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Analysis of natural gas — Biomethane — Determination of the content of compressor oil

Analyse du gaz naturel — Biométhane — Détermination de la teneur en huile de compresseur

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Foreword

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This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 408, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document supports the implementation of specifications for biomethane and biogas such as ISO 15403-1 or the EN 16723 series[9],[10] when used in the natural gas grids and when used as a transport fuel. Implementation of these specifications require fit-for-purpose measurement methods with known performance and acceptable metrological traceability to support the trade in renewable gases and conformity assessment.

Analysis of natural gas — Biomethane — Determination of the content of compressor oil

1 Scope

This document gives general guidance for the sampling and gas chromatographic analysis of compressor oil in biomethane or compressed natural gas (CNG). The compressor oil mass fraction is determined by sampling on coalescing filters under defined operational conditions (the two first cubic meters of gas referring to standard conditions, delivered at a refuelling station).

Compressor oils are lubricants used in mechanical devices where the purpose is to reduce the volume and increase the pressure of gases for use in a variety of applications.

The method is solely applicable to compressed gas (p>18 MPa).

The compressor oil content is expressed as mass fraction. The scope of this method is from 3 mg/kg – 30 mg/kg.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO 6974 (all parts), *Natural gas — Determination of composition and associated uncertainty by gas chromatography*

ISO 6976, *Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition*

ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories*

ISO 14532, *Natural gas — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532, ISO/IEC Guide 98-3 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

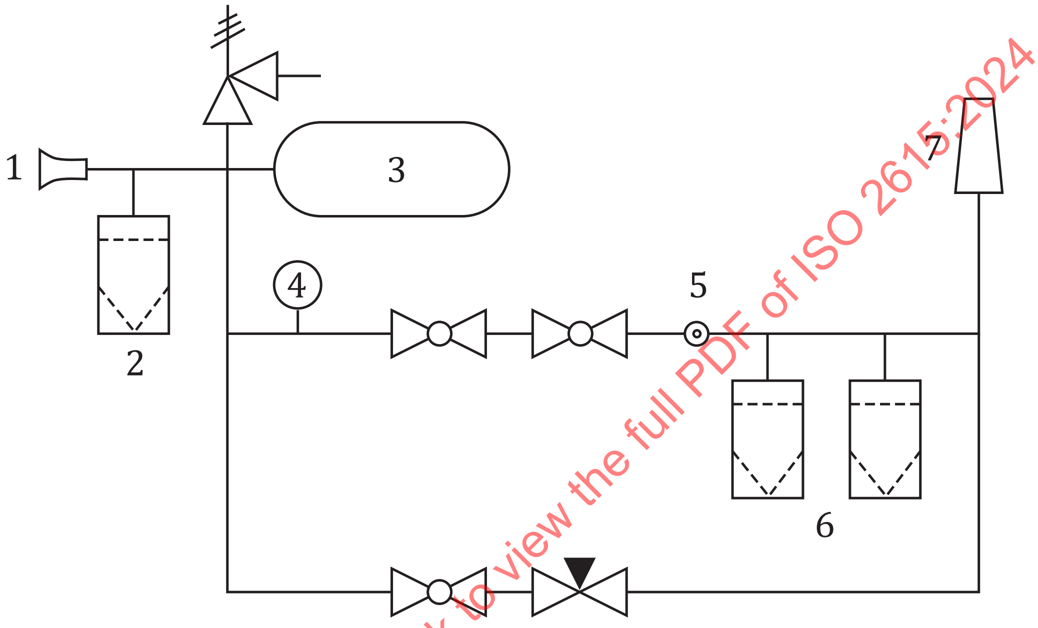
3.1
response
output signal of the measuring system, for a component that is measured as peak area or peak height

[SOURCE: ISO 6974-1:2012, 3.1, modified — The symbol y was deleted.]

4 Principle

This method is based on sampling a sufficiently large volume of gas and condensating the compressor oil on a coalescing filter by expanding the gas through a nozzle spray. The compressor oil thus collected is analysed using gas chromatography. The gas chromatograph is calibrated with calibrants ideally using compressor oil of the same make. The method uses a flame ionization detector (FID) or mass spectrometer (MS).

The pressure of the compressed 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. The oil that deposits in the buffer tank is recovered as well. For a typical sampling arrangement, see Figure 1.



Key

1	natural gas vent (NGV) 1 receptacle for car refueling or NGV2 receptacle for truck/bus refueling
2	pre-filter
3	buffer tank
4	pressure indicator
5	nozzle spray
6	filters
7	vent

Figure 1 — Compressor oil sampler

5 Chemicals and materials

5.1 Compressor oils

For calibration purposes, samples of all compressor oils used at the station or any other oils that can be present in the gas to be analysed shall be separately collected to be used for preparing the calibration standards. Please note that oil references should ideally come from the same production batch as the ones actually used at the station.

If not feasible, calibration should be made using equivalent oils. The closer the characteristics of the oil being used for the calibrants and the oil present in the gas, the better the performance of the method.

5.2 Solvent

Dichloromethane, pentane, hexane, analysis grade, or another suitable organic solvent of chromatrographic quality, for preparing oil calibration standards. This solvent should be of sufficient purity to ensure that it does not give rise to interferences during the analysis. Use only a solvent of recognized analytical grade. The same solvent should be used for preparing oil calibration standards and for sample extraction.

5.3 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.

5.4 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.

5.5 Calibration standards

Shall be prepared by diluting oil to the concentration of (1 to 10) mg/ml.

5.6 Nitrogen pure gas

Nitrogen of a minimum 99,999 % purity and a total hydrocarbon content (THC) of less than 0,5 µmol/mol.

5.7 Compressed liquid propane

Propane of a minimum 99,999 % purity.

6 Apparatus

6.1 Gas chromatograph

This is equipped with a mass spectrometer (GC/MS), electron ionization (EI) mode, or a flame ionisation detector (GC/FID). The liquid sample is injected with an automated microsyringe through a septum into a port at the head of the column.

6.2 Capillary column

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

6.3 Ultrasonic bath

With start at ambient temperature. Temperature increase due to sonication may be neglected.

6.4 Pressurised fluid extraction apparatus

Consisting of extraction cells which shall 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 shall be flushed with the extraction solvent.

6.5 Filter housing

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

6.6 Rotary evaporator, concentration apparatus

Designed to allow the solvent extract to be concentrated from more than 300 ml to (10-20) ml.

6.7 Laboratory glassware

6.7.1 Flat-bottomed flask, capacity 500 ml.

6.7.2 Measuring cylinder, capacity 500 ml or equivalent large enough to soak a whole filter.

6.7.3 Beaker, capacity 50 ml.

7 Sampling

7.1 Sampling apparatus

The sampler consists of a NGV1 connection, 1/2 inch tubing, a manometer, three ball valves (oasis engineering ltd or similar), a 12,5 l buffer tank, and two EU37/25 filter housings (with coalescing filters) connected in series after a spray nozzle of 0,3 mm hole diameter and union tees (see Figure 1).

7.2 Sampling steps

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 18 MPa (which corresponds to between (2,1 to 2,6) m^3 gas sampled). The sampler is then disconnected from the dispenser and brought aside.

NOTE 1 Unless specified otherwise, gas volumes stated in this document refer to standard conditions. If not specified otherwise, standard conditions are given in ISO 13443.

The gas sample is released through the vent by opening a ball valve until the pressure in the bottle reached 18 MPa [1] (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 release of gas can then be stopped when the pressure in the bottle reaches 10 MPa (approximately equivalent to 1 m^3 sampled), 12 MPa (approximately equivalent to 0,75 m^3 sampled) or 14 MPa (approximately equivalent to 0,5 m^3). These pressures are read when the temperature in the cylinder has reached equilibrium (the pressure is then stable). The correct gas volume is calculated from the actual buffer tank volume, V_{buffer}, and initial (at the start of gas release) and final (at the end of gas release) pressures and temperatures (p_{i}, T_{i} and p_{f}, T_{f}, respectively) as well as compressibility factors, z_{i} and z_{f}, at the respective conditions. The compressibility factor is calculated by the use of commercial or inhouse software/ 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 at least three samplings. The filters are removed after one sampling and new filters are installed in the filter housings.

NOTE 2 Compressibility factors at standard conditions can be computed using ISO 6976. Compressibility factors at other conditions can be computed using the ISO 12213 series, and ISO 20765-1.

Once all samplings are performed, the gas left in the bottle is released through the vent.

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[1] 0,1 MPa =10^5 Pa; 1 MPa = 1 N/mm^2

8 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.

a) After demounting the buffer tank which has been depressurized from the sampler, rinse at least three consecutive times with 250 ml solvent. Flush with nitrogen to remove all solvent.

b) Without demounting the buffer tank from the sampler, rinse at least three consecutive times with propane. Recover the propane into a 1 l glass bottle by setting the sampler upside down. The recovered propane fraction is then let opened in a well-ventilated place until the propane has totally evaporated. 10 ml of solvent is then added to the glass bottle to dissolve the oil that has deposited in the glass bottle. Finally, flush the buffer tank with nitrogen to remove all solvent.

9 Extraction procedure for coalescing filters

9.1 Procedure 1: Ultrasonic extraction – nitrogen flush

The procedure is composed of the following steps.

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

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

c) Perform a 30 min (±5 min) long extraction in an ultrasonic bath.

d) Turn the coalescing filter upside down and perform a 30 min (±5 min) long extraction in an ultrasonic bath.

e) Transfer the extraction solvent into a 500 ml flat-bottomed flask.

f) Place the filter into a filter housing. The solvent remaining on the filter is removed under a flow of pure nitrogen and recovered in a 50 ml beaker. The recovered solvent is added into the 500 ml flat bottomed flask.

g) Concentrate the extraction solvent to reduce the volume from (300–400) ml to 10 ml or less with a rotary evaporator [(35 ± 3) °C].

h) Transfer into a 10 ml volumetric flask and fill to the mark. Store the concentrated solvent extract cold (±4 °C) until the analysis is carried out.

9.2 Procedure 2: Pressurised fluid extraction

The procedure is composed on the following steps.

a) The filter is positioned in the extraction cell.

b) If the filter cannot completely fit in the cell, it can be cut in several pieces. In this case, the cutting devices shall also be rinsed with the extraction solvent to ensure the recovery of oil potentially present on the cutting device. The solvent used for rinsing the cutting devices shall be added before the evaporation step to the extract obtained after the filter extraction.

c) The cell is then completed with a neutral matrix, sand, to reduce the void volume in the cell and therefore the solvent consumption (the sand shall be previously extracted under the same experimental conditions as the sample to clean it and remove any potential interferences).

d) The extraction is then performed using the following conditions:

  - extraction solvent: hexane;
  - temperature: 100 °C;
  - number of extraction cycles: two cycles;

- time for an extraction cycle: 11 min;
- pressure: 12 MPa;

e) The extract is concentrated under nitrogen at a final volume of 10 ml. The extract is concentrated with an evaporator (40 ± 3 °C). Transfer into a 10 ml volumetric flask and fill to the mark.

f) Store the concentrated extract cold (±4 °C) until the analysis is carried out.

10 Analysis

10.1 GC/MS analysis

The mass spectrometer is tuned in accordance with the manufacturer’s instructions. Chromatograms are recorded in full scan [typically 32 amu to 450 amu (absolute mass units)]. Analyse the concentrated solvent extracts, the calibration standards and the extraction solvent.

Two examples of a GC/MS chromatogram obtained for a compressor oil and chromatographic conditions are given in Annex A and in Annex B.

10.2 GC/FID analysis

The operating conditions of the GC-FID are optimized in accordance with the manufacturer's instructions. Analyse the concentrated solvent extracts, the calibration standards and the extraction solvents with GC-FID.

An example of gas chromatographic conditions is given in Annex B. The description of the different types of oils is given in Annex C.

11 Calculations

Data from preferably three or more calibration standards are used to calculate a response factor (peak area divided by oil mass concentration in dichloromethane or other solvent, mg/ml) for each oil of interest. One (or more) ion(s) specific for the targeted oil should be extracted and used for the quantification. Oil mass, in mg, in a sample is calculated as the area of the oil characteristic ion(s) for the sample divided by the response factor multiplied by the volume of the concentrated extract.

Compressor oil amount is the sum of the oil amount recovered on the coalescing filters and the oil amount recovered in the buffer tank according to Formula (1) (see Reference [11]):

$$w_{\text{oil tot}} = w_{\text{filter}} + w_{\text{buffer}} \qquad (1)$$

where

$w_{\text{oil tot}}$	is the total mass fraction in the gas of compressor oil, expressed in mg/kg;
w_{filter}	is the mass fraction in the gas of compressor oil recovered on the coalescing filters, expressed in mg/kg;
w_{buffer}	is the mass fraction in the gas of compressor oil recovered in the buffer tank, expressed in mg/kg.

The mass fraction in the gas of compressor oil recovered on the coalescing filters, w_{filter}, is expressed in mg/kg gas according to Formula (2):

$$w_{\text{filter}} = m_{\text{oil coalescing}} / (V_{\text{gas coalescing}} \cdot \rho_{\text{gas}}) \tag{2}$$

where

$m_{\text{oil coalescing}}$	is the mass on the coalescing filter, expressed in mg;
$V_{\text{gas coalescing}}$	is the gas sample volume that passed through the coalescing filters, referred to standard conditions and expressed in m^3;
ρ_{gas}	is the density of the gas, referred to standard conditions and expressed in kg m^{-3}.

The mass fraction of oil recovered in the buffer tank shall be computed according to Formula (3):

$$w_{\text{buffer}} = \frac{c_{\text{oil buffer}} V_{\text{sol}}}{V_{\text{gas buffer}} \rho_{\text{gas}}} \tag{3}$$

where

$c_{\text{oil buffer}}$	is the concentration of the oil as determined by GC analysis, expressed in mg m^{-3};
V_{sol}	is the volume of the solution prepared from the extracted oil, expressed in m^3;
$V_{\text{gas buffer}}$	is the gas sample volume that passed through the buffer tank, referred to standard conditions, expressed in m^3.

The density (ρ, expressed in kg m^{-3}) shall be determined from an accurate determination of the gas composition and according to ISO 6974 series and the calculation shall be based on a composition using ISO 6976.

$V_{\text{gas buffer}}$ is determined as the sum of the initial filling volume (calculated from the volume of the buffer tank at standard condition and the initial filling pressure), and the refilling volumes needed to perform the series of three samplings.

The uncertainty of the mass fraction compressor $w_{\text{oil tot}}$ shall be calculated considering, among other, the following uncertainty sources:

— performance of the sampling and extraction method: can be evaluated by spiking coalescing filters with known amount of oil evaluation requires sufficient replicate measurements;

— calibration of the gas chromatograph;

— analysis of the sample.

12 Test report

A test report shall meet the requirements of ISO/IEC 17025. The test report shall contain, apart from the items listed in ISO/IEC 17025:2017, 7.8,

a) a reference to this document;

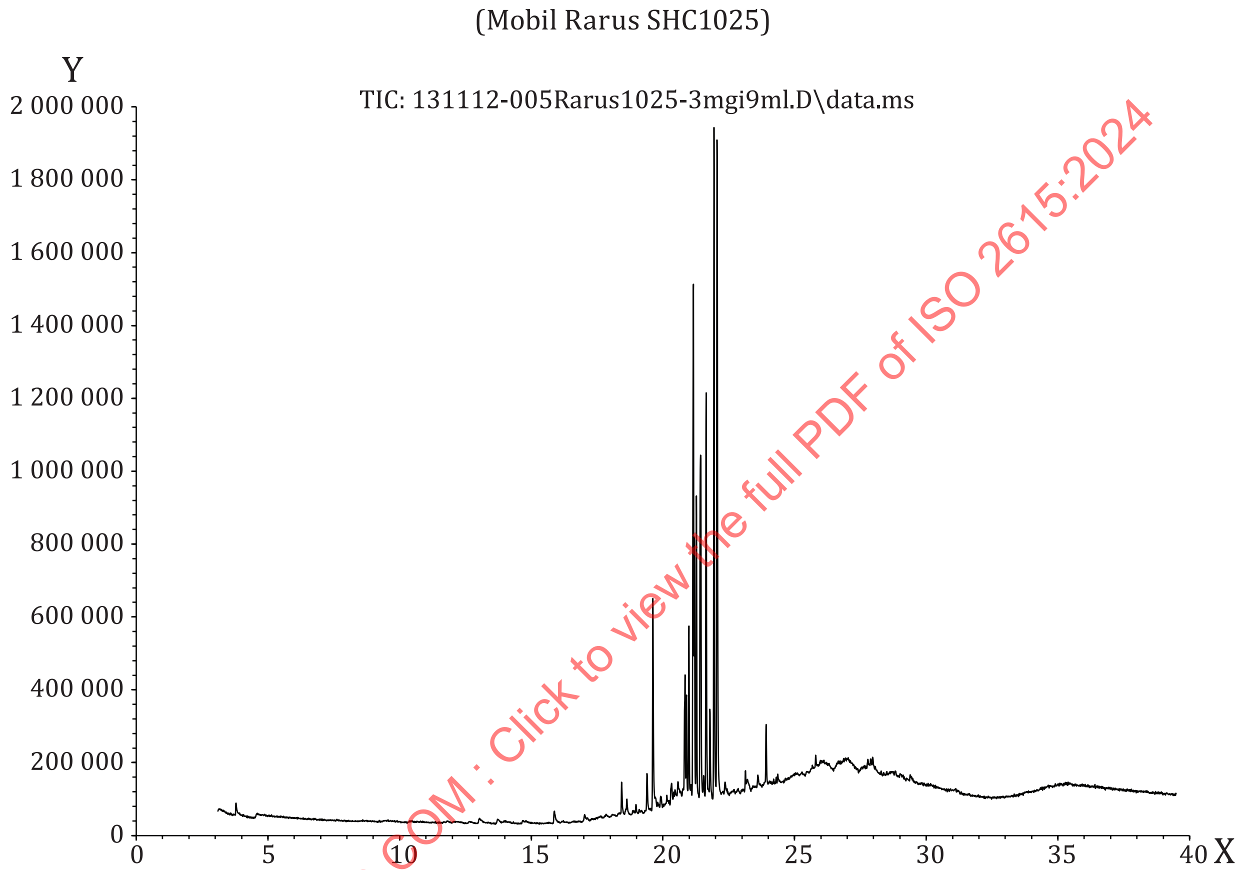
b) date and time of the sampling;

c) location of the sampling;

d) the result, including the measurement uncertainty.

Annex A
(informative)

Example of a GC/MS chromatogram obtained for a compressor oil (Figure A.1)



Key

X time

Y abundance

Figure A.1 — Chromatogram of a compressor oil with indication of the retention time in minutes

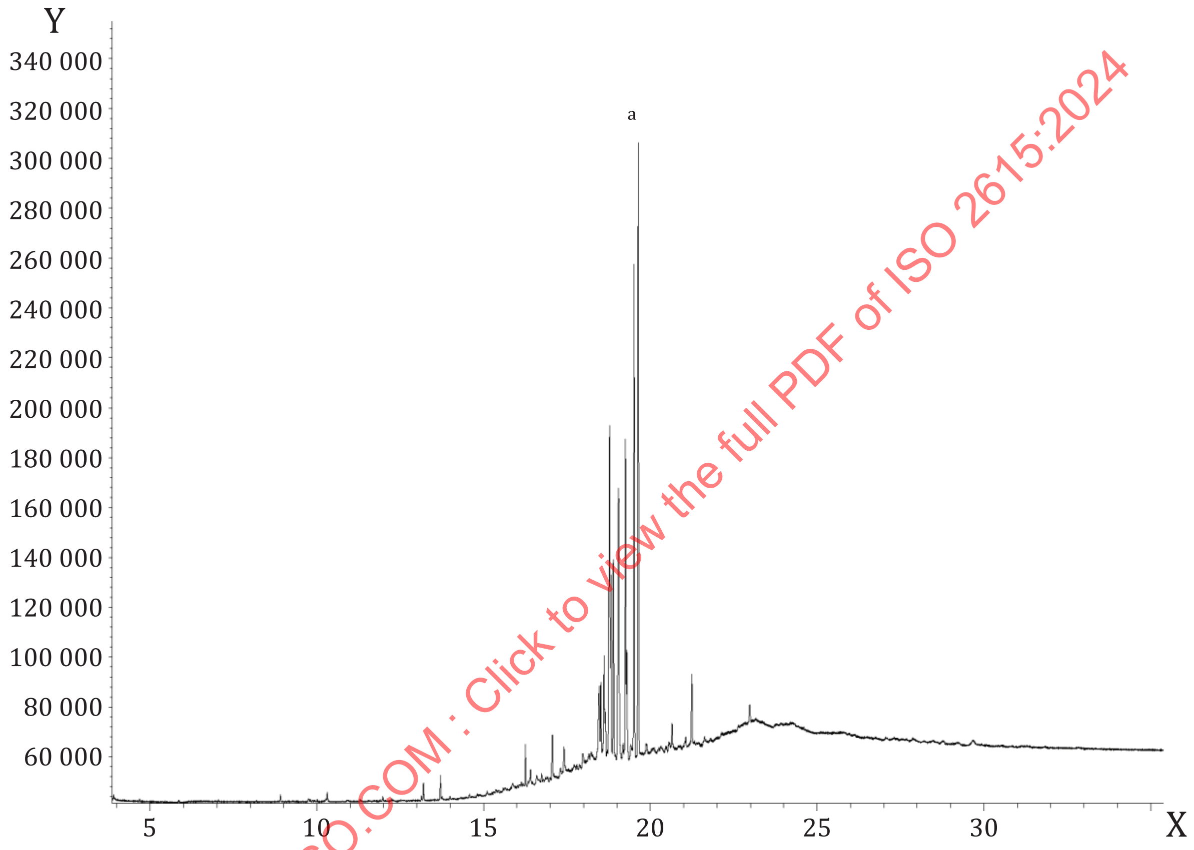
The configuration of the chromatographic system is given in Table A.1.

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

Annex B
(informative)

Example of a GC/FID chromatogram obtained for a compressor oil (Figure B.1)


(Mobil SHC 1025 oil)

Key

X	time
Y	abundance
[a]	Signal: 180411-037R arusny_3.D\FID 1A.ch (*).

Figure B.1 — Chromatogram of a compressor oil with indication of the retention time in min

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

Table B.1 — Configuration of the chromatographic system

Determination	
Column phase	Phenyl arylene polymer (DB-5ms)
Length	30 m
Internal diameter	250 µm
Film	0,25 µm
Temperature program	80 °C (2 min) to 325 °C (15 min) at 12 °C/min
Carrier gas	helium