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Introduction

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Date: xx/xx/20xx	Document: ISO/DIS xxxx
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1	2	(3)	4	5	(6)	7
MB	Clause No./ Subclause No./Annex (e.g. 3.1)	Paragraph/ Figure/Table/Note	Type of comment	Comment (justification for change) by the MB	Proposed change by the MB	Secretariat observations on each comment submitted
	3.1	Definition 1	ed	Definition is ambiguous and needs clarifying.	Amend to read '...so that the mains connector to which no connection...'	
	6.4	Paragraph 2	te	The use of the UV photometer as an alternative cannot be supported as serious problems have been encountered in its use in the UK.	Delete reference to UV photometer.	



DRAFT International Standard

ISO/DIS 6974-4

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

Part 4: Guidance on gas analysis

ICS: 75.060

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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.

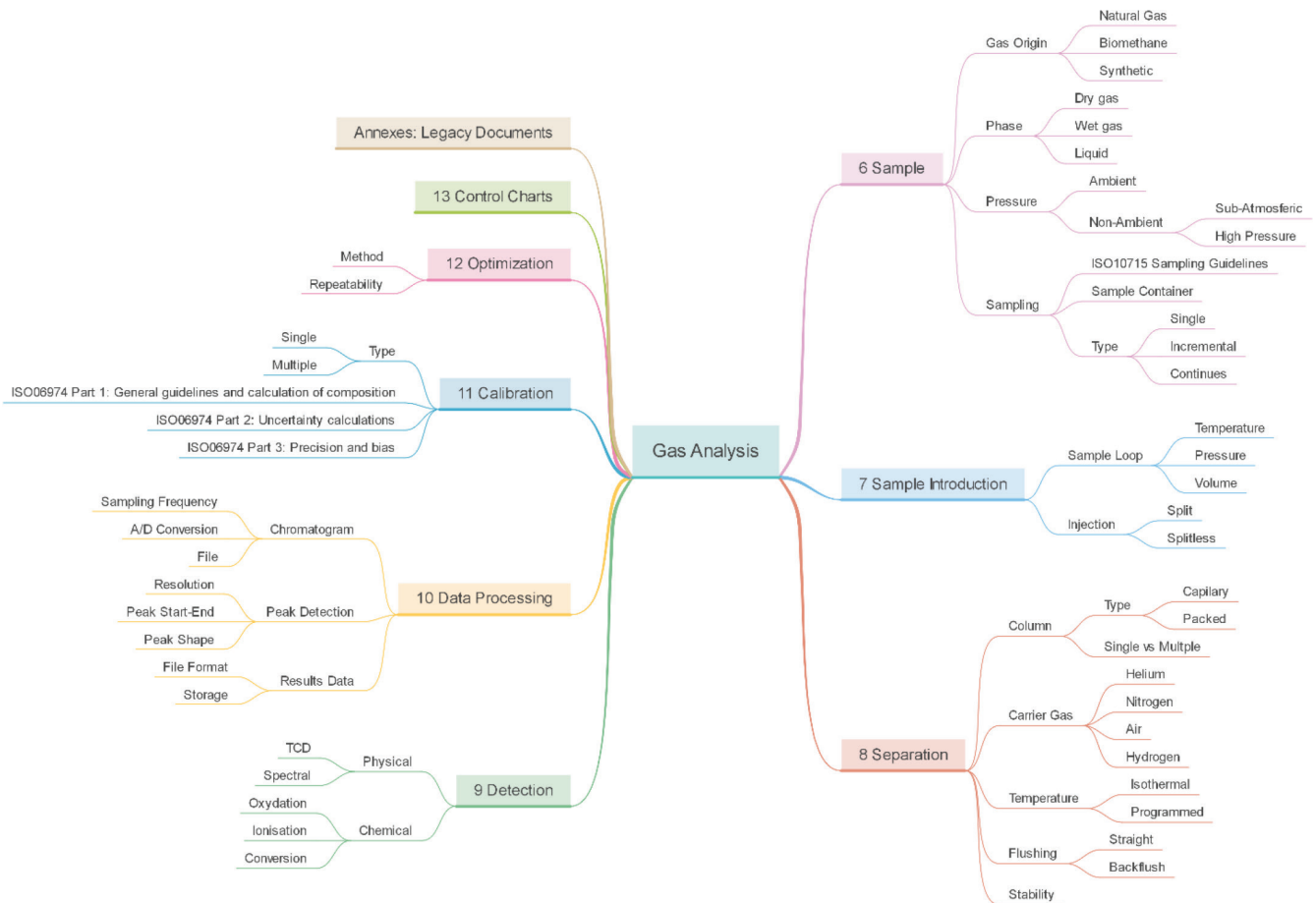


Figure 1 — Gas Analysis Overview

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.

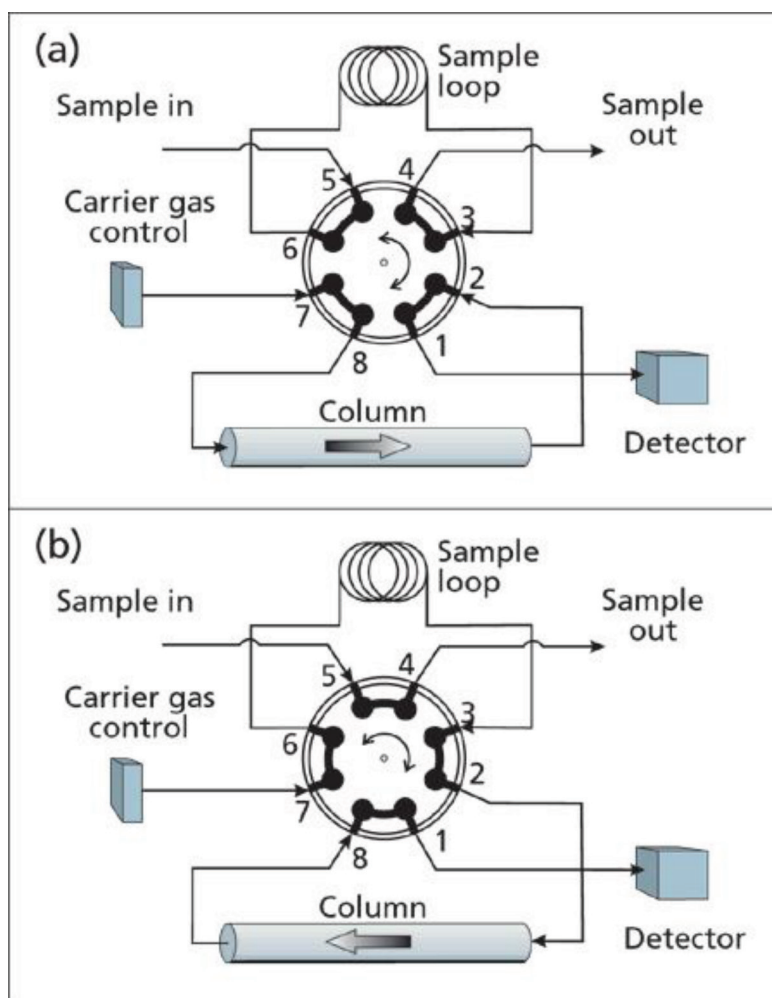


Figure 2 — Operation of a simple GC configuration using a switching valve; (a) sampling and (b) injection

Different types of Injection can be specified:

- Manual injection: if you don't have to analyze too many samples, manual injection can be used. Be aware that the injection should be repeatable in order to have repeatable results.
- Auto-sampling: in case of many samples, an auto-sampler can be a good option and also to have more repeatable injections and results. For gas samples, the auto-sampler could be more complicated than for liquid samples.
- Sample-loop: the capacity of the sample loop should be chosen based on the detection limit wanted and on the column dimension. The split flow also plays a role in this case.
- Time-based valve injection: this kind of valve can be used for a better repeatability of the injection and so, for the analysis

Injection using a Deans type switch. This is an effluent switching device based on controlling flows of carrier gas instead of mechanical valves in the analytical flow path. This technique offers high inertness and a wear-free operation.

In process GCs a combination of an autosampler with a time-based valve injection or Deans type switch is most often seen.

7.4 Vacuum injection

If the sample pressure is very low, or the amount of sample available is very small it may be necessary to first evacuate the sampling system prior to injection. By first removing any previous sample, air or carrier gas from the sample loop using a vacuum pump prior to introducing the sample will greatly reduce the amount of sample required to get a representative sample of the gas. See [Figure 3](#) for schematic overview.

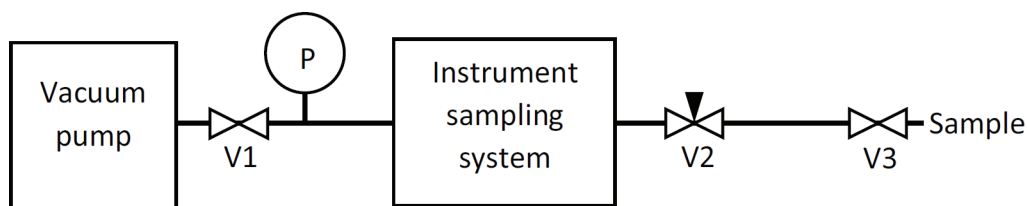


Figure 3 — Vacuum injection

Procedure:

1. Connect the sample, vacuum pump and pressure gauge as per the above figure, with all three valves closed.
2. Evacuate the sampling system by opening valve V1.
3. Once a suitable pressure (vacuum) is achieved (< 10 mbar) isolate the vacuum pump using valve V1.
4. Monitor the pressure indicator to ensure that ambient air is not leaking into the system, if the pressure is steadily increasing, check all the fittings and return to step 2.
5. The sample should then be slowly introduced to the system; valve V1 should be opened first then valve V2 can be slowly opened and used to control the flow. Once the pressure within the system reaches atmospheric pressure, close valves V2 and V3.
6. The sample can then be injected.
7. Repeat steps 2-6 until the required number of injections is achieved.

If there is sufficient sample it may be beneficial to omit step 6 after the first evacuation and re-pressurization cycle to ensure the sampling system is fully purged before injecting.

8 Separation

8.1 General

A separation system, consisting of one or more chromatographic columns, which allows consistent retention times and adequately separates all components of interest, is required to obtain reliable results.

This involves at least one column, usually more, in a temperature-controlled oven with a supply of carrier gas controlled either by pressure or by flow. Where multiple columns are used, the configuration is changed through the analytical cycle. This can be accomplished either by switching valves or by a Deans type pressure control. Either system uses timed events within the analyzer controller to create the changes.

To obtain optimum separation and reliable results the user has the possibility to select from a wide range of separation options, and with a wide range of combinations it is possible to have an analysis that produces the components of interest at adequate accuracy or analyses to give results as detailed as possible. The following sub-clauses highlight some of the system parts available for a gas analysis system configuration.

8.2 Columns

The gas chromatographic columns are a vital part of the analyser and can be chosen according to specifications:

- type of column (packed, capillary)
- stationary phase specification:
 - stationary phase thickness (capillary column)
 - characterization of solid phase (packed column)
- column dimensions

All these have an influence on the separation, retention time (speed of analysis) and sensitivity.

8.3 Carrier gas

The carrier gas is essential to the gas chromatographic separation of the injected sample. The choice of carrier gas depends on the analytes that are to be separated. In multi-column setup, different carrier gases can be selected in order to be able to analyze the complementary components, i.e. use helium as carrier gas to analyze for nitrogen and use nitrogen as carrier gas to analyze for helium.

8.3.1 Types of gases

Gases, supplied from cylinder or generator, used in GC analyses are divided by their use for the separation and detection. The most common carrier gases are:

- Helium
- Hydrogen
- Argon
- Nitrogen
- Air

The choice of gas can depend on the available gas supply, the detection method and safety concerns.

8.3.2 Carrier gas flowrate

Component retention times are a direct function of carrier gas flowrate, and so flow variations will have a possible effect on peak identification. With the thermal conductivity detector, which is concentration sensitive, increased flowrate will give smaller peak areas (but similar peak heights) and vice versa. With the flame ionization detector, which is mass sensitive, flowrate change will have a secondary effect on peak area measurement due to the fact that detector sensitivity varies with the carrier gas/hydrogen ratio.

Most common configurations of the carrier gas flowrate are:

- Constant velocity
- Constant pressure
- Programmed

8.3.3 Purity of the carrier and auxiliary gas

The purity of the carrier and auxiliary gas has an influence on the (long-term) performance of a separation column:

- A carrier gas purity shall be at least 99,99 % (4,0), but 99,999 % (5,0) or even 99,999 9 % (6,0) purity is preferred. The addition of a carrier gas filter can even further increase the purity of the carrier gas and, more importantly, shield the separation column from impurities like water, oxygen and hydrocarbons, inherent to the (lack of) purity or originating for instance from a carrier gas cylinder change. Be aware that the carrier gas filter should be preferably ordered, pre-filled or thoroughly rinsed (before use) with the same gas as the carrier gas to prevent transient effects. Maintenance of these filters is important and most filters have indicators to show when the filter needs replacement. Upon installation all connections should be checked for leakage.
- Carrier and auxiliary gases can be supplied from high pressure cylinders, compressors (air) or from generators. Especially for the use of hydrogen, a hydrogen generator can be a safer option. Generators for hydrogen, nitrogen and air can produce high purity gases from deionized water (hydrogen) or compressed air (nitrogen and air).
- A column that has been set-up for separation of “lighter” components will accumulate “heavier” components, either present in the sample-gas or in the carrier gas, especially when operating in isothermal mode. Periodically increasing the temperature to the maximum allowable temperature for some time is a good way to remove accumulated components, restoring the separating properties of the column, and should be part of the maintenance procedure.
- Components that are separated on the column but present in the carrier gas could appear as negative peaks, or ghost peaks in the next chromatogram. A series of blank runs, both without injection and with injection of the carrier gas, can provide useful insight to the baseline performance of the analyser and the actual purity of the carrier gas.

NOTE In this case, attention should be paid to the fact that some columns can be damaged if they are run without carrier gas

- For all supply lines for carrier gasses, fuel gasses and support gasses, impermeable tubing like copper or stainless steel, should be used to prevent impurities for permeating in or out. Special attention in this regard should be given to the use of hydrogen.

8.4 Temperature

Component retention times remain consistent if the column performance does not vary, and the oven temperature and carrier gas flowrate remain constant. This applies to both isothermal and temperature programmed operation, see [Figure 4](#), to each stage of the program in the latter case. Exact accuracy of the oven temperature is not critical, but consistency is. Changes in column temperature will have little or no effect on the peak size, but will cause alterations in retention times, with possible effects on peak identification.

The oven temperature can be set in different configurations:

- Isothermal; isothermal temperature programming is used generally to have more repeatable results and when the components are not too heavy and so the analysis is not too long. See top.
- Step-Programmed; programmed temperature generally is used when the components to be analyzed have a very wide, but clustered range of boiling points and to shorten the analysis total time in case of heavy compounds. In the temperature transition the baseline is more unstable and is less suited for separation purposes.
- Ramping; a continue rising temperature program, see [Figure 5](#). This type of programming is used when a sample contains a significant amount of higher boiling components. See bottom part of [Figure 4](#).

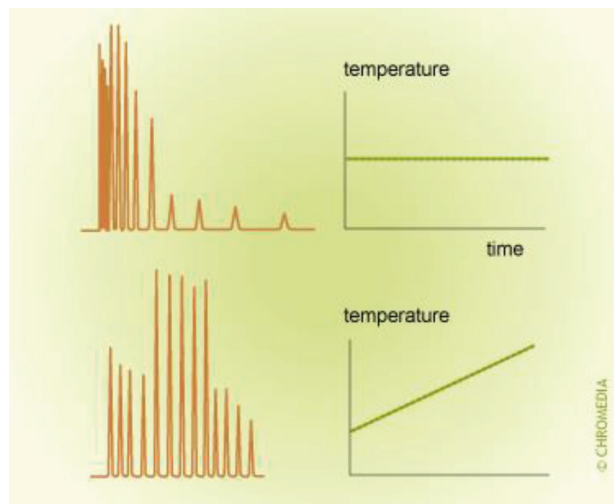


Figure 4 — Isothermal vs temperature ramp

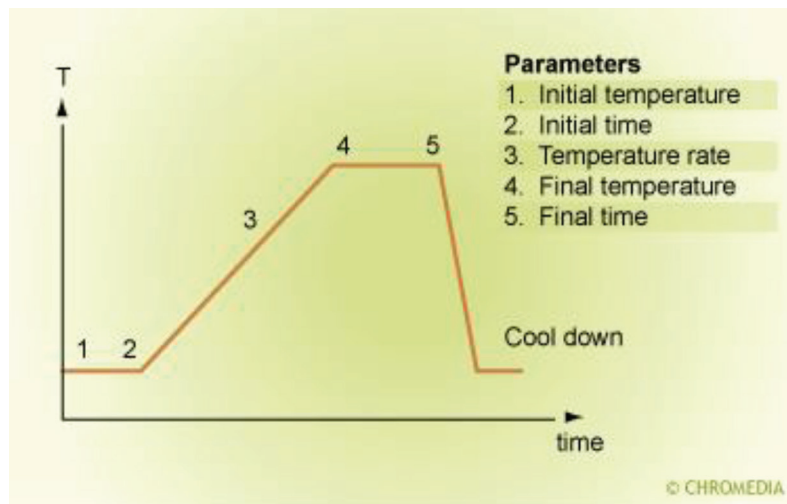


Figure 5 — Temperature programming

8.5 Separation columns

The separation column is the functional part of the gas chromatograph. Through interactions between the individual compounds in the sample and the stationary phase within the column separation occurs. Several types can be discerned:

- Packed or capillary phase. Packed columns are more common in process GCs or for the separation of bigger quantities of gas. Capillary columns give a better separation of the components since have a higher HETP but can cope with lower quantities of gas. Capillary columns can accept lower quantities of sample, so, a split flow should be regulated in order not to saturate the column.
- Stationary phase type. The choice of the stationary phase of a column should be based on the components of the mixture that are to be separated. It can be chosen to separate by polarity, functional groups, boiling point, etc.
- Dimensions of the column, diameter and length. It should be chosen based on what is the wanted separation(resolution) of the components of the mixture, and taken into account the quantities or the detection limit that should be reached.

8.6 Back-Flush

Back-Flush is a useful part of a chromatographic system and consists of a short column of which the flow after a determined time is reversed. Key advances are:

- Protection of the separation column against slow-eluting components.
- Maintaining a more stable baseline, by preventing ghost peaks from the previous injection.
- Gives an indication that the gas contains components that are beyond the GC's designed range but are in the gas nevertheless, if equipped with a detector.

It might be therefore prudent to equip every column with a Back-Flush, even the columns used for the "heavier" components.

An in-depth perspective on the use of the backflush technique on the C6+ components is given in [Annex F](#).

8.7 Maintenance related to column performance

A column that has been set-up for separation of "lighter" components will accumulate "heavier" components, either present in the sample-gas or in the carrier gas, especially when operating in isothermal mode, during an analysis period. Periodically increasing the temperature (and carrier flow) to the maximum allowable temperature for some time is a good way to remove accumulated components and restore the separating properties of the column, and should be part of the maintenance procedure, either during a non-analysis or a maintenance period.

The available GC-columns typically used, have very stable characteristics. The exception is the Molecular Sieve type, which is only used for natural gas if oxygen/argon/nitrogen separation is required. Molecular Sieve (aluminum oxide) is a desiccant and adsorbs water at trace levels in carrier and sample gases. This reduces its activity and causes retention times to reduce with consequential loss of resolution. If a molecular sieve column is used in the system, this column should be conditioned at high temperature (above 200 °C) for some hours (see the manufacturer's instructions) every 5-6 months or every time the resolution between peaks decreases.

8.8 Environmental conditions

The environmental conditions surrounding the GC influence its results and stability. This influence maybe gradual of nature or more abrupt. Examples are:

- Ambient pressure. When a GC sample loop is filled with the gas to be analyzed, the pre-injection stabilization of the sample loop pressure to ambient pressure causes the injected amount to be proportional to the ambient pressure. If the GC does not use pressure compensation for the sample loop pressure, the results are to be corrected for the pressure measured in the vent line as close to the sample loop as possible with a high-accuracy barometer, at the moment of injection.
- Temperature. Although fluctuations in the normal temperature range will influence the operation of a GC, the sample too is influenced by the surrounding temperature. A temperature conditioned room or cabinet will increase the stability of the produced analytical results. The reduction of the sample pressure to the injection pressure should also take place in that room or cabinet.
- Pressure variations. Detectors like, for instance, FID or TCD are also influenced by pressure pulses (caused, for instance, by the opening and closing of a door to the analyser cabinet or to a laboratory operating in under- or over-pressure). These pressure peaks cause false peaks in the chromatogram, which may lead prematurely starting or ending the analytes' peak, resulting in a misreading.
- Unless the humidity is beyond the permissible range, stated by the manufacturer, no influence is to be expected from the ambient humidity.

8.9 General setup

The configuration of the GC determines the range of possibilities a GC has. A proper setup gives the user enough options to optimize the analysis method for varying compositions. Most seen option are:

- Single or multiple columns: the choice for a single or multiple columns depends on the analysis to be performed. If the mixture to be analyzed is complex with different kinds of compounds (e.g. hydrocarbons and permanent gases and sulfur compounds), it could be advisable to use multiple columns in order to have good separation and short times of analysis.
- Single or multiple carriers: usually it is more practical to use a single carrier, but in some cases where the compound to be analyzed has the same or very similar properties as the carrier gas, it is advisable to use multiple carriers (e.g. hydrogen determination with helium carrier)
- With or without back-flush: The back-flush is useful in combination with a pre-column, when there are compounds in the mixture that have longer retention times in the column and there is no interest in them, so to clean the column and have a shorter time for the analysis, back-flush can be a good option. Back-flush can be used also for the determination of heavier compounds that are useful as one peak (as for example, the determination of C6+ in natural gas analysis)
- With or without pre-column: a pre-column can be used in combination with back-flush to do a pre-separation of a family of compounds in order to shorten the time of analysis, but also to protect the column against contamination.

8.10 Correction for the presence of oxygen and argon

8.10.1 General

Normally, natural gas does not contain oxygen or argon. If, however, natural gas samples are found to contain oxygen or argon, this may be due to contamination by improper sampling of the gas. In such a case, the mole fraction of nitrogen and all other components shall be corrected according to the following procedures.

NOTE A historic benchmark for deciding how to correct for oxygen is 0,02 % oxygen. Depending on the sampling method and circumstances, it can be decided whether or not to correct for air.

8.10.2 Gas containing oxygen.

If the gas contains oxygen, correct the mole fraction of nitrogen according to [Formula \(1\)](#):

$$x_{N_2,C} = x_{N_2} - \frac{78,084}{20,946} \cdot x_{O_2} \quad (1)$$

where

$x_{N_2,C}$ is the mole fraction, expressed as a percentage, of nitrogen after correcting the mole fraction for air contamination;

x_{N_2} is the mole fraction, expressed as a percentage, of nitrogen in the sample after normalization;

x_{O_2} is the mole fraction, expressed as a percentage, of oxygen in the sample after normalization.

In [Formula 1](#) it is assumed that the TCD responses for N₂ and O₂ are equal. To minimise the error for this correction, the respective response factors (of the nearest calibration points) should be taken into account.

This correction applies in most cases to spot sampling.

The mole fraction, $x_{j,C}$, expressed as a percentage, of component j in the sample corrected for the presence of oxygen is normalized to 100 % according to [Formula 3](#):

$$x_{j,C} = \frac{x_{j,S}^*}{\sum_{j=1}^{n-2} x_{j,S} + x_{N_2,C}} \quad (3)$$

where

$x_{j,S}$ is the normalized mole fraction, expressed as a percentage, of component j in the sample;

$x_{j,S}^*$ is the non-normalized mole fraction, of component j in the sample;

n is the total number of components;

$n-2$ is the total number of components except oxygen and nitrogen, determined separately on both the molecular sieve 13X and PR column.

8.10.3 Gas containing argon

In certain biomethane producing processes, i.e. air is added to reduce the production of gaseous sulphur components during fermentation, or nitrogen is added to adjust the physical properties of final gas. In the latter case, the origin of this nitrogen will in most cases specifically remove only oxygen, so the produced nitrogen gas will still contain the remaining air components, like the noble gasses.

The amount of argon, present in air, accounts for 0,934 volume percent. This means that for every 100 00 mol ppm of nitrogen in the final gas, also 120 mol ppm of argon is introduced.

When analysing for oxygen in such a process, a separation column must be set up in such a way that argon is sufficiently separated from oxygen. Otherwise, argon's peak area will significantly add to oxygen's peak area, resulting in an overcorrected nitrogen content, and should therefore be calculated for based on the nitrogen content and deducted from the oxygen peak area, before calculating and correcting for oxygen.

8.10.4 Air contamination correction for natural gas spot samples

Often oxygen is found in samples of natural gas from sources where no oxygen should be present, this is primarily due to contamination of atmospheric air during the sampling process. If oxygen is found the best possible course of action would be to acquire a new sample free from contamination; however this is often not possible due to remote analysis or samples taken at a particular time being of interest. This annex will provide a method for the correction of air contamination for natural gas spot samples which come from sources which are known to be oxygen free. Particular care should be taken in this regard since differing fuel gas sources are often comingled with natural gas and some of these sources may contain oxygen.

8.10.5 Correction when the amount of argon has been determined

Since atmospheric air has a well-defined composition it is possible to determine the amount of atmospheric nitrogen and argon in a sample using the ratio of oxygen to nitrogen and argon. The correct nitrogen value can be determined as per [Formula 4](#) below

$$x_{N_2,C}^* = x_{N_2} - \frac{78,084}{20,946} \cdot x_{O_2} \quad (4)$$

where

$x_{N_2,C}^*$ is the mole fraction, expressed as a percentage of nitrogen after correcting the mole fraction for air contamination;

x_{N_2} is the mole fraction, expressed as a percentage of nitrogen in the sample after normalization;

x_{O_2} is the mole fraction, expressed as a percentage of oxygen in the sample after normalization.

Trace argon is sometimes present in natural gas, if argon is also measured and nitrogen is corrected for air contamination the argon must also be corrected via [Formula 5](#).

$$x_{Ar,C}^* = x_{Ar} - \frac{0,0934}{20,946} \cdot x_{O_2} \quad (5)$$

where

$x_{Ar,C}^*$ is the mole fraction, expressed as a percentage of argon after correcting the mole fraction for air contamination;

x_{N_2} is the mole fraction, expressed as a percentage of argon in the sample after normalization.

NOTE It is possible that if all of the argon in the mixture is from air contamination that $x_{Ar,C}^*$ could possibly be negative due to slight biases within the measurement system. If this occurs then $x_{Ar,C}^*$ should be considered to be zero. If $x_{Ar,C}^*$ is significantly negative it would suggest strongly that air contamination is not the source of oxygen present in the gas.

Once the corrected values have been determined the mixture must be re-normalised according to [Formula 6](#) for all components except for oxygen, nitrogen and argon

$$x_{j,C} = 100 \cdot \frac{x_{j,S}}{100 - x_{O_2} - (x_{N_2} - x_{N_2,C}^*) - (x_{Ar} - x_{Ar,C}^*)} \quad (6)$$

where

$x_{j,S}$ is the normalized mole fraction, expressed as a percentage, of component j in the sample prior to air contamination correction;

$x_{j,C}$ is the normalized mole fraction expressed as a percentage of component j in the sample after air contamination correction.

To determine the corrected normalised amount of nitrogen and argon we can use [Formula 7](#)

$$x_{j,C} = 100 \cdot \frac{x_{j,C}^*}{100 - x_{O_2} - (x_{N_2} - x_{N_2,C}^*) - (x_{Ar} - x_{Ar,C}^*)} \quad (7)$$

where $x_{j,C}^*$ is the un-normalized mole fraction, expressed as a percentage of component j in the sample after air contamination correction.

The corrected normalised oxygen value $x_{O_2,C} = 0$.

8.10.6 Correction when the amount of argon has not been determined

When the argon is not separated from the oxygen and the two components co-elute the composite peak is typically assumed to be oxygen.

The composite peak will contain the oxygen and argon, this method assumes all of the argon in the sample is from air contamination, and that the bulk material the sample was taken from contains no argon; however if the bulk material does contain argon this will introduce a bias to the measurement.

The method also assumes that argon and oxygen have the same response factor, this will also introduce a bias to the measurement. These biases should typically be small but can be eliminated by separating and measuring the oxygen and argon.

The corrected nitrogen value can be determined as per [Formula 8](#) below

$$x_{N_2,c}^* = x_{N_2} - \frac{78,084}{20,946 + 0,0934} \cdot x_{O_2} \quad (8)$$

where

- $x_{N_2,c}^*$ is the mole fraction, expressed as a percentage of nitrogen after correcting the mole fraction for air contamination;
- x_{N_2} is the mole fraction, expressed as a percentage of nitrogen in the sample after normalization;
- x_{O_2} is the mole fraction, expressed as a percentage of oxygen (and argon) in the sample after normalization.

Once the corrected values have been determined the mixture must be re-normalised according to [Formula 9](#) for all components except for nitrogen and oxygen

$$x_{j,c} = 100 \cdot \frac{x_{j,S}}{100 - x_{O_2} - (x_{N_2} - x_{N_2,c}^*)} \quad (9)$$

where

- $x_{j,S}$ is the normalized mole fraction, expressed as a percentage of component j in the sample prior to air contamination correction;
- $x_{j,c}$ is the normalized mole fraction, expressed as a percentage of component j in the sample after air contamination correction.

To determine the corrected normalised amount of nitrogen we can use [Formula 10](#)

$$x_{N_2,c} = 100 \cdot \frac{x_{N_2,c}^*}{100 - x_{O_2} - (x_{N_2} - x_{N_2,c}^*)} \quad (10)$$

The corrected normalised oxygen value $x_{O_2,c} = 0$

9 Detection

9.1 Typical detectors for natural gas analysis

The choice of the detector depends on the purpose of the gas analysis results. Most common detectors are:

- Thermal conductivity (TCD): It is a universal detector, as long as there is enough difference of the conductivity between the carrier gas and the components of the mixture. Being universal, it is not very specific, and the detection limit can be insufficient in case of low concentrations.
- Flame ionization (FID): it is a detector suitable for the analysis of hydrocarbons, since it responds proportionally to the carbon number in the components.

The most used detector is the TCD, as it does not require a support gas and is a very compact detector.

Other types of detection are available that give a better detection of certain types of components and for lower concentrations. For example, mass spectrometry (MS), which can be used specially to identify unknown compounds. It is a universal detector, but it is expensive and more complicated to use compared to the TCD.

9.2 Peak resolution

It is important that all components are measured without interference from others, see [Figure 7](#). For each component to be quantified independently, the resolution between neighboring peaks shall exceed 1,5. This can be assessed by measuring peak resolution.

Gas-chromatographic resolution is a characteristic of the separation of two adjacent peaks and is measured as twice the distance between the maxima of the named peaks divided by the sum of the intercepts on the baseline made by tangents drawn to the peaks at half their height (see [Figure 6](#)). The resolution R_{AB} may be expressed by following [Formula 11](#):

$$R_{AB} = 2 \cdot \frac{[d_R(B) - d_R(A)]}{[w(A) + w(B)]} \quad (11)$$

where

$d_R(A)$ and $d_R(B)$ are the retention distances of the eluted components A and B;

$w(A)$ and $w(B)$ are the widths of the respective peaks at their base.

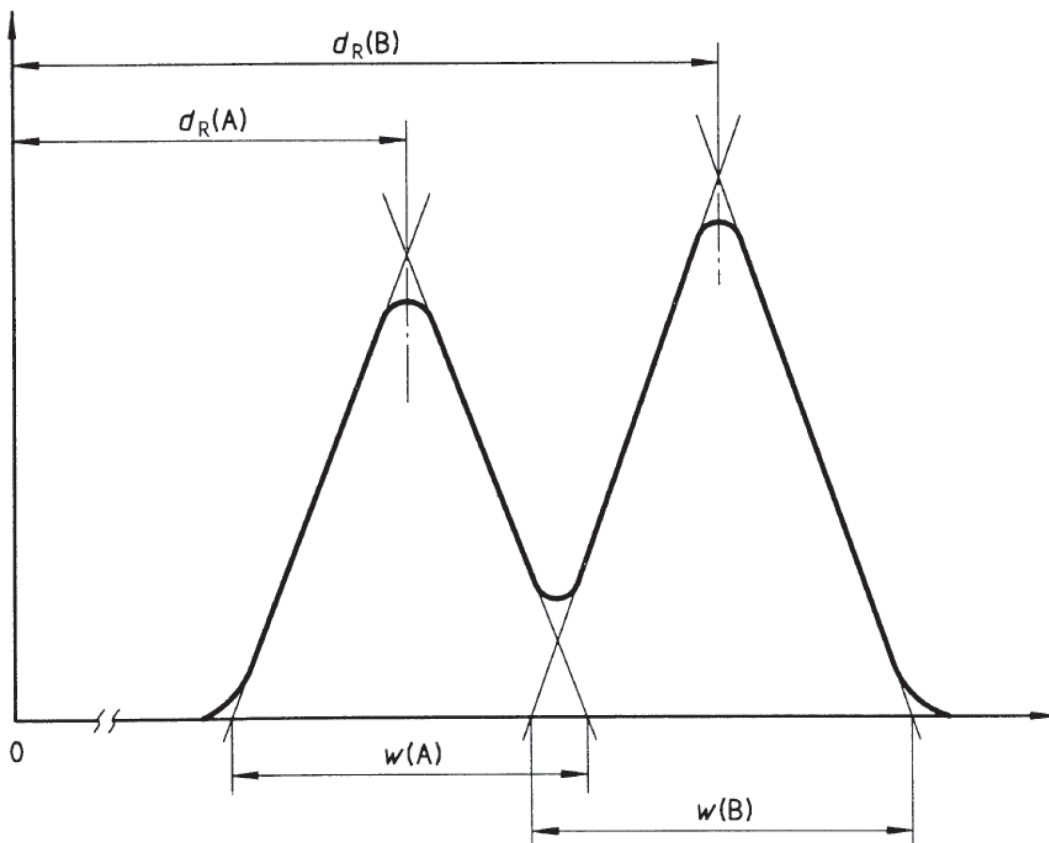


Figure 6 — Resolution of two adjacent peaks

Although the resolutions of all peaks are important, there are particular pairs of peaks which are critical: their satisfactory resolution ensures that of other pairs. A reference for peaks resolution that allows obtaining the limit precision values, is given in Annex [A.5.2.1.1](#) and Annex [C.6.3.4](#) of this document.

Ideally, component peaks should start from and finish at the baseline. The data system evaluates the area bounded by the peak profile and the calculated position of the baseline if the peak had not been there. This baseline calculation is more reliable if the data system can assess the baseline position both before and after the peak and hence project a straight line between the two. This is not always possible, particularly if there are time constraints on the analytical cycle, and the signal between adjacent peaks does not return to the baseline (or where it would have been) so that there is some overlap between peaks. See [Figure 6](#).

Where overlap occurs, there is inevitably some misallocation of the areas (quantitative measurements) of the two peaks. If the peaks are symmetrical (approximately Gaussian) and of comparable size, the loss from one balances the gain from the other, and the area allocations are close to being correct. If, as would be the case with iso and normal butane, the responses are very similar and the properties almost identical, then the errors involved in calculating their contributions to calorific value, for example, would be small. If the peaks are of substantially different sizes and the respective substances have different physical properties, then more significant errors will arise.

A good example is nitrogen and methane, where the peak resolution is complicated by the asymmetry of the methane peak in particular. See [Figure 8](#).

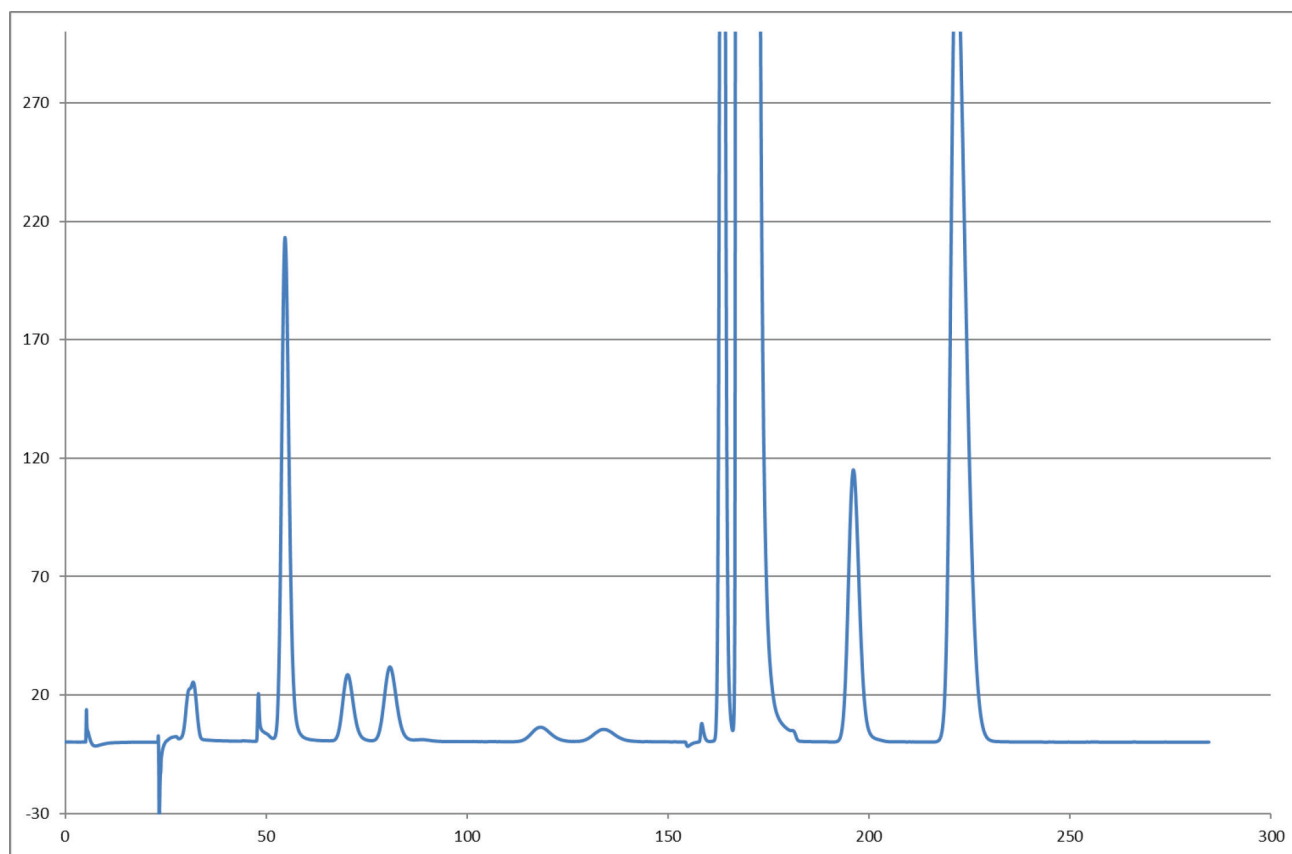


Figure 7 — Example of overlapping peaks

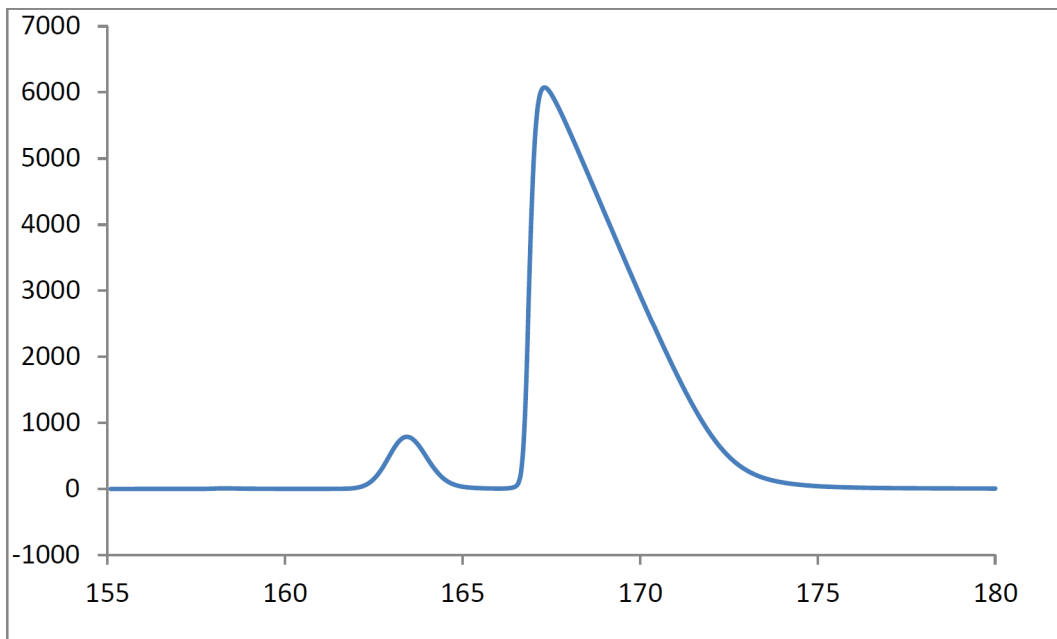


Figure 8 — Good separation, but asymmetry for the methane peak (right)

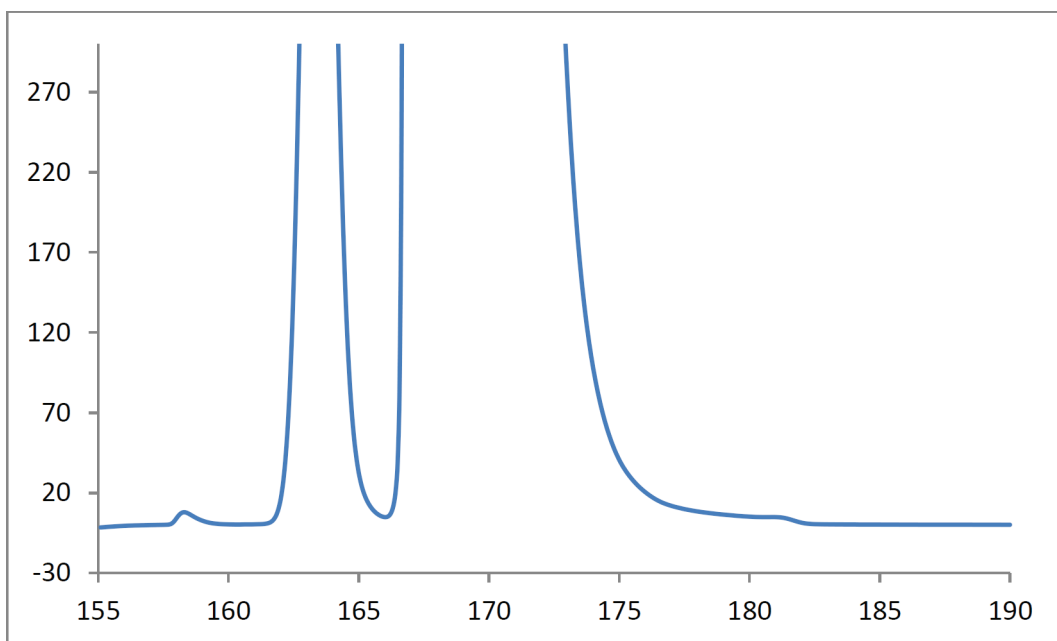


Figure 9 — [Figure 8](#), zoomed in

This is illustrated in the chromatograms shown, which uses the data and recreates the chromatogram from a typical C6+ analyzer. The full chromatogram ([Figure 7](#)) is shown at the top, and the nitrogen/methane pair below it ([Figure 8](#)), at different scales (see [Figure 8](#) and [Figure 9](#)) to allow the tangents to each peak to be plotted. The calculated peak resolution is 0,98. Conventional wisdom would say that this is unacceptably low, and a value of 1,5 or higher should be aimed for. It would need considerable change to the chromatography to achieve a value of 1,5, and almost certainly a longer analysis time. It would also be debatable whether a resolution of 1,5 would give a better result than the existing 0,98.

If the resolution is less than desirable or resolving would require an unproportional amount of time or money, then an (off-line) optimization of the integrating parameters (for the components range of interest) combined with an investigation for linearity could be the most effective way to go.

9.3 Detector

The detector(s) should be chosen in order to be suitable for all the separated components of interest and has a stable and repeatable response characteristic for the separated components.

The thermal conductivity detector (TCD) is the most widely used for natural gas analysis. Its ability to measure non-flammable gases (principally nitrogen and carbon dioxide) means that it is the only choice for single-operation analysis. It can also measure sufficiently low amounts of C4 and C5 hydrocarbons (and the pseudo-component C6+) to be satisfactory for calculation of the more common properties, such as CV, SG and WI.

The thermal conductivity detector responds to conductive heat loss (hence its flow sensitivity). However, in GC applications thermal conductivity is the main effect. The most important parameter is the temperature difference between the sensing element (filament or thermistor) and the detector body.

If a TCD is chosen for the analysis, it should be taken into account that the thermal conductivity of the carrier and of the components to be determined should be sufficiently different to have a sensible signal (for example, in the case of the determination of hydrogen, helium as carrier is not a good choice since they have almost the same thermal conductivity; in this case argon or nitrogen are good choices for carrier gas).

The flame ionization detector (FID) can be used for hydrocarbons, but only in the context of multi-operation analysis. An FID cannot detect inert gases, (high levels of) methane or hydrogen. It is more sensitive to higher hydrocarbons than a TCD. In conjunction with TCD an FID is more suited for CV determination where the gas contains higher amounts of higher hydrocarbons.

The most complete GC for Natural Gas analysis is a setup with both a TCD and FID. However, it requires (much) more support gas and has more safety requirements. In combination with a Boiling Point separating column is also suitable for Hydrocarbon Dew Point calculations.

Hence, we need to be aware of:

- 1) The sensing element temperature, which is a function of the current flowing through it.
- 2) The detector block temperature. The detector can be mounted in the column oven, which sets it to the column temperature (only practical for isothermal analysis) or, more commonly, in a separate heated enclosure. In this latter case the constraint on the temperature value is that it should not be lower than the minimum column temperature (or the maximum temperature programmed value) to avoid condensation of column bleed (effluent/analyte) in the detector. The temperature stability is important for baseline stability and consistency of response.
- 3) The detector pressure. The amount of analyte is directly influenced by the pressure in the detector. Although it would be difficult to actively correct the detector output for the pressure, it is recommended to shield the detector from sudden pressure shifts as much as possible. For instance, this can be achieved by using soft closing doors to the laboratory and installing a "delay line" (tubing-volume-tubing) between the detector and the vent-line. Sudden pressure shifts appear to have a particular propensity for the starting or ending zone of a peak.

10 Data processing

10.1 Data

10.1.1 General

The data of the chromatograph uses a data handling system which converts the analogue detector output into qualitative (what is the component?) and quantitative (how much of it?) data.

10.1.2 Conversion

The data system converts the analogue detector signal to a series of digital sums for each component. If necessary, it converts these sums to molar quantities according to the calibration. From these quantities

it calculates physical properties from the resulting composition. It also provides time-based commands to control valve or flow switching during the chromatogram. In a fully automated system, it controls repeated analyses on a regular basis with calibration carried out at selected intervals.

10.1.3 Allocation or peak identification

The analogue to digital conversion is trouble-free. The correct allocation of peak area depends upon the system recognizing the start and finish of each peak. The system should allow for baseline drift without confusing it with the start or finish of peaks and not confusing electrical spikes or baseline noise with real signals. It must also handle peaks which are not fully resolved. In this case the signal between the peak maxima does not reach the 'true' baseline. It creates a 'valley' point between the peaks, and defines a perpendicular line from the valley to the baseline. This represents the end of the first peak and the beginning of the second. In particular circumstances, the system will create a tangent skim whereby the second peak is deemed to be sitting on the tail of the first one.

How these decisions are made can be checked by inspection of the chromatogram generated by the data system. The location of the peak start and finish is usually identified on the chromatogram and the projected baseline under the peak is shown. If the user does not agree with the decisions made, changing the integration parameters, such as peak width, slope sensitivity and turning integration on and off should lead to more acceptable results. The subtlety of these allocations and adjustments are such that specification of how the system should make decisions can hardly be more instructive than "ensure correct operation". The operator's experience is the critical input.

10.1.4 Data file format

A convenient way to transfer data between systems is the XML file format, as described in ISO 23219.

The XML file format is useful for output from ISO 6974-1 for composition, and ISO 6974-2 for uncertainty, and for input for ISO 10723 for performance evaluation. Typically, these would be the gas composition as provided on an analysis certificate, or results from a performance evaluation that would be read into an Excel spreadsheet for data processing.

XML is defined by the tags – keywords enclosed in angular bracket, e.g. <gas>, with a terminating tag with / in front of the keyword, e.g. </gas>

The schema is short but defines the file format that has flexibility to be of use for all natural gas data.

The schema has (up to) four levels:

— Level 1 (top level)	<natgas>	
— Level 2	<gas>	g. tags
— Level 3	<data>	d. tags
— Level 4 (bottom level)	<param>	p. tags

Within each level the layout is basically: keyword, value, units and uncertainty.

The XML tags defined in the schema are case sensitive (they are all lowercase) and have no leading or trailing spaces. The tags have no attributes, i.e. no name="value" within the tag.

The content of the tags, e.g. keywords, are case insensitive, and leading and/or trailing spaces are ignored. In the examples (see [annexes B](#) to [E](#)), the contents are in uppercase; often with trailing spaces in order to improve readability.

The only likely need for lowercase is to distinguish the S.I. prefixes of m (milli) and M (mega). Keywords should not contain spaces.

For more detailed information, see ISO 23219, Natural gas – XML Data File Format.

10.2 Peak integration

10.2.1 General

Peak integration is basically the numerical processing of the detector signal during or after sample analysis to obtain a component response proportional to the component content in the sample being analyzed.

10.2.2 Principle

The principle and challenge of integrating the peaks in a chromatogram is finding the balance between baseline noise and peak resolution. The simplest way to integrate a peak is to start the integration when the signal has risen significantly above the noise of the baseline and stop integration after the signal has peaked vice versa, when the signal can no longer be discriminated from the baseline noise.

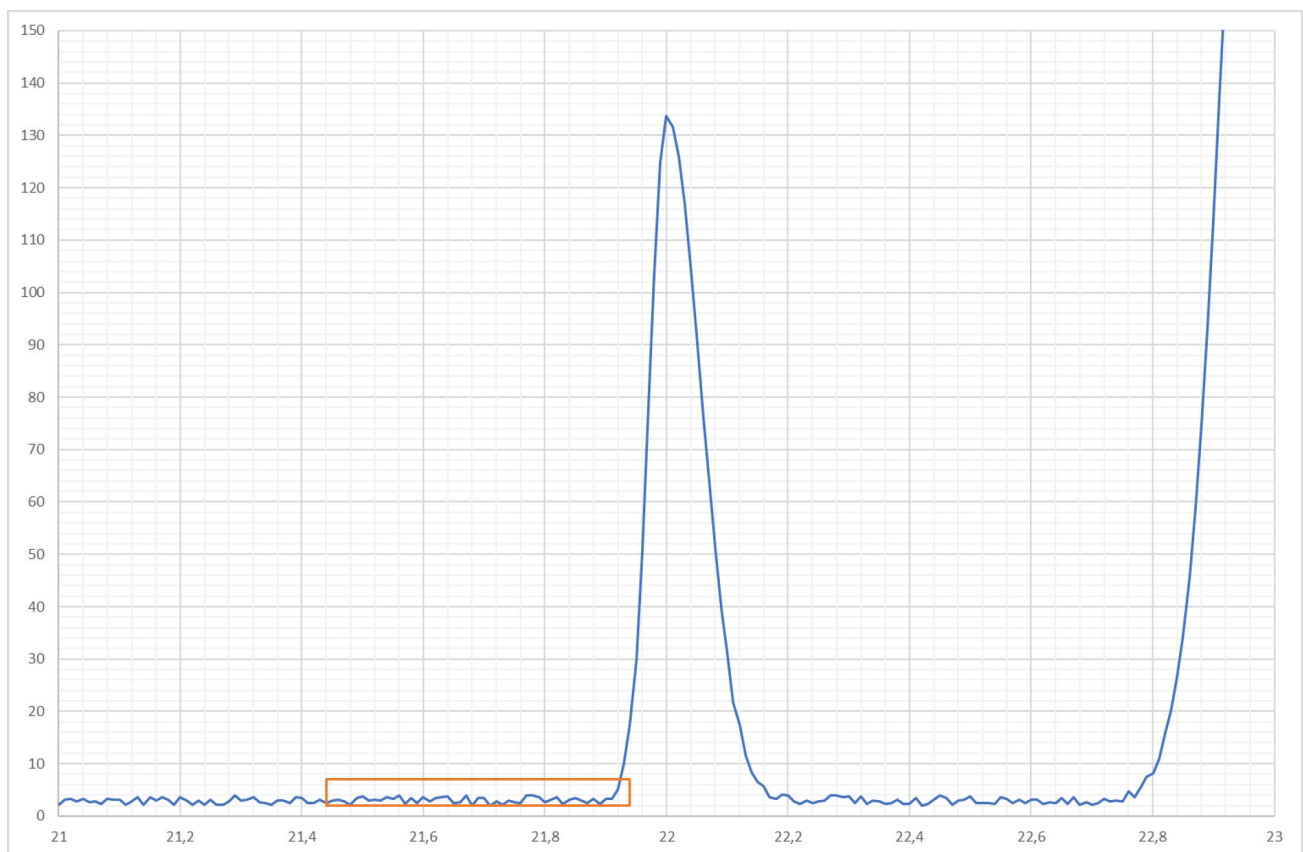


Figure 10 — Example of the Peakwidth-Threshold box

Above, [Figure 10](#) is an example of peak detection, set by peakwidth and threshold (box); the signal is no longer within the threshold range during the peakwidth time range. The moment this occurs, is defined as the start of the peak. Vice versa, the same logic is used for detecting the end of the peak.

Most GC manufacturers are providing a wide range of peak detection types and parameters, and, also, provide all information necessary to obtain optimum solution for the component range of interest.

10.3 Chromatogram

10.3.1 General

A chromatogram is a visual representation of the detector signal of the analysis run, and is often combined with per-peak information, i.e. peak name and retention time, either during analysis or afterwards.

10.3.2 File

Chromatogram files are commonly stored in a GC producers' proprietary file type, a binary file or another type of compressed file type.

10.3.3 A/D Conversion

The analogue signal from the detector needs to be digitized to be processed digitally. The bit depth of this step needs to be in agreement with the signal level to produce an optimal signal to noise ratio. An automatic bit depth-level, based on the signal level, may also be available.

10.3.4 Sampling frequency

The sampling frequency is set such to allow the detection of the peak of interest with smallest peak width with sufficient resolution, so reliable peak detection can be performed. Setting the sampling frequency to high will not lead to better peak detection, but only increase the file size of the chromatogram data.

11 Calibration

Calibration is described in ISO 6974 part 1, the associated uncertainty in ISO 6974 part 2.

12 Optimization

12.1 General

The correct way to integrate peaks in a chromatogram is to set integration parameters that lead to the best calibration fit with the lowest polynome for the composition range of interest.

12.2 Method

The following steps, using the two-factorial or Design of Experiments approach, for the optimization of the integration parameters are recommended:

- 1) Unless proper integration demands it, do not start integration directly after injection. The pressure difference caused by injection or backflush can result in a substantial baseline swing. Start integration a few seconds before the first peak, 10 % of its retention time (RT) is a good guideline.
- 2) Assuming a components determination has already been performed, optimization of integration parameters starts at the first peak in the chromatogram.
- 3) Inject the lowest concentration of reference gas for the current peak in the calibration range once.
- 4) In the chromatogram, determine the peak width at half-height (PW) of the current peak. This is the lowest value in the PW-range to be investigated, PWmin.
- 5) Inject the highest concentration of reference gas for the current peak in the calibration range once. Determine the peak width at half-height (PW). This is the highest value in the PW-range to be investigated, PWmax.
- 6) Determine the noise level at the current RT by injecting a zero-gas or by performing a run without injection. Within the time period of PWmin, find the difference between the lowest and highest baseline level. This is the minimal threshold for integration, THmin.
- 7) Analyse all reference gasses at least 10 times.
- 8) Recalculate following a fractional or DoE approach to obtain the optimal integration parameters, in the following range:
- 9) $PW_{min}/2$ to $2 \cdot PW_{max}$, in an odd amount of steps