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ISO 6974-1

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Natural gas — Determination of composition with defined uncertainty by gas chromatography —

Part 1: Guidelines for tailored analysis

Gaz naturel — Détermination de la composition avec une incertitude définie par chromatographie en phase gazeuse —

Partie 1: Lignes directrices pour l'analyse spéciale

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 6974 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 6974-1 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This part as well as the other five parts of ISO 6974 cancel and replace ISO 6974:1984 which specified only one method.

ISO 6974 consists of the following parts, under the general title *Natural gas — Determination of composition with defined uncertainty by gas chromatography*:

— *Part 1: Guidelines for tailored analysis*

— *Part 2: Measuring-system characteristics and statistics for data treatment*

— *Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8 using two packed columns*

— *Part 4: Determination of nitrogen, carbon dioxide and C_1 to C_5 and C_{6+} hydrocarbons for a laboratory and on-line measuring system using two columns*

— *Part 5: Determination of nitrogen, carbon dioxide and C_1 to C_5 and C_{6+} hydrocarbons for a laboratory and on-line process application using three columns*

— *Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8 using three capillary columns*

Annexes A and B of this part of ISO 6974 are for information only.

Introduction

This part of ISO 6974 gives guidelines for the "tailored" analysis of natural gas with the aim of determining the mole fractions of the principal components.

ISO 6974 (all parts) describes methods of analysis of natural gas with definable levels of uncertainty. The approach is suitable for the calculation of calorific value and other additive physical properties of the gas, again with a definable uncertainty.

Part 2 of ISO 6974 describes the determination of the measuring system characteristics and the statistical approach to data handling and error calculation with the aim of defining the uncertainties in the component mole fractions.

Part 3 and subsequent parts of ISO 6974 describe different possible methodologies for tailored analyses, which can only be applied in conjunction with parts 1 and 2 of ISO 6974.

Parts 1 and 2 represent the body of ISO 6974. The method chosen from Part 3 and subsequent parts or from any other source requires compliance with parts 1 and 2 of ISO 6974.

Informative annex A gives a comparison of the characteristics of typical analytical methods as described in part 3 and subsequent parts of ISO 6974.

ISO 6974 (all parts) is designed for the measurement of H_2, He, O_2, N_2, CO_2, individual hydrocarbons and/or a total figure for hydrocarbons for example above C_5 defined as C_{6+}. It is not applicable to other minor components where their contribution to physical properties is not significant or can be regarded as constant. Among these are potentially natural components such as Ar, H_2O and sulfur compounds, and components arising from gas treatment such as methanol, glycols and amines.

The described method allows air contamination in the sample to be recognized and measured in the case of spot sampling and laboratory analysis, but not necessarily for on-line analysis.

Although "tailored" analysis itself is relatively simple, it can produce an analysis with high accuracy, provided that elaborate preparations are carried out. These include outlining the structure of the analysis, defining the working ranges and establishing the analytical procedure. However, in practice, only a limited number of steps are necessary for setting up the method to meet the requirements for specific application. The amount of work and calculations necessary will then be relatively restricted.

This part of ISO 6974 describes all the essential steps for setting up a "tailored" analysis.

Assuming that the analytical results follow the normal distribution, control charts give an indication as to whether the measuring system and the established method is working satisfactorily. For this reason the use of control charts is described in informative annex B of this part of ISO 6974.

ISO 6974 (all parts) can be used in daily practice in a laboratory and for on-line field applications and covers the following options or alternatives.

— Straight-line or polynomial calibration plots.

— Single-point or multi-level calibration.

— Recombination of components by backflushing to vent, recombination of components by backflushing to measure, or forward elution of all components.

— Calibration one-to-one, or by relative response factors to a reference component.

— The use of a thermal conductivity detector (TCD) is necessary and in certain cases a flame ionisation detector (FID) may be used in addition.

When setting up a tailored analysis, a series of choices are to be made from these options. The consequences of the combination chosen should be assessed. The procedure for this assessment is described in this part of ISO 6974. If the assessment shows that the performance is poorer than desired, another combination can be chosen, in which case the assessment is to be repeated in full.

Natural gas — Determination of composition with defined uncertainty by gas chromatography —

Part 1: Guidelines for tailored analysis

1 Scope

This part of ISO 6974 gives guidelines for the quantitative analysis of natural-gas-containing constituents within the application ranges given in Table 1.

Individual methods, as described in part 3 and subsequent parts of ISO 6974, may have more restricted application ranges than those in Table 1, but in all cases they will fall within this overall scope of the ranges given.

Table 1 — Application ranges

Component	Mole fraction range %
Hydrogen	0,001 to 0,5
Helium	0,001 to 0,5
Oxygen	0,001 to 5
Nitrogen	0,001 to 60
Carbon dioxide	0,001 to 35
Methane	40 to 100
Ethane	0,02 to 15
Propane	0,001 to 25
Butanes	0,000 1 to 5
Pentanes	0,000 1 to 1
Hexanes and heavier	0,000 1 to 0,5

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 6974. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 6974 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6974-2, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for data treatment.*

ISO 6974-3, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8 using two packed columns.*

ISO 6974-4, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and C_1 to C_5 and C_{6+} hydrocarbons for a laboratory and on-line measuring system using two columns.*

ISO 6974-5, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and C_1 to C_5 and C_{6+} hydrocarbons for a laboratory and on-line process application using three columns.*

ISO 6974-6, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8 using three capillary columns.*

ISO 6975, *Natural gas — Extended analysis — Gas-chromatographic method.*

ISO 10715, *Natural gas — Sampling guidelines.*

3 Terms and definitions

For the purposes of this part of ISO 6974, the following terms and definitions apply.

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

3.2
reference component
component present in a working-reference gas mixture (WRM) (see 3.9), which is used to calibrate the analyser response to other, similar components in the sample which are not themselves present in the working-reference gas mixture

NOTE For example, if the WRM contains hydrocarbons up to and including *n*-butane, but no pentanes or higher, then *n*-butane contained in the WRM can be used as a reference component for the quantification of pentanes and heavier components in the sample. The reference component should have a response function which normally is a first-order polynomial with zero intercept, i.e. a straight line through the origin.

3.3
relative response factor
K_j
ratio of the molar amount of component j to the molar amount of reference component which gives an equal detector response

3.3.1
relative response factor for flame ionisation detector (FID)
calculated as the ratio of the carbon number of the reference component to the carbon number of the sample component

NOTE The values of the relative response factors are described in ISO 6974-2.

3.3.2
relative response factor for thermal conductivity detector (TCD)
determined using reference gas mixtures as described in ISO 6974-2

3.4
other components
components in the gas sample which are not measured by tailored analysis in accordance with ISO 6974 (all parts) and/or can be regarded as being present at a constant mole fraction

NOTE The mole fraction of these components, except methanol and sulfur, can be determined by extended analysis in accordance with ISO 6975.

3.5
group of components
components with mole fractions so low that their measurement as individuals would be difficult or require excessive time, and which are measured as a group

NOTE This can be achieved by particular chromatographic techniques, such as backflushing, or by data handling, such as integrating a succession of components as if they were a single component.

3.6
accuracy
closeness of agreement between a measurement result and the true value of the measurand

NOTE The term accuracy, when applied to a set of measurement results, describes a combination of random components and a common systematic error or bias component.

3.7
uncertainty
estimate attached to a measurement result which characterizes the range of values within which the true value is asserted to lie

NOTE In general, the uncertainty of measurements comprises many components. Some of these components may be estimated on the basis of statistical distribution of the results of series of measurements and can be characterized by experimental standard deviation (SD). The estimates of other components can only be based on experience or other information.

3.8
certified-reference gas mixtures
CRM
mixtures which are used for the determination of the response curves of the measuring system

NOTE Certified-reference gas mixtures may be prepared gravimetrically in accordance with ISO 6142[1] or ISO 13275[2] or certified and validated by comparison with primary standard gas mixtures of closely related composition in accordance with ISO 6143[3] (see ISO 14111[4]).

3.9
working-reference gas mixtures
WRM
mixtures which are used as working standards for regular calibration of the measuring system

NOTE Working-reference gas mixtures may be prepared by a gravimetric method in accordance with ISO 6142[1] or certified and validated by comparison with CRM of closely related composition in accordance with ISO 6143[3].

3.10
direct measurement
measurement by which individual components and/or groups of components are determined by comparison with identical components in the working-reference gas mixture

3.11
indirect measurement
measurement by which individual components and/or groups of components which are themselves not present in the working-reference gas mixture are determined using relative response factors to a reference component in the working-reference gas mixture

3.12
repeatability
value below which the absolute difference between two single measurement results obtained using the same method, on identical measurement material, by the same operator, using the same apparatus, in the same

laboratory, within a short interval of time, (repeatability conditions), may be expected to lie with a specified probability; in absence of other indication the probability is 95 %

3.13
control gas
high-pressure gas mixture of known composition containing all the components present in the working-reference gas mixture

NOTE 1 A control gas can be either a gas sample with a composition determined in accordance with ISO 6143[3] or a multicomponent mixture prepared in accordance with ISO 6142[1] or ISO 13275[2]. A control gas is used to calculate the mean (μ) and the standard deviation (σ) of component mole fractions detected for the preparation of the relevant control charts.

NOTE 2 For on-line analysis the working-reference gas mixture may be used as a control gas.

3.14
working range
restricted mole fraction range within the application range of Table 1, that is specific for methods of tailored analysis

4 Symbols and subscripts

4.1 Symbols

a_j,b_j,c_j,d_j	polynomial constants of component j
K_j	ratio of the response factor of component j to the response factor of the reference component
R	response expressed as the number of counts
x	normalized mole fraction
x^*	non-normalized mole fraction

4.2 Subscripts

c	air contamination
j	component j
mc	main components to be analysed using direct measurement
oc	components which are not measured and/or can be regarded as being present at a constant mole fraction
rcwrm	reference component of the working-reference gas mixtures
rrf	components or groups of components to be analysed using indirect measurement
s	sample
wrm	working-reference gas mixture

5 Principles of analysis

All significant components or groups of components to be determined in a gaseous sample are physically separated by means of gas chromatography and measured by comparison with calibration data obtained under the

same set of conditions. Therefore the calibration gas(es) and the gas sample shall be analysed with the same measuring system under the same set of conditions. The mole fraction of non-measured components can influence the accuracy of the method and shall therefore be known.

After the working ranges of all components are defined, an evaluation shall be carried out to define which components are to be considered

— as components or groups of components to be analysed using direct measurement against identical components or groups in the working-reference gas mixture (x_{mc}),

— as components or groups of components to be analysed using indirect measurement against a different reference component in the working-reference gas mixture (x_{rrf}), and

— as other components which are not to be measured, and whose mole fraction can be assumed to be constant (x_{oc}).

The sum of the mole fractions of components measured directly and indirectly, as well as other components is equal to 1 as follows:

$$x_{mc} + x_{rrf} + x_{oc} = 1$$

6 Materials

6.1 Certified-reference gas mixture (CRM), consisting of components the mole fractions of which cover the working range (see 10.2.1, step 1) and which are used for the determination of the response curve of the measuring system.

Depending upon the working range and the accuracy required, more than one CRM may be needed.

The working range shall not necessarily cover the whole application range of this part of ISO 6974.

6.2 Working-reference gas mixture (WRM), consisting of components, the mole fractions of which have a value situated within the working range to which the working reference applies.

The WRM shall contain all those components that are measured by direct comparison.

7 Apparatus

7.1 Measurement system, comprising a sample introduction and transfer unit, a separation unit, a detection unit, an integrator and a data reduction system.

Part 3 and subsequent parts of ISO 6974 give different configurations of laboratory and on-line measuring system which have been found to be suitable.

NOTE Annex A summarizes the comparative characteristics of parts 3 to 6 of ISO 6974.