16ENG05 – METROLOGY FOR BIOMETHANE

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

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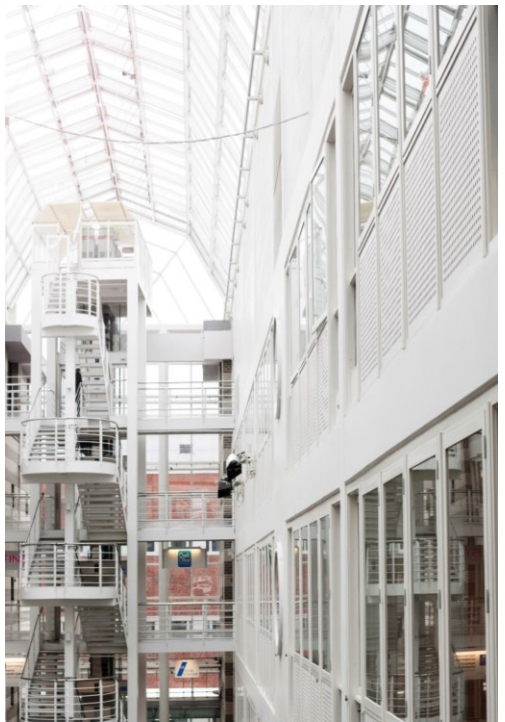


SHORT INTRODUCTION

- Problems associated with oil in biomethane
- What do ISO16723 standards say about oil – what is ISO8573-2?
- Measurement challenges
- Introduction to principle of coalescence
- RISE sampler
- What has been done during the project ”Metrology for biomethane”?

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

Standard EN16723-2:2017

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/m^3	-	15	ISO 8573-2

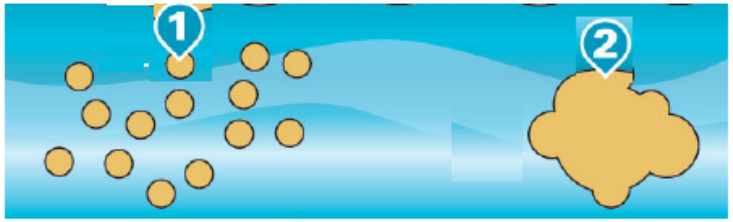
[e] The test method is "SP 5184 Oil: Biomethane/CNG – Oil carryover sampling and determination"

[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.

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)



1 **Aerosols** - Minute droplets of oil suspended in the air stream

2 **Vapors or oil mist** - Vaporised oil in a cloud form

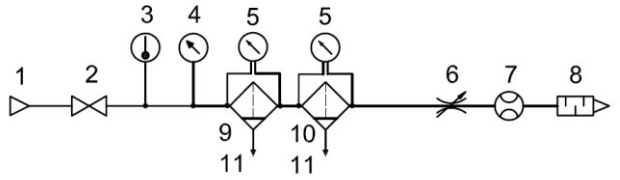
While aerosol can be trapped on coalescing filters (widely used in compressor stations), vapour oil cannot be filtered by them unless pressure and/or temperature decreases causing the evapourized oil to condense

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

Sampling + Analytical procedures

- Method A: sampling on coaleascing filters +volume or weight measurement

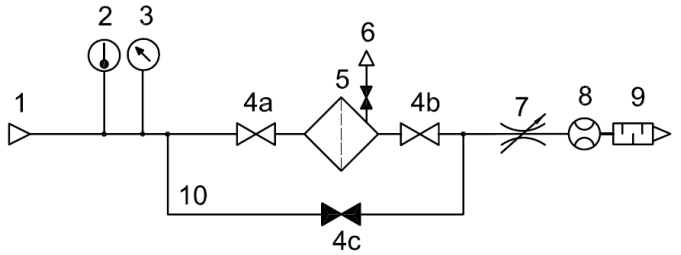
- Method B1 and B2: the oil collected on a microfiber membrane is dissolved in a suitable solvent and the amount determined by infrared spectrometry or by gas chromatography/FID



A

Key

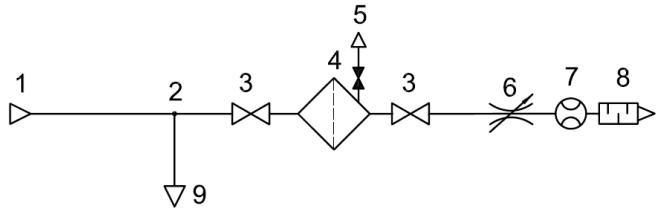
1	compressed air sampling point	7	flow sensing/measuring
2	full-flow ball valve	8	silencer
3	temperature sensing/measuring	9	sampling filter
4	pressure sensing/measuring	10	back-up filter
5	differential pressure gauge	11	liquid collection
6	multi-turn flow control valve		



B1

Key

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



B2

Key

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

Measurement challenges

At compressor stations, lack of sampling points where the sampling train proposed in the 8573 standards (constant flow…) can be installed

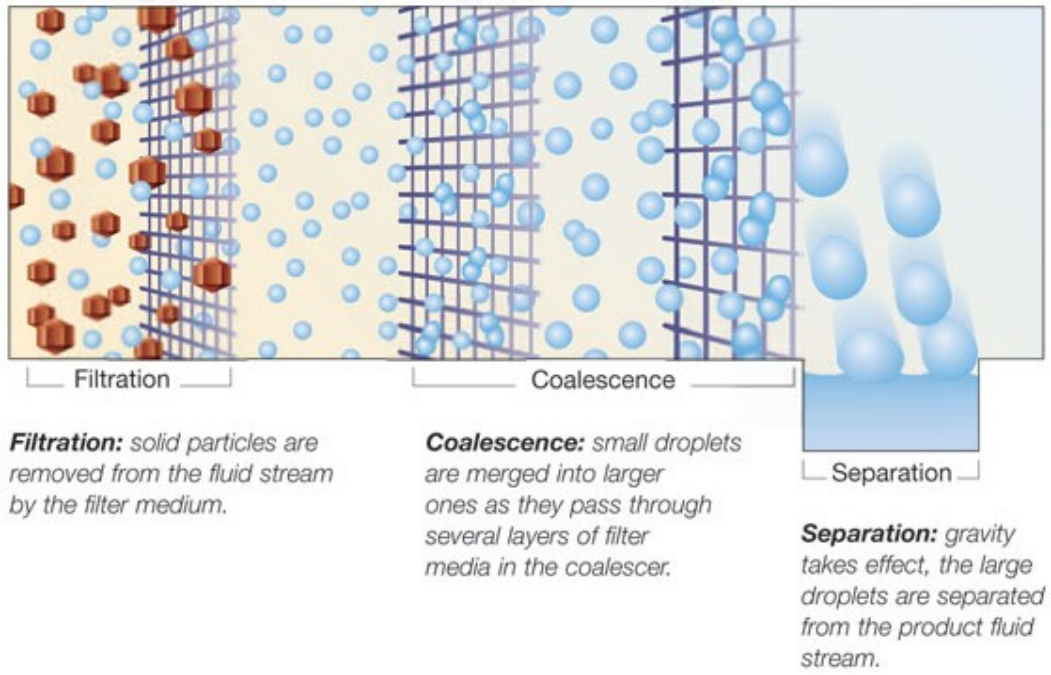
Taking samples using the ISO8573 standards is a challenge at the dispenser for at least 2 reasons:

1) The flow is not constant (it varies with the volume of gas in the car tank)
2) There are security systems that immediately stop a refueling if you try to fill to an open end

RISE DEVELOPED A NEW METHOD USING COALESCING FILTERS AND A SAMPLER WITH A BUFFER TANK ADAPTED TO DISPENSERS WITH NGV1 or NGV2 CONNECTIONS

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



Oil carryover sampling and determination

4) The rest of the gas in the buffer is safely released through a chimney

3) Filter house containing the main coalescing filter
80 bar of the gas in the buffer tank passes the filters after quick reduction of the pressure through a hole located just before the filters

2) Buffer tank
12 liter, fills
With 200 bar gas

Filter house containing the backup coalescing filter

1) NGV1 or NGV2 connection

What has been done during 16ENG05?

We worked on:

- ❑ Improving methods to extract oil from the coalescing filters
- ❑ Improving methods to recover deposits in the buffer tank
- ❑ Improving analytical procedures, lowering measurement uncertainties

  - ○ 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)

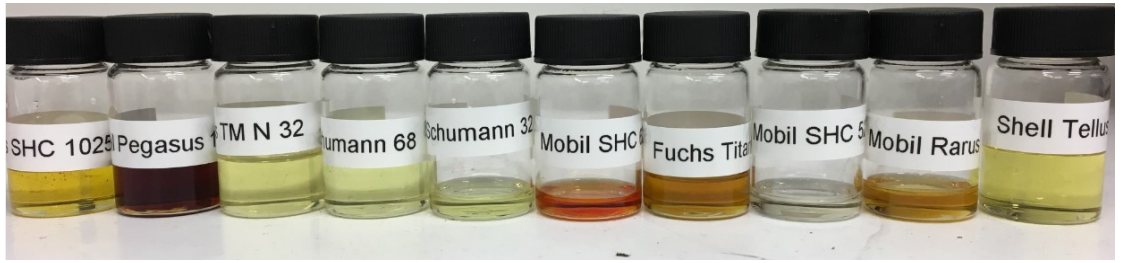
NWIP Compressor oil

- Foreword, scope, normative references, terms and definitions, symbols, principle, chemicals and materials, apparatus
- Sampling
- Methods to recover the oil from the buffer tank
- Extraction procedure for coalescing filters
- Analysis
- Calculations

Chemicals and materials

Compressor oils

For calibration purposes. Samples of all compressor oils used at the station to be tested or any other oils that can be present in the gas to analyse shall be separately collected to be used for preparing the calibration standards. Please note that oil references need to come from the same production batch as the ones actually used at the station. If not feasible, calibration can be made using equivalent oils.



Dilution solvent and extraction solvent

Dichloromethane or hexane, analysis grade, for preparing oil calibration standards. This should be of sufficient purity to ensure that it does not give rise to interferences during the analysis. Use only solvent of recognized analytical grade.

Calibration standards

Can be prepared by diluting amounts of oil (from 1 mg to 10 mg) in 1 ml of dilution solvent.

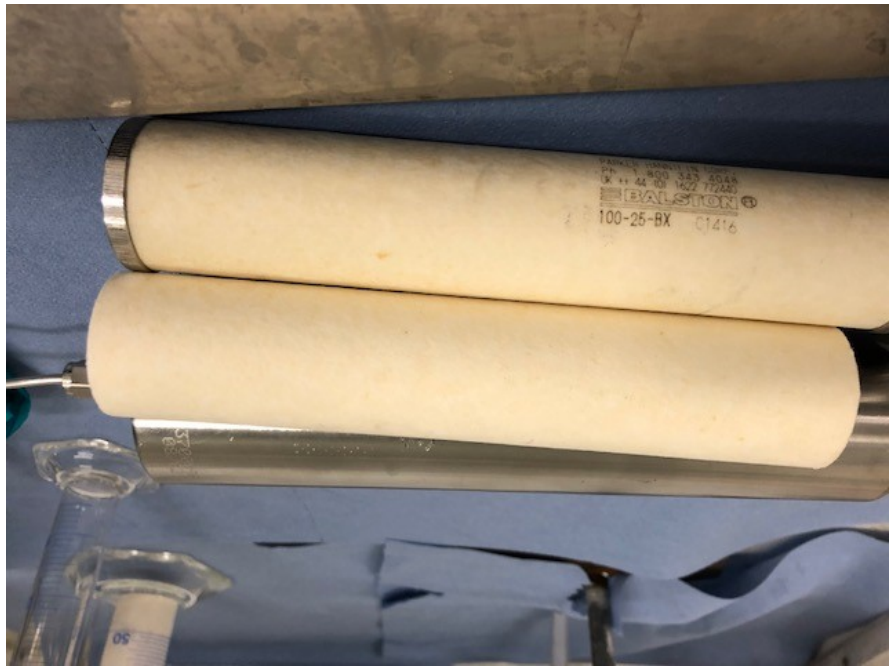
Chemicals and materials

Sampling filters

- The sampling filters are a high-efficiency coalescing filter made of borosilicate microfibers with fluorocarbon resin binder with more than 99.99% efficiency at 0.01 µm. Flow rate through the sampling filter shall not exceed the manufacturers' recommendation for the test pressure.

Backup filters

- This filter is identical to the sampling filter and, in the event of malfunction of the sampling filter, collects any oil, that passes through it.



Apparatus

Gas chromatography/mass spectrometer (GC/MS), EI mode or gas chromatography/flame ionisation detector (GC/FID)

Procedure 1

Ultrasonic bath, with start at ambient temperature. Temperature increase due to sonication can be neglected.

Filter house, equipped with an inlet for gas (nitrogen, high purity) and an outlet for gas and liquid at the bottom of the filter house.

Rotary evaporator, concentration apparatus, that is designed to allow the solvent extract to be reduced from more than 300 ml to 10 - 20 ml.

Procedure 2

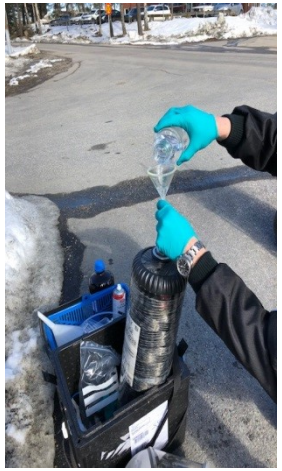
Pressurised fluid extraction apparatus. Consisting of extraction cells which can be heated to 150°C at static pressures up to 10 MPa. The device should be programmable regarding the temperature, duration and number of extraction cycles. The cells must be flushed with the extraction solvent.

Methods to recover the oil from the buffer tank

Oil that eventually has been deposed in the buffer tank is recovered by one of the two following methods:

1) After demounting the buffer tank from the sampler, rinse with at least 3 consecutive times with 250 ml pentane. Rinse with nitrogen to remove all solvent

2) Without demounting the buffer tank from the sampler, rinse at least 3 consecutive times with propane. Recover the propane by setting the sampler upside down. Rinse with nitrogen to remove all solvent



Pentane method

Propane method

Extraction procedure for coalescing filters

Procedure 1: Ultrasonic extraction – nitrogen flush

Transfer a coalescing filter to a measuring cylinder large enough to soak a whole filter

Introduce the extraction solvent into the measuring cylinder so the whole filter is soaked.

Perform two 30-minutes (± 5 minutes) long extraction in an ultrasonic bath

The solvent remaining on the filter is removed under a flow of pure nitrogen.

Concentrate the solvent extract to reduce the volume from 300-400 ml to 10-20 ml with a rotary evaporator (35 ± 3°C).

Extraction procedure for coalescing filters

Procedure 2: Pressurised fluid extraction

The filter is positioned in the extraction cell. (filter can be cut in several pieces).

The cell is then completed with a neutral matrix, clean sand, to reduce the void volume in the cell and therefore the solvent consumption

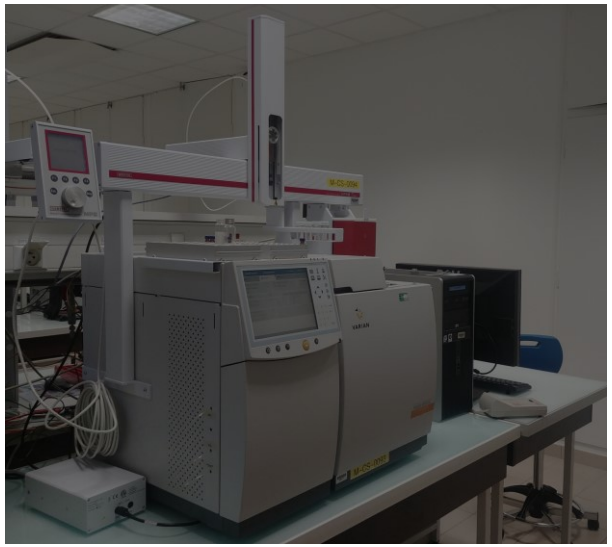
The extraction is then performed using the following conditions:

- ❑ Extracting solvent: hexane
- ❑ Temperature: 100 °C
- ❑ Number of extraction cycles: 2 cycles
- ❑ Time for an extraction cycle: 11 minutes
- ❑ Pressure: 120 bars

The extract is concentrated under nitrogen at a final volume of 10 mL.

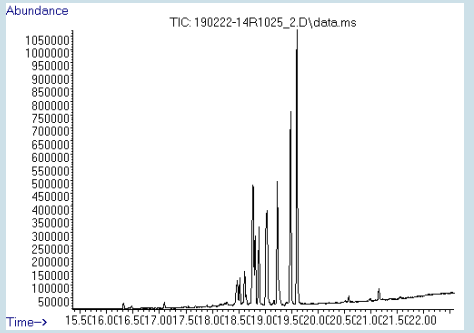
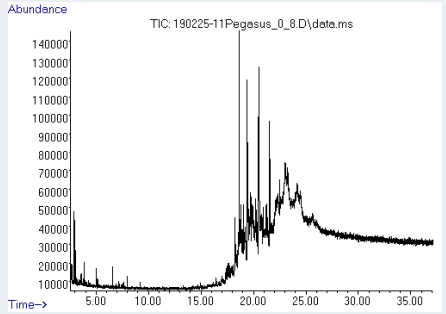
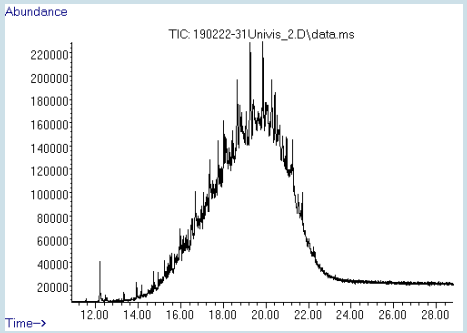
Analytical methods

Gas Chromatography / Mass Spectrometry
Calibration with oils to be analysed (from 0.1 to 6 mg/ml in dichloromethane)
Extracted ions to increase selectivity



Gas Chromatography / Flame ionization detector
Calibration with oils to be analysed
(from 0.2 to 6 mg/ml)

GC profiles of different types of oils

Oil	Type	
Mobil Rarus SHC 1015	Type 1: GC characteristic: well separated peaks	
Mobil Pegasus 1	Type 2: Globally unresolved peaks with some dominant peaks	
Mobil Univis TM N32	Type 3: Unresolved mixture	

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Calculations

- Data from calibration standards is used to calculate a response factor (area/mg oil in 1 ml dichloromethane) for each oil of interest. One (or more) ion(s) specific for the targeted oil should be extracted and used for the quantification (for the GC/MS method). Oil quantities in mg in a sample are calculated as the area of the oil characteristic ion(s) for the sample divided by the response factor divided by the volume of the concentrated solvent extract.
- Oil carryover is the sum of the oil recovered on the coalescing filters and the oil recovered in the buffer tank.
- The density (ρ expressed in $kg.Nm^{-3}$) may be determined from an accurate determination of the gas composition (according to ISO6974) and calculation based on composition using ISO 6976.

Calculations

Parameters needed:

- $V_{gas\ coal.}$ volume of gas sampled on a coalescing filter
- $V_{gas\ buffer.}$ total volume of gas sampled during one test (-) minus the volume of gas that has passed through the coalescing filters.

The oil recovered on the coalescing filters is expressed in mg/kg according to the following equation:

- Oil recovered on the coalescing filter in mg/kg
- $m_{oil\ coalescing\ (mg)} / (V_{gas\ coal.(Nm3)} \cdot \rho_{gas\ (kg.Nm-3)})$

The oil recovered in the buffer tank is expressed in mg/kg according to the following equation:

- Oil recovered in the buffer tank in mg/kg
- $m_{oil\ buffer\ (mg)} / (V_{gas\ buffer\ (Nm3)} \cdot \rho_{gas\ (kg.Nm-3)})$

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Thank You

RI. SE