

Biomethane/CNG – Oil carryover

1 Scope

This document gives general guidance for the sampling and analysis of oil carryover in biomethane/CNG. The oil carryover is determined by sampling on a coalescing filter under defined operational conditions (the two first Nm³ delivered at a refueling station). The oil carryover is expressed in ppmM.

2 Term and definition

3 Principle

The pressure of the gas to analyse is drastically reduced by forcing the gas to pass through a nozzle spray with a limited hole diameter (which implies that the temperature of the gas also drops) so as to make the oil condense as droplets and deposit on a coalescing filter. Two filters are connected in series, a main filter and a backup filter.

4 Chemicals and materials

4.1 Compressor oils, for calibration purposes. Samples of all compressor oils used at the station to be tested or any other oils that may 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.

4.2 Dilution solvent, dichloromethane, for preparing oil calibration standards. This should be of sufficient purity to ensure that it does not give rise to interferences during the GCMS analysis.

4.3 Extraction solvent, dichloromethane. This should be of sufficient purity to ensure that it does not give rise to interferences during the GCMS analysis.

4.4 Sampling filters, the sampling filters are a high-efficiency coalescing filter made of borosilicate microfibers with fluorocarbon resin binder with more than

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99.99% efficiency at 0,01 µm. Flow rate through the sampling filter shall not exceed the manufacturers' recommendation for the test pressure.

- 4.5 **Backup filters**, this filter are identical to the sampling filter and, in the event of malfunction of the sampling filter, collects any oil, that passes through it.
- 4.6 **Calibration standards**, can be prepared by diluting amounts of oil (from 1 mg to 20 mg) in 3 ml of dilution solvent.

5 Apparatus

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

5.2 **Capillary column**, for gas chromatography, fused silica coated with a non-polar bonded phase which performs equivalent to a 5% diphenyl, 95% dimethylpolysiloxane.

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

5.4 **Rotary evaporator, concentration apparatus**, that is designed to allow the solvent extract to be reduced from 500 ml to 10 to 20 ml.

5.5 **Laboratory glassware**

5.5.1 **Flat-bottomed flask**, capacity 500 ml

5.5.2 **Measuring cylinder**, capacity 500 ml

6 Sampling

6.1 **Sampling line**

The sampler consists of a NGV1 connection, 1/2" tubing, a manometer, 3 ball valves (oasis engineering ltd), a 12.5 liter composite CNG bottle, and two EU37/25 filter houses (with coalescing filters) connected in series after a spray nozzle of 0.3 mm hole diameter and union tees.

6.2 **Sampling**

The sampler is connected to the dispenser through the NGV1 connection. A refueling is started and manually stopped (if necessary) when the pressure in the bottle has

reached at least 180 bar (which corresponds to between 2.1 to 2.6 Nm³ gas sampled). The sampler is then disconnected from the dispenser and brought aside.

The gas is released through the chimney by opening a ball valve until the pressure in the bottle reached 180 bar (this pressure has been chosen as it supposedly can be achieved in all stations even the ones working at slightly lower pressures than average). The pressure is read when the temperature in the cylinder has reached equilibrium (the pressure is then stable). The gas is then led through the coalescing filters by opening the two other ball valves. As the gas passes first through the hole of the nozzle, the pressure drops resulting in a temperature drop and the oil is trapped on the filter.

The sampling can then be stopped when the pressure in the bottle reaches 100 bar (approximately equivalent to 1 Nm³ sampled), 120 bar (approximately equivalent to 0.75 Nm³ sampled) or 140 bar (approximately equivalent to 0.5 Nm³). These pressures are read when the temperature in the cylinder has reached equilibrium (the pressure is then stable). The correct gas volume is calculated by division with the appropriate compressibility factor, which is calculated by the use of commercial or inhouse software/Excel worksheets based on literature. Input data are pressure, ambient temperature and gas composition. Preferably, the sampler is then refilled with the gas to analyse in the same way to perform several samplings. The filters are removed after one sampling and new filters are installed in the filter houses. Once all samplings are performed, the gas left in the bottle is released through the chimney.

7 Extraction procedure

- 7.1 Transfer a coalescing filter to a 500 ml measuring cylinder
- 7.2 Introduce 350 ml extraction solvent into the measuring cylinder.
- 7.3 Perform a 30 minutes (± 5 minutes) long extraction in an ultrasonic bath
- 7.4 Turn the coalescing filter upside down and perform a 30 minutes (± 5 minutes) long extraction in a ultrasonic bath
- 7.5 Transfer the extraction solvent into a 500 ml flat-bottomed flask
- 7.6 Introduce another 250 ml extraction solvent into the measuring cylinder
- 7.7 Perform a 30 minutes (± 5 minutes) long extraction in a ultrasonic bath
- 7.8 Transfer the extraction solvent from the second extraction into the flat-bottomed flask containing the extraction solvent from the first extraction
- 7.9 Concentrate the solvent extract to reduce the volume from 500 ml to 10-20 ml with a rotary evaporator ($35 \pm 3^\circ\text{C}$). Note down the final volume. Store the concentrated solvent extract cold until the GCMS analysed is carried out.

8 GCMS analysis

The quantification can be done using either a FID or a MS detector. The mass spectrometer is tuned in accordance with the manufacturer's instructions. Chromatograms are recorded in full scan (typically 32 to 450 absolute mass units (amu). Analyse the concentrated solvent extracts, the calibration standards and the extraction solvent.

9 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. 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 then expressed in ppmM (part per million by weight) according to the following equation:

$$\text{Oil carryover in ppmM} = m_{oil (g)} V_{gas} (Nm^3) \cdot \rho (g.Nm^{-3}) \cdot 10^6$$

The density (ρ expressed in $g.Nm^{-3}$) may be determined from an accurate determination of the gas composition (according to ISO6974) and calculation based on composition using ISO 6976. V_{gas} is the volume of gas sampled on the coalescing filter.

10 Bibliography

SGC 2013:290, Development and validation of methods for test of CNG quality inclusive of oil carryover, K. Arrhenius, H. Yaghooby, P. Klockar,
<http://www.sgc.se/ckfinder/userfiles/files/SGC290.pdf>

ISO 6974-3,4,5,6:2000/2002, "Natural gas -- Determination of composition with defined uncertainty by gas chromatography"

ISO 6976:1995, "Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition".

AGA Report No. 8, Compressibility Factor of Natural Gas and Related Hydrocarbon Gases (1994)
<http://www.techstreet.com/aga/products/294>

Annex A
(Informative)

Example of a chromatogram obtained for a compressor oil
(Mobil Rarus SHC1025)

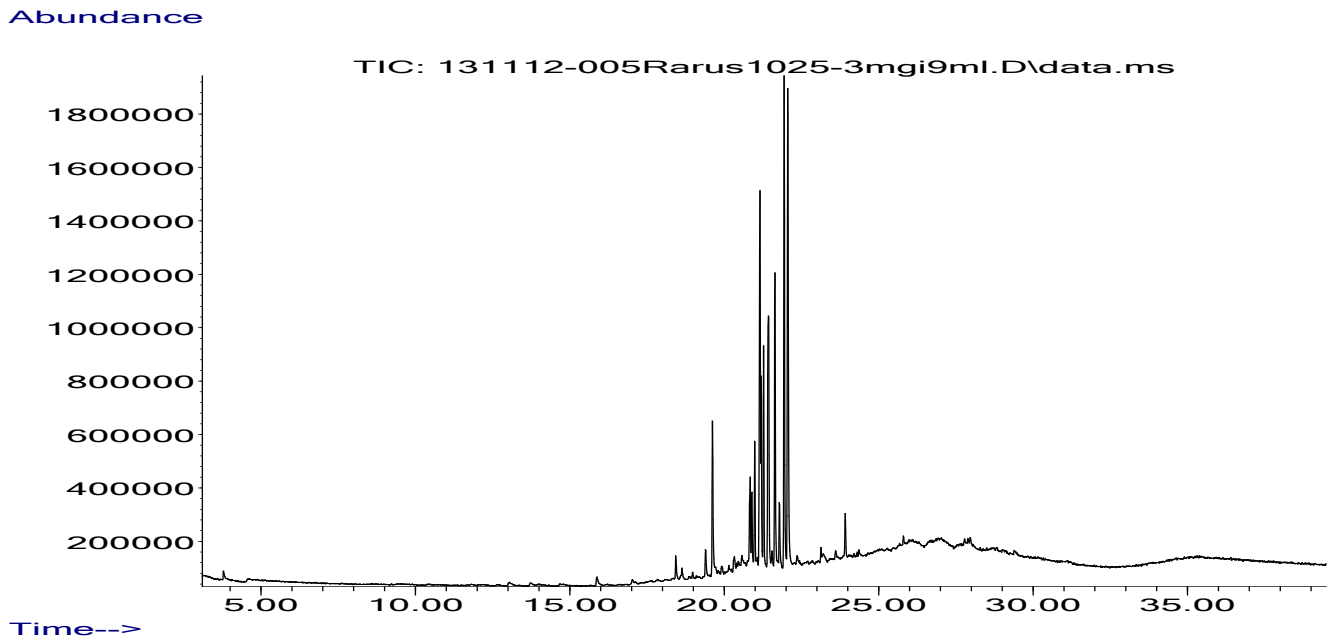


Figure A.1 – chromatogram of a compressor oil with indication of the retention time in minutes

The configuration of the chromatographic system is given in Table A.1.

Table A.1 - Configuration of the chromatographic system

Determination	
Column phase	arylene-stabilized 5% phenyl/95% methyl polydimethylsiloxane (PDMS)
Length	30 m
Internal diameter	250 µm
Film	0,1 µm
Temperature program	35°C (5 min) to 400°C (5 min) at 10°C/min
Carrier gas	Helium