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Zemeljski plin - Določanje sestave in s tem povezane negotovosti s plinsko kromatografijo - 4. del: Navodilo za analizo plina (ISO/DIS 6974-4:2025)

Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 4: Guidance on gas analysis (ISO/DIS 6974-4:2025)

Erdgas - Bestimmung der Zusammensetzung und der damit verbundenen Unsicherheit durch Gaschromatographie - Teil 4: Leitfaden für die Gasanalyse

Gaz naturel - Détermination de la composition avec une incertitude définie par chromatographie en phase gazeuse - Partie 4: Détermination de l'azote, du dioxyde de carbone et des hydrocarbures C1 à C5 et C6+ pour un système de mesurage en laboratoire et en continu employant deux colonnes

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Part 4:
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This edition cancels and replaces the previous editions of ISO 6974-3:2000, ISO 6974-4:2000, ISO 6974-5:2014, ISO 6974-6:2002 and ISO 6975:1997, which in part have been technically revised.

The main changes compared to the previous edition(s) are extensive, as this document is the compilation of the formentioned documents, added to a collection of knowledge on natural gas chromatography.

A list of all parts in the ISO 6974 series can be found on the ISO website.

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

The composition of natural gasses varies immensely, and the addition of biogas, biomethane, hydrogen, syngas and other natural gas substitutes only adds to chromatography spectrum. The gas chromatographic system should be designed not only to separate the components of economic (short-term) interest, but also for components considered as trace or of no-interest. These trace components could be potentially problematic for public health, safety or assets.

A precise and stable analysis of the main and trace components of the gas can be obtained by an analyser that is fit-for-purpose. Satisfactory performance of a natural gas analyser requires that the method has good precision and response characteristics which allow component concentrations over the range of interest to be accurately compared with the equivalent components in the reference mixture (calibration).

This document elaborates on all steps involved with gas chromatography, and is comprised of extracts from older parts of this standard, and other standards. Added to the extracts is guidance, originating from common sense and experience, which may help the user and manufacturer to ascertain that their analyser is fit-for-purpose and that optimum analysis results are obtained from the analyser.

Natural gas — Determination of composition and associated uncertainty by gas chromatography —

Part 4:
Guidance on gas analysis

1 Scope

This document gives guidance for obtaining the best analysis results possible from a gas chromatograph (GC) when analysing natural gas and natural gas substitutes for combined use with the most recent versions of ISO 6974's part 1, 2 and 3 (examples are given).

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 6974-1, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO 6974-2, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

ISO 6974-3:2018, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 3: Precision and bias*

ISO 7504:2015, *Gas analysis — Vocabulary*

ISO 10715:2022, *Natural gas — Gas sampling*

ISO 14532:2014, *Natural gas — Vocabulary*

ISO 23219:2022, *Natural gas — Format for data from gas chromatograph analysers for natural gas — XML file format*

3 Terms and definitions

For the purposes of this document, the terms and definition used are taken from ISO 14532 and ISO 7504.

ISO and IEC maintain terminological 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/

4 Symbols

The table below, Table 4-1, lists the symbols used in the main text of this document.

Table 4-1 — Symbols

symbol	explanation	unit
$x_{N_2,C}$	mole fraction of nitrogen after correcting the mole fraction for air contamination	mol/mol
x_{N_2}	mole fraction of nitrogen in the sample after normalization;	mol/mol
x_{O_2}	mole fraction of oxygen in the sample after normalization;	mol/mol
$x_{j,S}$	normalized mole fraction of component *j* in the sample;	mol/mol
$x^*_{j,S}$	non-normalized mole fraction, of component *j* in the sample;	mol/mol
n	total number of components;	-
$x^*_{Ar,C}$	mole fraction of argon after correcting the mole fraction for air contamination;	mol/mol
x_{Ar}	mole fraction of argon in the sample after normalization;	mol/mol
$x_{j,c}$	normalized mole fraction of component *j* in the sample after air contamination correction;	mol/mol
$x^*_{j,C}$	Is the non-normalized mole fraction of component *j* in the sample after air contamination correction;	mol/mol
R_{AB}	peak resolution	-
$d_R(B), d_R(A)$	retention distances of the eluted components A and B	s
$w(B), w(A)$	widths of the respective peaks at their base	s

5 Overview

This guidance document covers a wide range of subjects in relation to the analysis of natural gas.

Below, in Figure 1, a schematic overview is given, the main clauses are indicated according to the process-sequence.

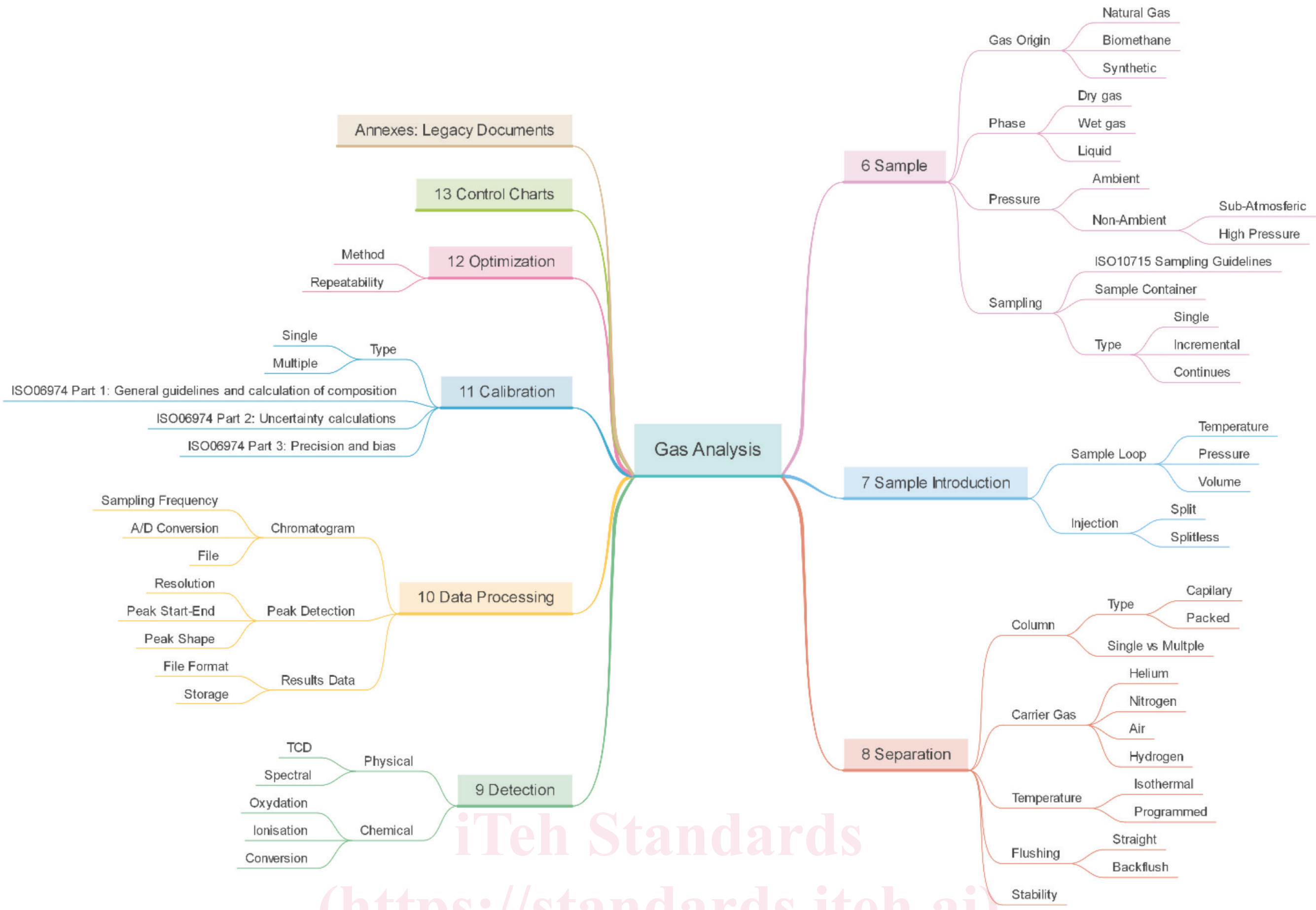

Figure 1 — Gas Analysis Overview

6 Sample

6.1 General

All gas analysis starts with a sample. The origin and physical state of the sample are of importance to the subsequent steps in the analytical process. This clause describes the most common concerns in the first step of that process. More detailed methods of sampling can be found in ISO10715.

6.2 Gas origin

A good understanding of the gas production process and the consequences for possible trace components should be consulted for. Although a periodic in-depth investigation of these components seems like a wise way of operating, it has the innate possibility to miss the (near) out-of-spec occurrences.

A few examples from the field of biomethane:

- Periodic replacement of activated carbon filters is a clear and common way of operating, but the flooding of a filter is primarily caused by contaminant concentration times flow, and not by time alone. A small investment in an extra separation column or back-flush with detector option provides up-to-date information of the contaminant-level and leads to better prediction of the filter-pack efficiency and proper moment of replacement.
- Biomethane usually contains nitrogen, which, more often than not, originates from the air added to the fermentation process to decrease the production of hydrogen sulfide and other sulphur compounds. When analyzing for oxygen in the produced biomethane, argon should be sufficiently separated from oxygen because argon will be present in a 0,934 0 to 78,084 ratio to nitrogen, whereas the oxygen might

be lower in concentration, because it is used in the process. For instance, at 5 mol% nitrogen this adds up to about 600 ppm argon.

— Water should be identified in the chromatogram to determine co-elution or even calibrated for, because a high level (> 50 ppm) is quite common and could get as high as 1 vol%. Measurement of the water concentration with a water dewpoint analyser provides a way to prevent a mismeasurement.

Syngas or other gasses from synthetic sources may contain unsaturated hydrocarbons or other volatile components that are low in concentration individually, but could amount to be significant when lumped together, either in total concentration or in calorific content.

Natural gas has a wide range of concentration for all occurring components. In some cases, the gas has quite a high amount of higher hydrocarbons and aromatic compounds, but could also be almost pure methane. This wide range of component concentrations has implications for the set-up of the gas analyser (and will be detailed further on in this document).

6.3 Phase of sample

For most applications the sample phase will be gaseous (with low water dewpoint and low hydrocarbon dewpoint, i.e. dry gas), but it may very well be that the sample has a high hydrocarbon or water dewpoint or is liquified.

This document will not treat samples that are liquid, multiphase or have a propensity towards multiphase behavior, and for this document it is assumed that the introduced sample is entirely gaseous. There are various solutions available for such samples, ranging from heated sample container cabinets and heat-traced sample lines up to very advanced evaporation systems.

6.4 Sample pressure

Although pressure (and temperature) of the sample is closely related to phase behavior of the gas, it also is of concern for the sampling part of the analyser:

— If the sample is at ambient, sub-atmospheric or high pressure it needs to be decided if the sample is to be compressed, pumped or reduced for sampling.

— The gas wetted valves and tubing used need to be assessed accordingly.

— The sample loop pressure needs to be able to equilibrate within the time between filling and injection.

— The sample flow needs to be enough to properly purge the sample line, from the sample container to the sample loop, so a representative sample is taken.

— The sample pressure and flow should not overload the vent system (e.g. of the lab or of other analyzers).

These items are treated in more detail further in this document.

6.5 Sampling

The sampling of the gas of interest at its source is not treated in this document but is described extensively in ISO 10715, along with guidelines on the materials used for the sample container and the sample line.

In relation to the configuration of the gas analyser mainly two types of sampling occur:

— Single, from a sample container

— Continuous, from e.g. a gas supply line or process

Being closely related to the next step, sample introduction, this is treated in more detail in the next clause.

7 Sample introduction

7.1 General

A consistent means of sample introduction is required so that equivalent amounts of sample and reference mixture are compared.

7.2 Sample loop

7.2.1 General

In most applications, a switching valve is used for sample introduction. The sample is purged through a loop. This defines the sample size and when the valve operates. The loop is switched into the carrier gas stream. The loop contents are swept by the carrier gas onto the separation system, see Figure 2. An alternative for micro-GCs uses pressure switching for a selected short time to achieve the effect. There are some viscosity influences, and it is not considered here.

The sample loop has a defined volume, but the size of injected sample is influenced by the temperature and pressure of the contained gas. The sample loop is sufficiently flushed until the volume of sample or reference gas has fully purged the previous loop contents.

We therefore need to consider the following.

7.2.2 The temperature of the sample loop

The sample loop can be controlled separately or fitted in the column oven. The size is not usually critical, but the stability is. Temperature variations will cause different effective sample amounts and hence poorer repeatability.

Higher temperature stability can be achieved by adding masses of metal around the sample-loop and sample-valve. Combination with insulation and shielding the analyzer from airflows (e.g. air-conditioning vents and analyser exhausts) will further improve stability.

7.2.3 The pressure within the loop

The sample line usually purges to atmosphere (possibly through a vent line extending outside the laboratory or analyzer housing). If the sample flowrate and the resistance of the vent line create a backpressure, the pressure in the sample loop will vary with flowrate. Usually the flows of calibration gas and sample gas are controlled by different means and may be set to different values, so there may be a difference in effective sample size between the two and hence the possibility of bias error.

When using pressure correction it is advisable to connect the (high-accuracy) barometer as closely as possible to the sample-loop, i.e. connect the barometer directly to the exit of sample shut-off valve outlet. This prevents measuring the fluctuating under- or overpressure of the laboratory.

Also, be aware of the possibility of automatic pressure correction, installed by the manufacturer of the GC. It should either be disabled, removed or have the capability to be externally calibrated.

7.2.4 Sample shut-off before injection

This is a common procedure. Stopping the sample (or calibration gas) flow a few seconds before injection allows the loop pressure to decay to atmospheric. As a result, it will only vary according to atmospheric pressure variations, which can be significant.

The optimum sample shut-off time is influenced by the stability (or deterioration) of the sample. This is caused by sample composition, the sample-loop material and sample-loop temperature.

7.2.5 The atmospheric pressure effect

The atmospheric pressure effect can be measured at the exact time of injection and corrected for or ignored. If ignored and the method is a single operation one, normalization will correct it, since sample loop pressure has the same relative influence on all components. In fact, for single operation, atmospheric pressure correction followed by normalization (pressure correction alone never sets results to 100 %) gives the same result as normalization alone.

However, in multipoint calibration no component has the same calibration function. As a consequence, any pressure different from standard will give a slightly different correction on the raw analyzer output compared to the other components. This effect occurs both during calibration and analysis, so for multipoint calibration and subsequent analysis, pressure correction should be applied.

7.3 Injection

When only a small sample volume is available, or the GC is not equipped to handle atmospheric samples, a direct injection (e.g. by syringe) on the GC injector is a good alternative.

Most GC are equipped with a split/splitless injector, a small heated chamber that either flushes the sample on to the column (splitless mode) or flushes a portion of the sample into the column (split mode).

In split mode, a part of the mixture of sample and carrier gas in the injection chamber is exhausted through the split vent. Split injection is preferred when working with samples with high analyte concentrations.

Splitless injection, see Figure 2, is best suited for trace analysis with low amounts of analytes. In splitless mode the split valve opens for a pre-set amount of time to flush the sample on the separating column. This pre-set time should be optimized, a shorter time ensures less tailing but loss in response, a longer time increases tailing but also signal.