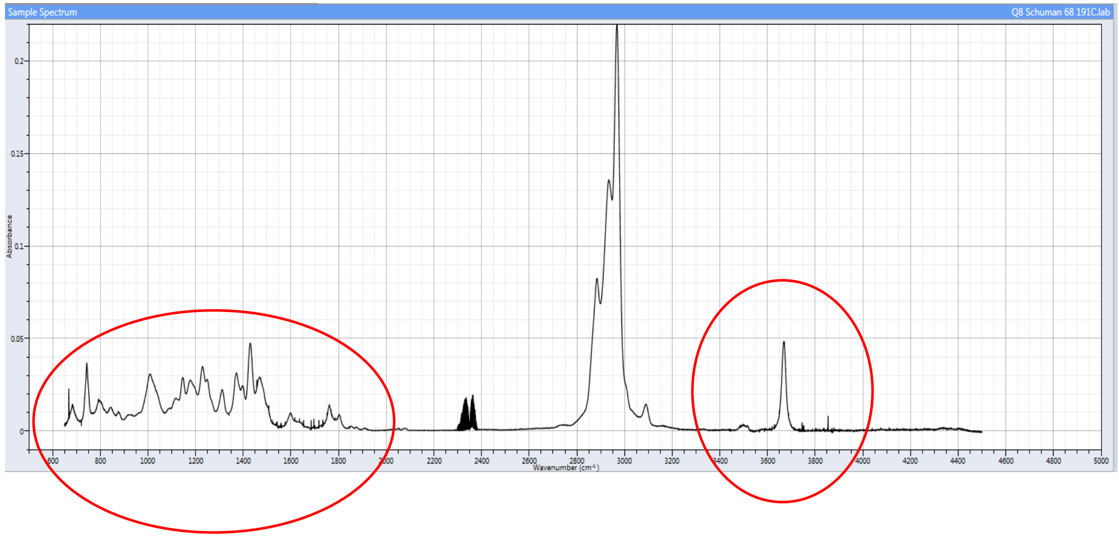
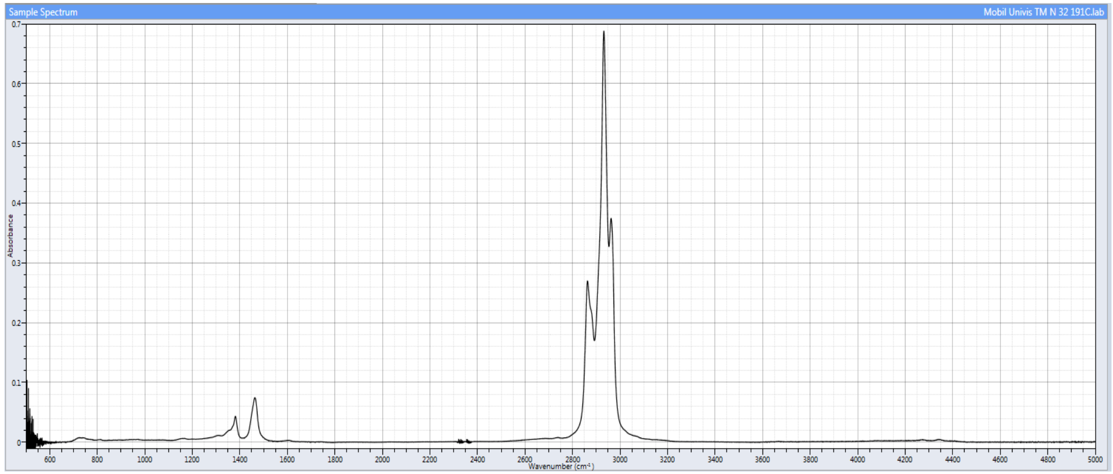
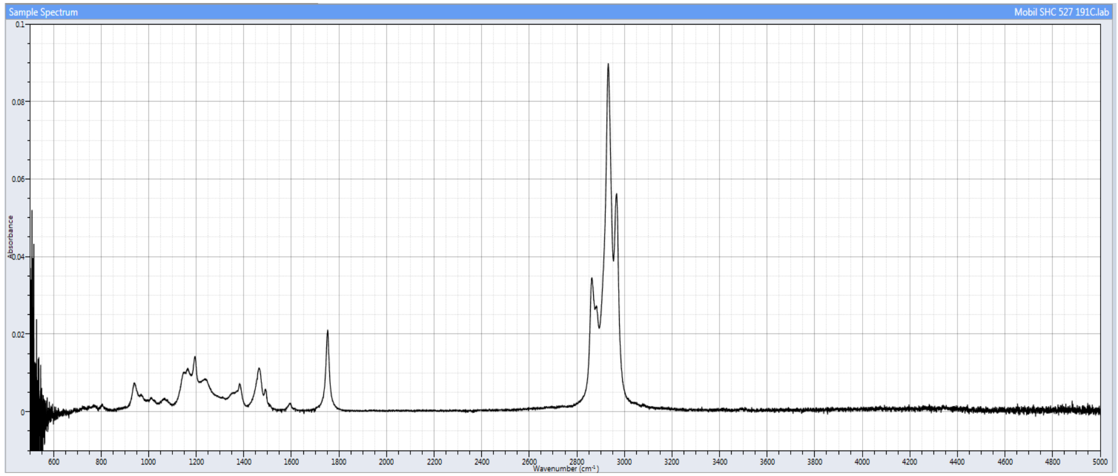
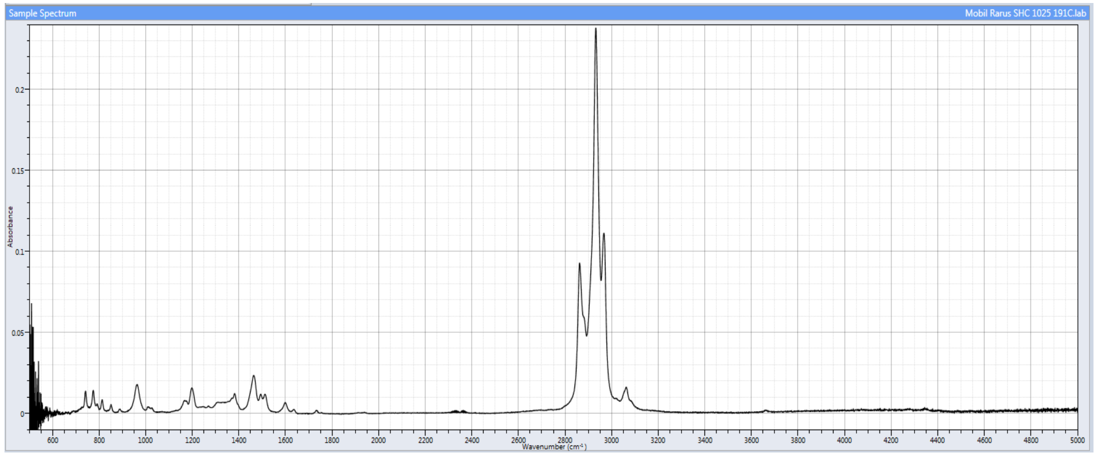
IR Spectrum of oils









Characterization of the oils with regards to metals (ISSI)

Work performed by ISSI (Innovhub Stazioni Sperimentali Per l´industria)

	Mobil Pegasus I	Rarus SHC 1025	Univis TM N32
	ppm	*ppm*	*ppm*
Al	<6	<6	<6
Mn	<5	<5	<5
Fe	<2	<2	<2
Ni	<5	<5	<5
Si	<8	<8	<8
Cr	<1	<1	<1
Cu	<2	<2	<2
Ti	<5	<5	<5
Mo	<5	<5	<5
P	486	1398	431
Zn	530	<5	<5
Sn	<10	<10	<10
V	<1	<1	<1
Ca	1340	<5	50
Pb	<5	<5	<5
Na	<7	<7	<7
Ba	<0,5	<0,5	<0,5
Cd	<1	<1	<1
Mg	<5	<5	<5
K	<5	<5	<5
Ag	<0,5	<0,5	<0,5
B	<4	<4	<4

Assuming 1 mg/Sm³ of compressor oil in biomethane
400-1400 ng/Sm³ P

ISSI results

INNOVHUB STAZIONI SPERIMENTALI PER L'INDUSTRIA
Innovazione e ricerca
STAZIONE SPERIMENTALE PER I COMBUSTIBILI

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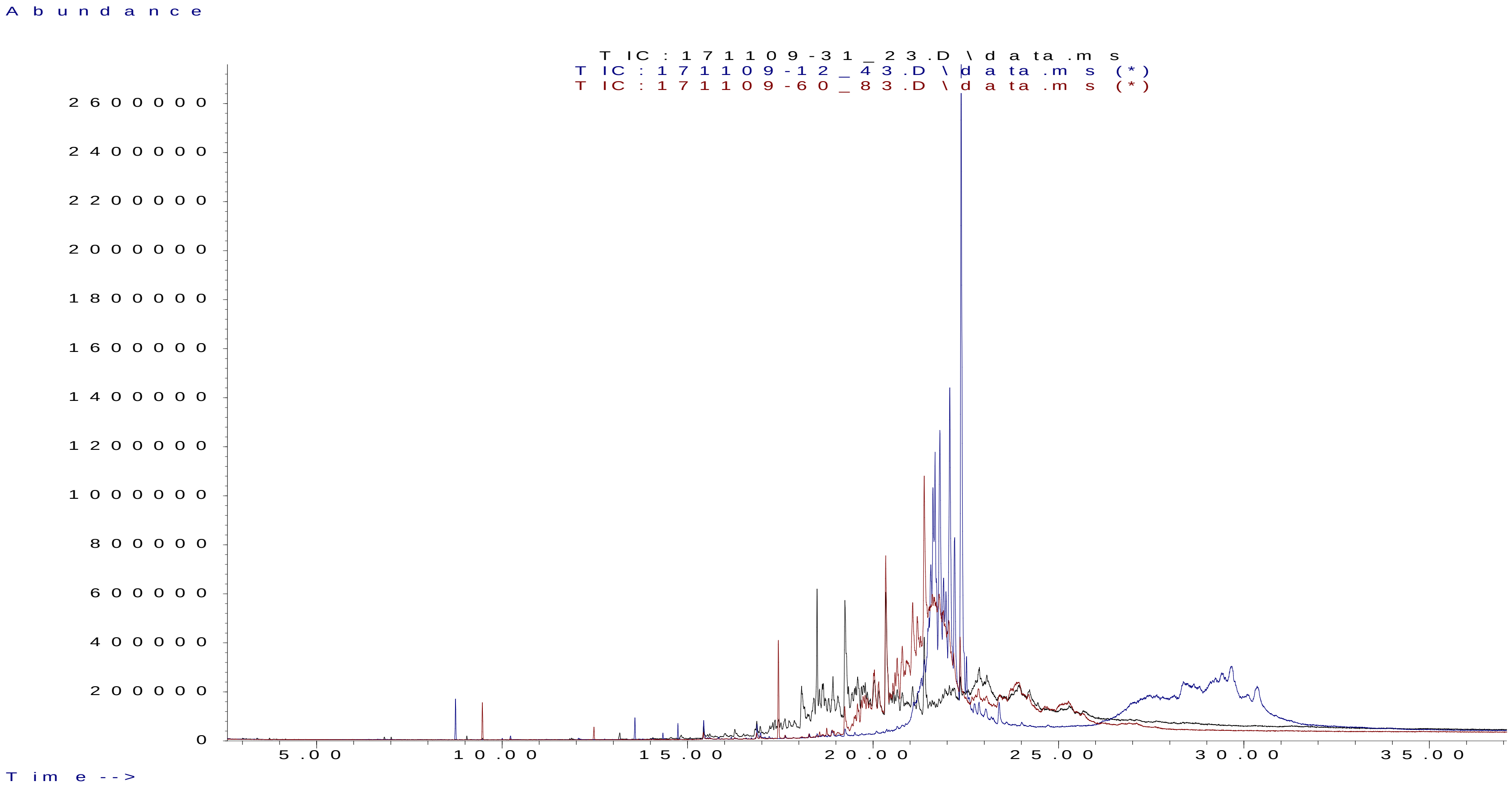
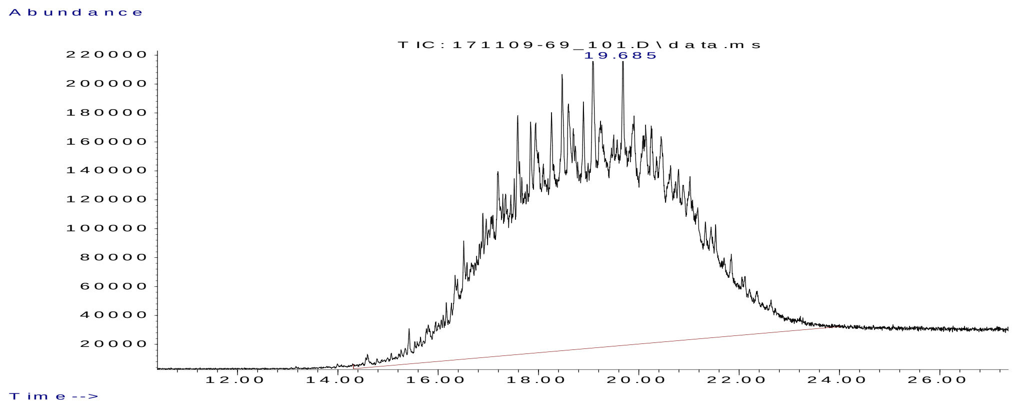
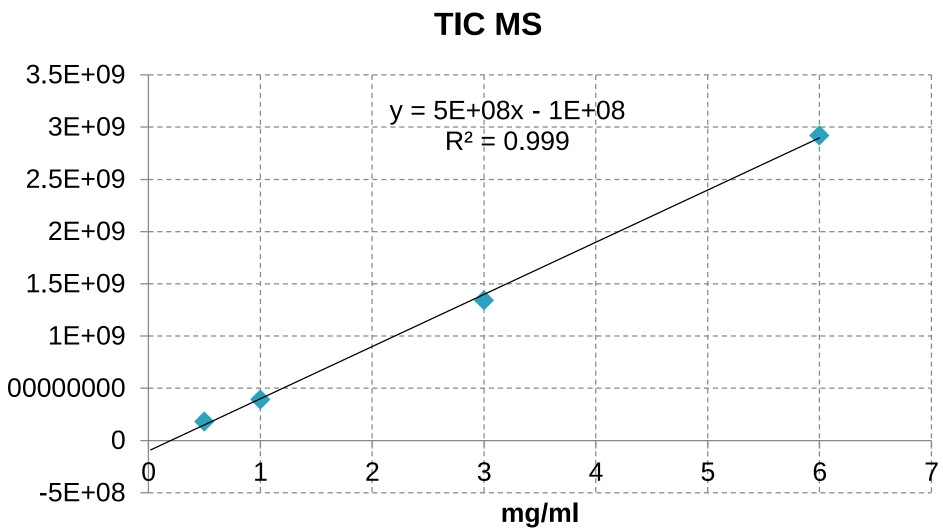
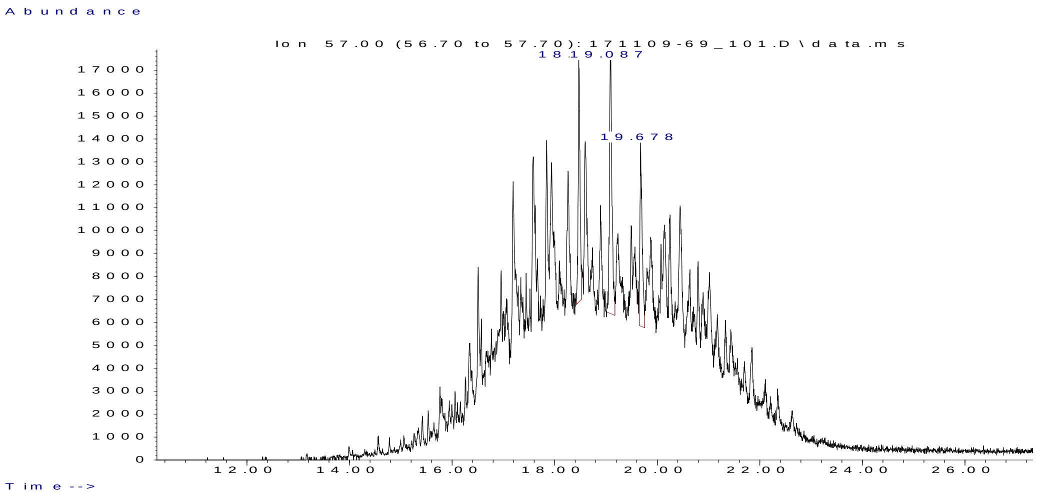
Poor GC selectivity, however normally only one or two oils are used in a compressor

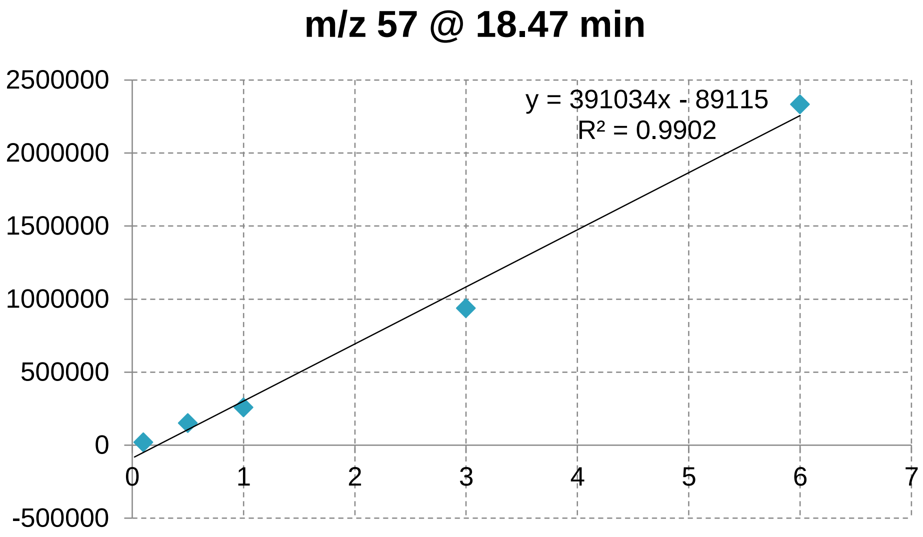


Development of GC/MS methods for the quantification of the oils: linearity



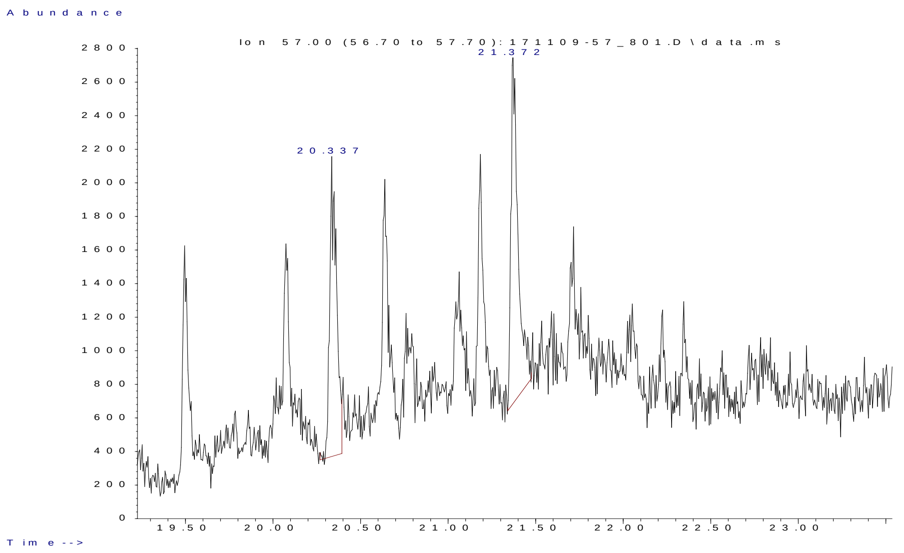




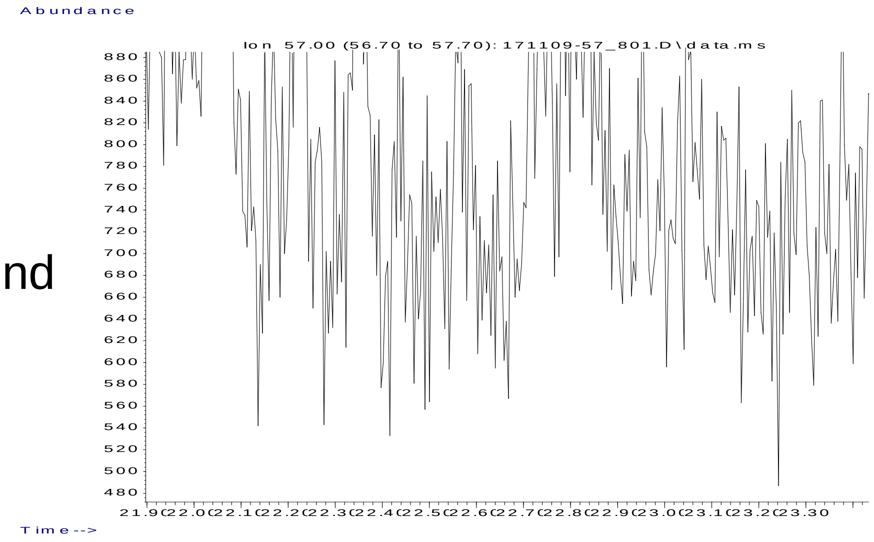


Development of GC/MS methods for the quantification of the oils: limit of detection

	Height	mg/ml		
m/z 57				
at 19.26	1200	0,1		
at 20.36	1400	0,1		
at 21.39	700	0,1		
Background	500		LOD	LOQ
			S/N = 3	S/N = 10
m/z 57	S/N		mg/ml	mg/ml
at 19.26	2,4		0,1	0,4
at 20.36	2,8		0,1	0,4
at 21.39	1,4		0,2	0,7

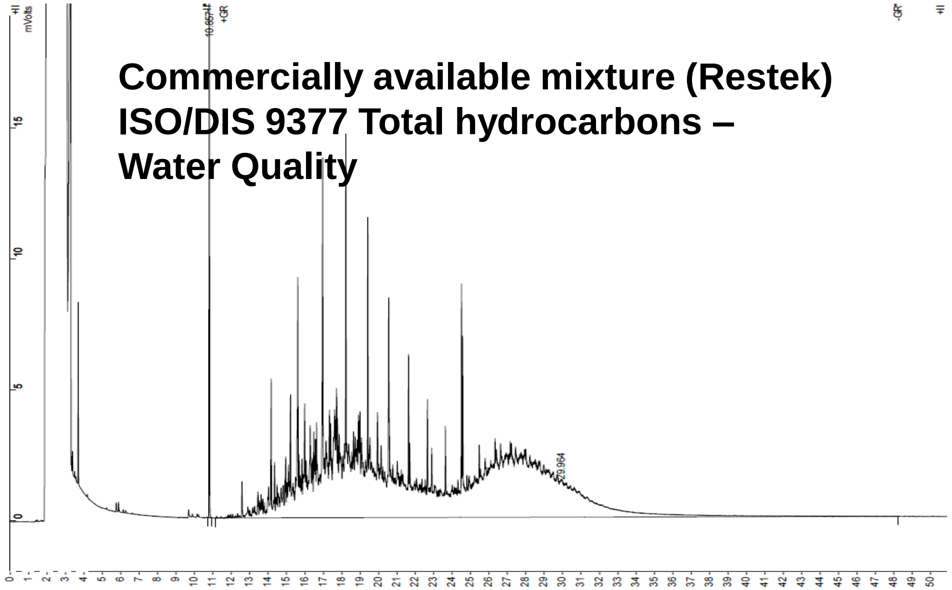


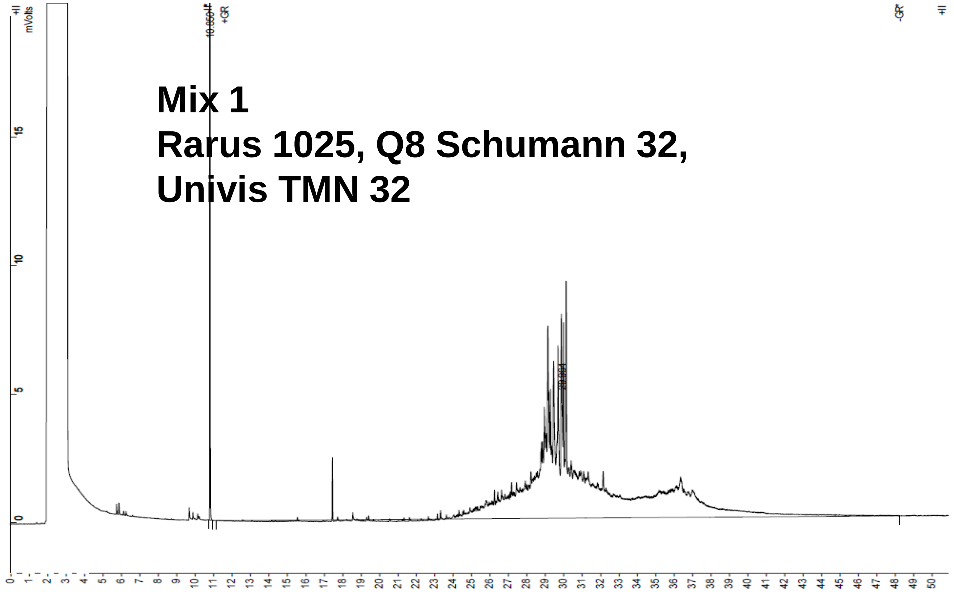
Background

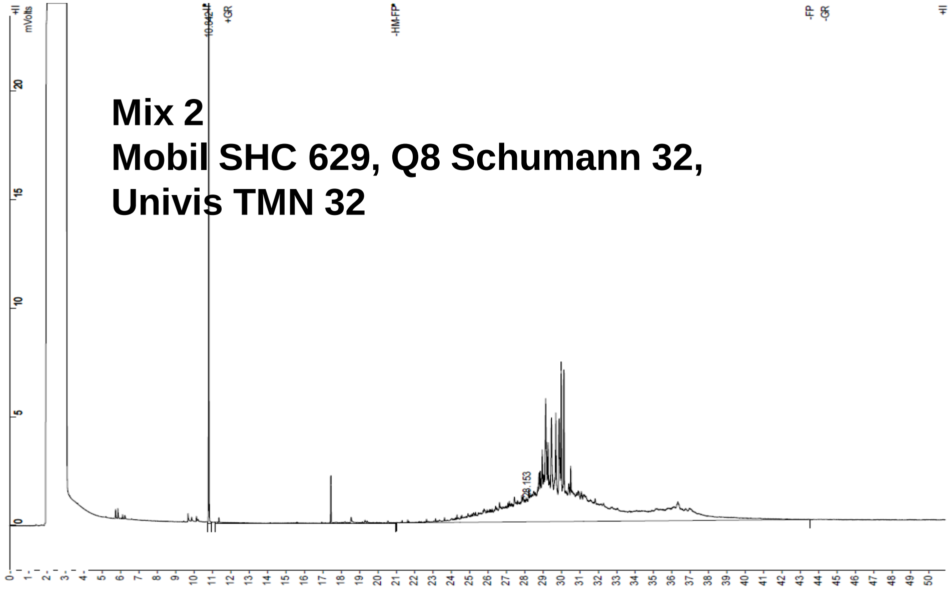


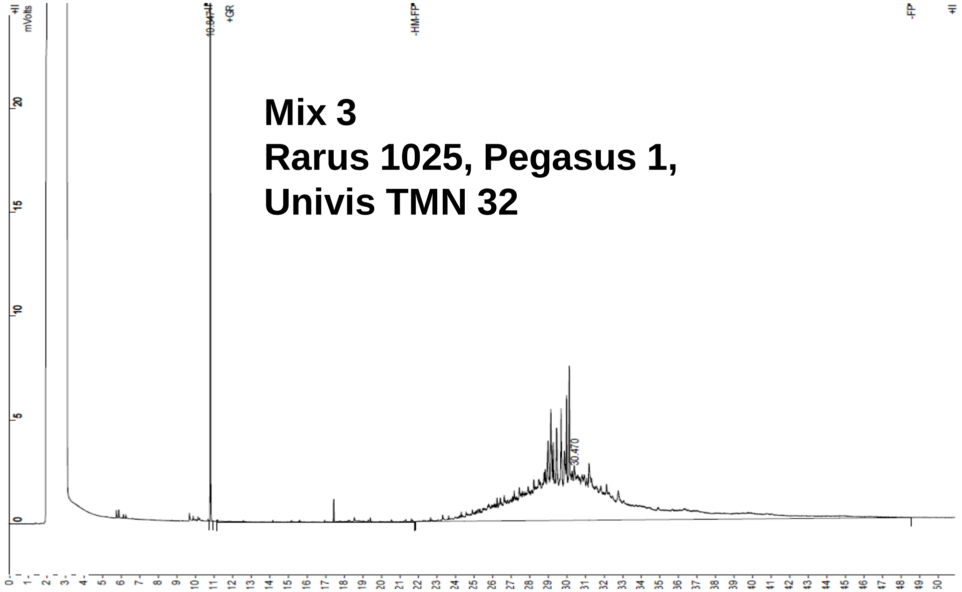
Profiles of the quantification standards used

ISO 9377-2 Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography

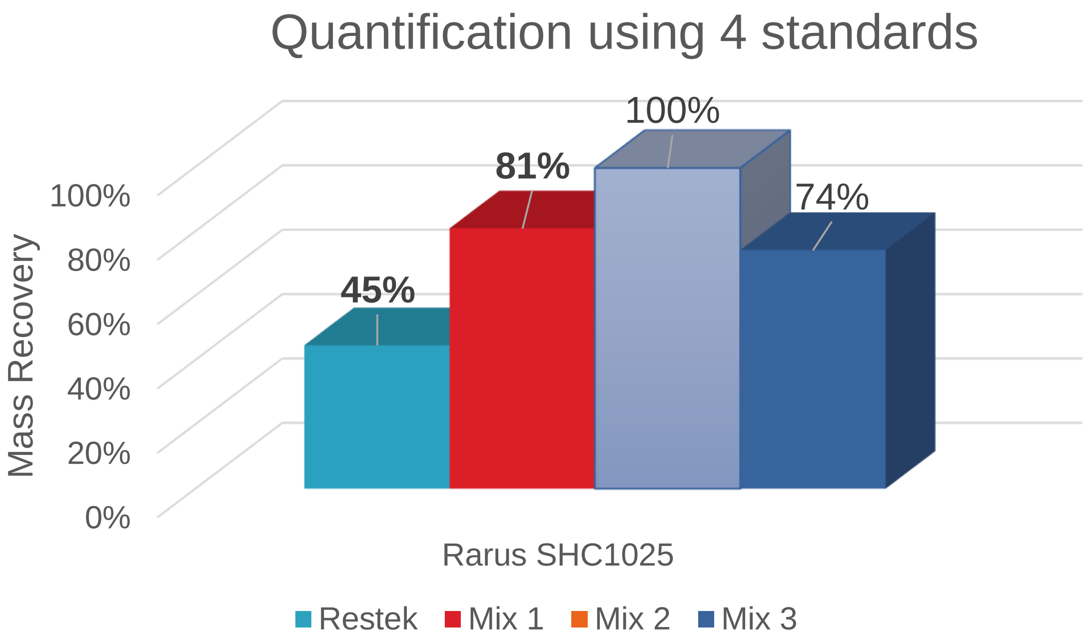


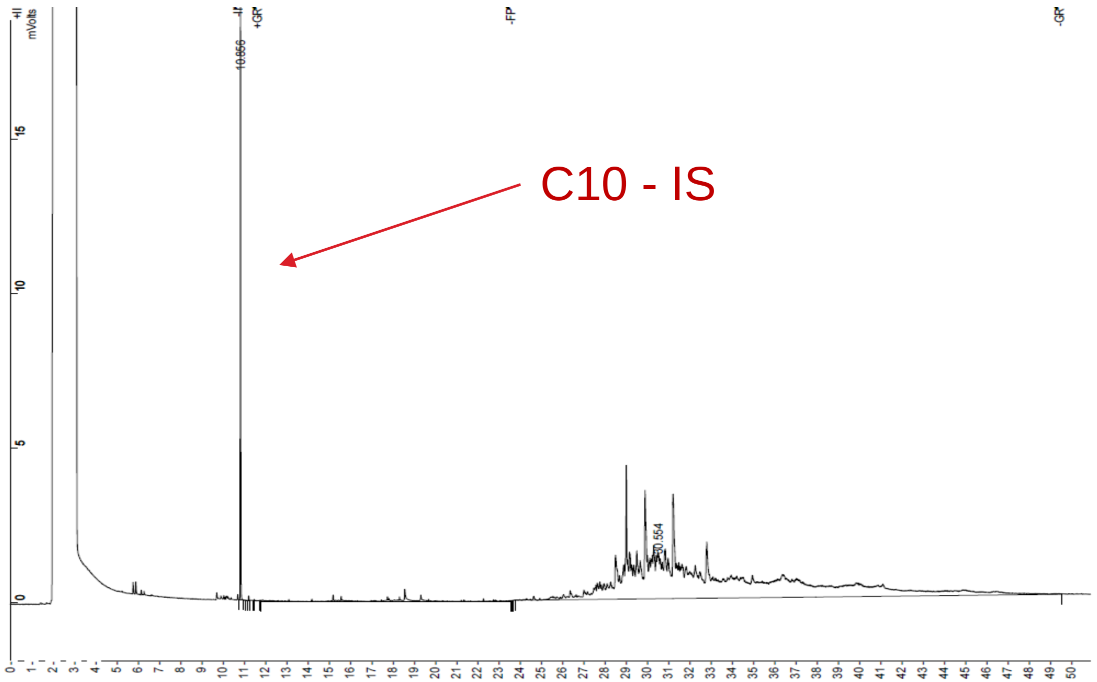






Example: quantification of Pegasus 1





- **Quantification using mix 2 (Mobil HSC 629, Q8 Schumann 32, Univis TMN 32) lead to 100% recovery.**
- **Recovery is underestimated with the 3 other standards, due to the difference of density and composition of oil mix.**

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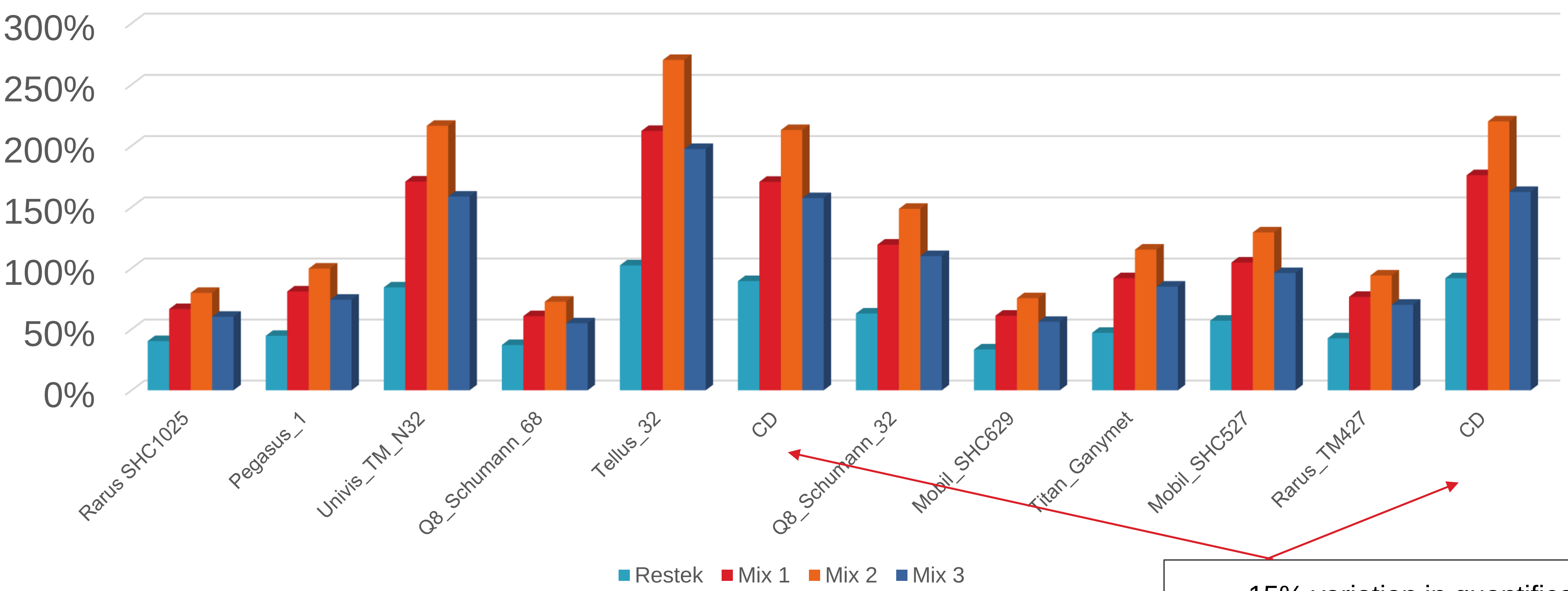
Quantification of the 10 oils using the 4 different standards mixtures



~15% variation in quantification process

Restek mix used as Qualiy Control (CD)

- Quantification with mixture could be under or over estimated depending on the standard choice for analysis.

➔ Oil from the station used for the analytical calibration will lead to more accurate result but can represent limitation to carry out on a large scale or with time (ageing of oil)

➔ Due to large composition of oils, using a mixture of oil for calibration will increase uncertainty measurement

Development of a method based on thermal desorption tube (TDT)-FTIR

- **Samples collected on TDT**
  - Solvent extraction not required
  - TDTs can be reused
- **Samples directly analysed by FTIR**
  - Analysis time of ~ 2-4 min per sample
  - Total oil concentration measured
  - Method based on carbon ladder analysis to determine similar CH_2 to CH_3 ratios
  - Equipment resilient to contamination by sample
  - Sensitivities of pg/l in biomethane

A2.4.2: Development of FTIR method

Direct injection of oils into the gas cell of an FTIR spectrometer using a calibrated syringe

The FTIR spectrometer was operated with a resolution of 4cm^{-1} (wavenumbers) and incorporated a 16µm cutoff liquid nitrogen cooled MCT IR detector.

- Gas cell: 5.11m pathlength, 200ml internal volume.
- The syringe injection: 10µl/min of oil into the gas cell, maintained at a constant temperature of 191°C, with a flow of nitrogen.
- Conclusion: gas cell used not appropriate for the application in terms of operating temperature. Gas cell materials not suitable for higher temperature operation
- New prototype developed (higher temperature, continuous flow gas cell (lower internal volume) & DTGS detector.
- The new FTIR spectrometer with 300°C gas cell tested in December 2018, a re-run of the compressor oil sample analysis completed by the end of January 2019.

Syringe pump assembly

WAVERTON Analytics

- Syringe pump
  - Oil injected at 10 µl/min flow
- Heated lines
  - Nitrogen carrier flow
  - Actual Run Temp 191°C inlet and outlet

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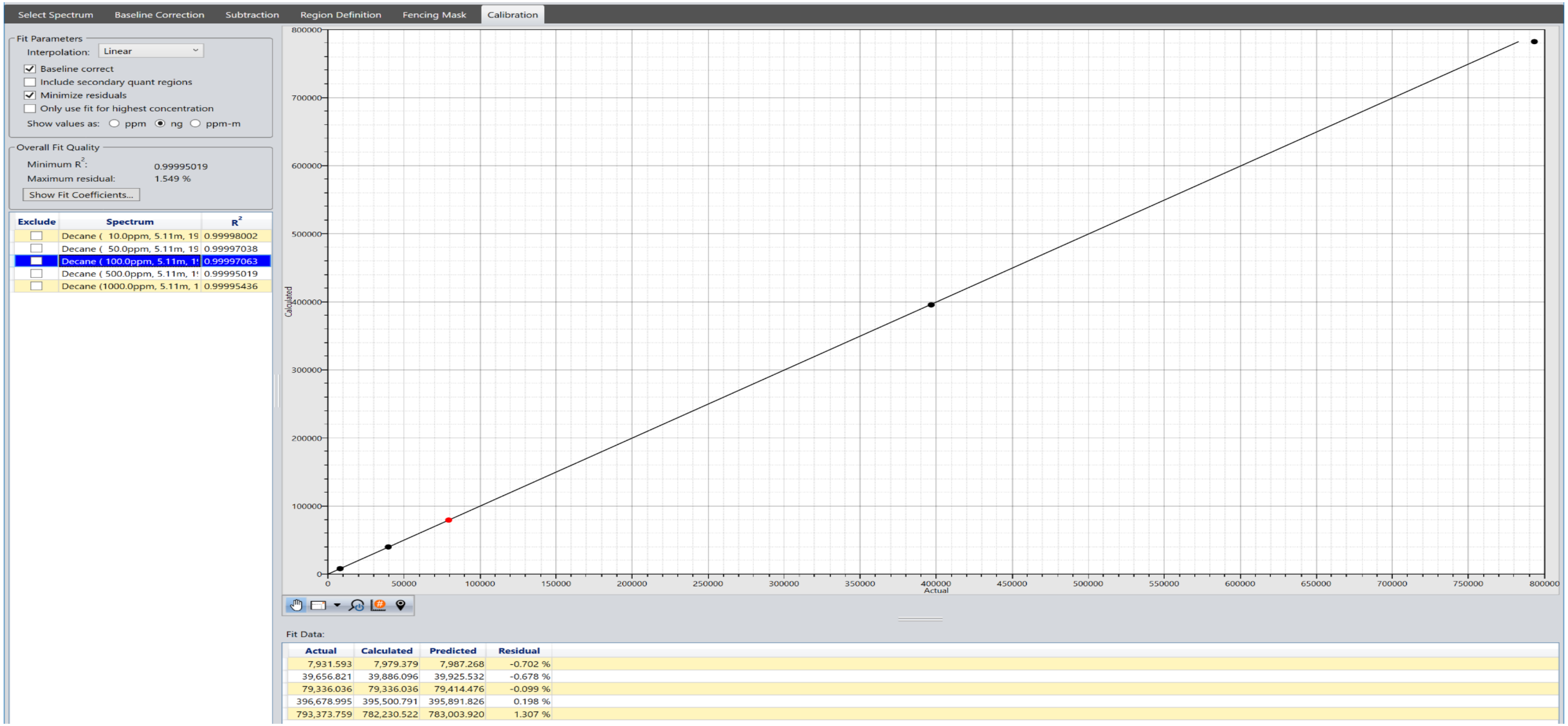
Calibration plot for decane



Linear calibration from 0 – 800,000 ng

Ongoing work

Produce a prototype GC-FTIR that has the capability of operating at much higher gas cell temperatures

→ Allow to see a greater proportion of the compressor oil sample.

Ongoing actions to reduce the cost and complexity of the method

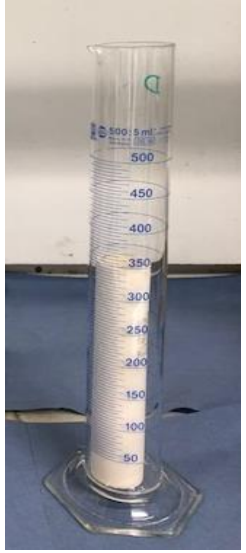
→ Be more attractive to the Biogas industry.

Currently: running initial tests with the prototype and later on running further compressor oil samples over the next couple of months.

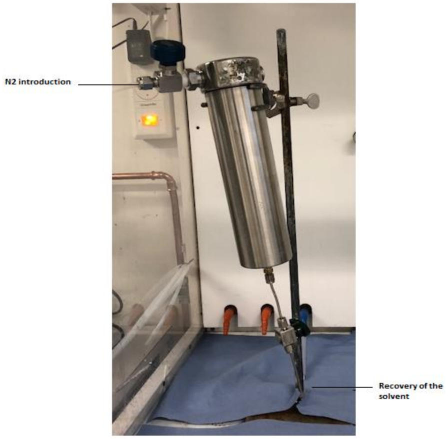
Improving methods to extract oil from the coalescing filters

Method 1: Extraction in dichloromethane and ultrasonic bath
The filters are introduced in a 500 ml measuring cylinder and dichloromethane is added
so the filter is completely immersed in the solvent
Ultrasonic bath – 60 min – then the volume of sovent is reduced to 10 ml using a rotavapor

Good efficiency, time consuming, large volume of solvent needed, some oil remains on the
filter together with the solvent absorbed



Method 2: The filter is introduced in a filter house containing 100 ml dichloromethane
The dichloromethane is removed from the filter using a flow of nitrogen, the solvent is
Recovered at the bottom of the filter house. Then the volume of sovent is reduced to 10 ml using a rotavapor

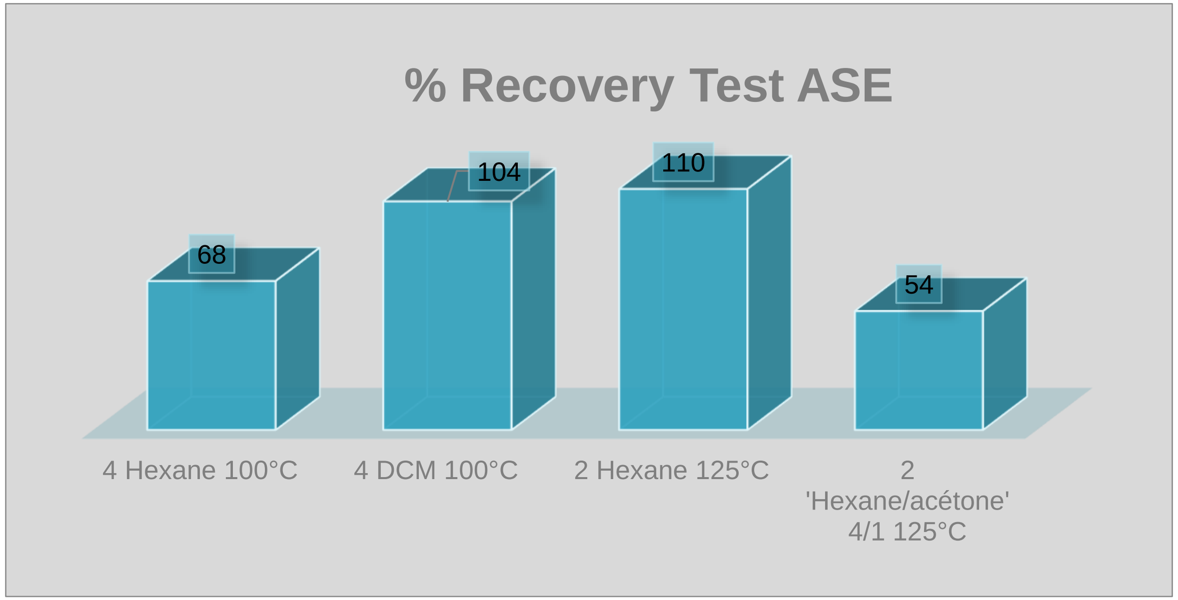


Difficulty to recover all dichloromethane (some evaporation?), small volume of solvent,
Time OK

Improving methods to extract oil from the coalescing filters

Method 3: Extraction of oil (Rarus 1025 QSP) from coalescing filters, using ASE (Accelerated Solvent Extraction)

-4 cycles with Hexane (100°C)
-4 cycles with dichloromethane (100°C)
-2 cycles with Hexane (125°C)
-2 cycles Hexane/Acetone 4/1 (125°C)



The filter need to be cut to fit in the ASE:
- Risk of losing oil (rinsing cutting devices)
- Time OK,
- Volume of solvent ok,
- Efficiency OK with DCM and hexane

Conclusions & perspectives

- **Sampling of oil is carried out through a buffer tank on coalescing filters**

➔Several methods for recovering oil adsorbed onto buffer tank have been investigated

➔Extraction methods of coalescing filters are under development

- **Analytical methods were studied using spectrocopic and chromatographic methods**

- **On-going work to validate analytical method (determination of limit of quantification, precision, robustness,…)**

RI.
SE

Questions?

Thank You