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

Part 2:
Measuring-system characteristics and statistics for processing of data

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

Partie 2: Caractéristiques du système de mesure et statistiques pour le traitement des données

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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 6974-2 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 processing of data*

— *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, B and C of this part of ISO 6974 are for information only.

Introduction

This part of ISO 6974 describes the data processing for the "tailored" analysis of natural gas.

This part is to be used in conjunction with part 1 of ISO 6974 which gives the guidelines for "tailored" analysis.

Any method of analysis, either one of those in part 3 of ISO 6974 and subsequent parts or another method of choice can only be applied in conjunction with parts 1 and 2 of ISO 6974.

The calculation of the composition of the gas using response curves, a working-reference gas mixture and relative response factors are described in part 1 of ISO 6974, while the elaboration of these formulae is described in this part of ISO 6974.

The working-reference gas mixture and the gas sample are analysed with the same analytical system under the same set of conditions. Components not measured by this method will influence the accuracy of the method and should therefore be known.

If no working-reference gas mixture is used for the regular calibration of the analytical system, a number of equations given in this part of ISO 6974 will change. Such changes are indicated for each of these equations.

Once the working ranges of the components have been defined, an evaluation is carried out to determine whether components are to be considered as:

⎯ main components or groups of components to be analysed using direct measurement (directly measured components);

⎯ components or groups of components to be analysed using indirect measurement, as a function of a different, reference component in the calibration gas (indirectly measured components);

⎯ components that are not measured and whose mole fraction can be assumed to be constant (components not measured).

The sum of the mole fractions of the main components, the indirect components and the fixed components is equal to 1.

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

Part 2:
Measuring-system characteristics and statistics for processing of data

1   Scope

This part of ISO 6974 describes the data processing for the tailored analysis of natural gas. It includes the determination of the measuring system characteristics and the statistical approach to data handling and error calculation with the aim of defining the uncertainty in the mole fractions of the component measured.

This part of ISO 6974 is only applicable in conjunction with part 1 of ISO 6974.

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 6974-1, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis.*

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

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

NOTE   Response is expressed in counts.

3.2
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. The estimates of other components can only be based on experience or other information.

3.3
certified-reference gas mixture
CRM
mixture which is 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]).

3.4
working-reference gas mixture
WRM
mixture which is used as a working standard 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].

3.5
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

3.6
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

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4   Symbols and subscripts

4.1   Symbols

a_i, b_i, c_i, d_i	polynomial coefficients of the component i
a_{mc}, b_{mc}, etc.	polynomial coefficients of the components or groups of components to be analysed using direct measurement as a function of identical components or groups in the calibration gas
h_s	number of replicates of the sample
h_{wrm}	number of replicates of the working-reference gas mixture
K	relative response factor with respect to the reference component
m	order of the response function fitted
n	total number of analyses used in the regression
q	number of direct components plus number of indirect components
R	instrument response, expressed as raw data, e.g. area counts or peak height
R_f	response factor (based on a single point calibration)
s_{MSE}	residual mean square (MSE)
s_{MSR}	mean square due to regression (MSR)

s^2_{SSE}	residual sum of squares (SSE)
s^2_{SSR}	sum of squares due to regression (SSR)
$s(\hat{x})$	standard deviation of the predicted value
$s(x)$	standard deviation of a normalized mole fraction
$s(x^*)$	standard deviation of a non-normalized mole fraction
$s(x_{c,WRC})$	standard deviation of a mole fraction in the WRM (from the certificate of WRM)
$s(R)$	standard deviation of the responses at one mole fraction level
T_i	the difference in slope between the tangent of the optimal response function in $R_{wr,i}$ and calibration line based on the single point method of the WRM only
t	reduced variable of the t-distribution
$x_{c,wrm}$	mole fraction of the WRM (given on the certificate)
$\hat{x}$	predicted value of the mole fraction according to a response function
x^*	non-normalized mole fraction
x	normalized mole fraction
$x_{L,wr}$	lowest mole fraction in the working range
$x_{U,wr}$	highest mole fraction in the working range
ν	number of degrees of freedom

4.2 Subscripts

c	certified
i	component i
j	mole fraction level j
h	number of replicates h
L	lowest
mc	main components or groups of components to be analysed using direct measurement as a function of identical components or groups in the calibration gas
MSE	residual mean square
MSR	mean square due to regression
oc	other components that are not measured and/or can be regarded as being present at a constant mole fraction

rrf	components or groups of components to be analysed using indirect measurement as a function of a different reference component in the calibration gas
ref	reference component
SSE	residual sum of squares
SSR	sum of squares due to regression
s	sample
U	highest (upper limit)
wr	working range
wrm	working-reference gas mixture

5 Procedure

5.1 Step 1: Determination of the optimal response functions

5.1.1 General remarks

Detector response functions are determined using certified reference gas mixtures (CRMs).

For each of the direct components, select the most optimal detector response function which gives the best relationship between response signal and component quantity of the CRM. Carry out this step in the following cases:

— initial installation of the system by the supplier;

— return to operation after a maintenance of the system;

— return to operation after replacement of a major part of the system, e.g. injection valve, column, detector;

— return to operation after failure to pass a routine check of the system using test gas(es).

NOTE   It may be necessary to determine the best statistical curve fit of the results. Although quadratic and cubic curves may give a better fit to the data, for a series of gases this may not be feasible. It is more important to obtain consistent results for the different gases. In practice, this consistency can often be obtained by simply drawing the relative-response (= absolute response/mole fraction) versus mole-fraction curves.

5.1.2 Selection of reference gases

To define the response functions, different mole fraction levels of the direct components are analysed. The number of levels needed depends on the order of the response curve that has to be fitted. The minimum number of levels needed is the same as the number of polynomial coefficients (see below) in the equation to be fitted. However it is recommended to use a few more mole fraction levels than necessary. In most cases, the order of the response curve is unknown beforehand but by increasing the number of data points, the response curve is less influenced by measurement error. Therefore, a minimum of seven levels is recommended although another number of mole fraction levels may be sufficient to obtain a good curve fit.

Choose these levels so as to spread them uniformly across the specified working range of each component and to cover a range which is slightly larger than the anticipated mole fraction range. This can be made possible by using a set of multi-component mixtures, each containing different mole fractions of all the direct components.

NOTE 1   The components can possibly be tested as binary mixtures in methane. However, this would greatly lengthen the testing process, as a separate set of cylinders would be needed for each non-methane component.

NOTE 2   It is obviously not possible to make a mixture with every component at the highest level required, or at the lowest, so most of the multi-component reference gas mixtures will have compositions which are quite different from normal natural gases. Provided that the mixtures are shown to be stable in storage and use, this will not create a problem.

NOTE 3   Prior to the use of a WRM it is necessary to prove that there is no contradiction between the multi-point calibration, made by CRMs, and the mole fraction values of the WRM.

5.1.3   Measurement procedure

Analyse each of the CRMs, containing the direct components, at least twice (preferably 5 to 10 times) using the gas chromatograph. Tabulate the data for the individual responses R_{ijh} of each component i, at each mole fraction j and for each replicate h. Before proceeding, inspect the data for outliers. Inspect the results of each group by component and level from one calibration interval for outliers or stragglers using Grubb's test or some other suitable outlier test. Reject the possible determined outliers.

NOTE   In any set of data, individual results may be found which are not consistent with the other data of that set. These are regarded as outliers or stragglers and shall, under the correct circumstances, be eliminated from the set of data. Possible causes of outliers can be identified, for example transcription errors or carryover from the previous CRM which was not fully purged from the system before the results from the new CRM were recorded.

5.1.4   Selection of the response function

5.1.4.1   Introduction

The response function shall be selected from the following polynomial functions. If a more complex function is needed, this means that the method is unsuitable for this application.

$$x_i = (a_i +) b_i R_i \qquad \text{first order} \tag{1}$$

$$x_i = (a_i +) b_i R_i + c_i R_i^2 \qquad \text{second order} \tag{2}$$

$$x_i = (a_i +) b_i R_i + c_i R_i^2 + d_i R_i^3 \qquad \text{third order} \tag{3}$$

The a_i term (intercept) is placed between brackets because the intercept is tested independently of the order of the model, so each of the above listed response functions may also appear without the intercept term.

Choose the response function with the following assumptions in mind:

— the most likely response is a straight line through the origin;

— a zero intercept, implying no response to a component in its absence, is likely for most components;

— curvature of the response function can be described by a second order term possibly by a third order term;

— it is unlikely that a higher order term will have greater significance than a lower order term in the same equation;

— the presence of a maximum or a minimum in the plot of calculated mole fractions versus response within the working range is not acceptable.

5.1.4.2   Regression analysis

For the data obtained in 5.1.3, carry out regression analysis using a computer program capable of:

— performing a least squares regression of component mole fractions, x_i, as the dependent variable as a function of the individual responses, R_{ijh}, as the independent variable;

— performing a least squares regression of x_i as a function of R_{ijh} and R_{ijh}^2 ;

— performing a least squares regression of x_i as a function of R_{ijh}, R_{ijh}^2 and R_{ijh}^3;

— producing output for each of the fitted response functions of the:

  — confidence interval for each coefficients;

  — sum of squares due to regression (SSR), s_{SSR}^2;

  — residual sum of squares (SSE), s_{SSE}^2;

  — mean square due to regression (MSR), s_{MSR};

  — residual mean square (MSE), s_{MSE};

  — number of degrees of freedom (ν) associated with s_{MSR} and s_{MSE};

  — predicted values of the component mole fractions $(\hat{x}_i)$;

  — standard deviations of the predicted values $\left[s(\hat{x}_i)\right]$.

5.1.4.3 Calculation

Calculate the significance of each of the response functions for each of the components using the following procedure (see reference [5] in the Bibliography).

Calculate the value of t (critical values of t are given in Table A.1 of annex A) for the first order regression $t(1)$, relating to b_i, as

$$t(1) = \sqrt{\frac{s_{SSR}^2(1)}{s_{MSE}(1)}} \tag{4}$$

The order of the regression, given in parentheses is as follows:

  (1) refers to data from the first order regression;

  (2) refers to data from the second order regression;

  (3) refers to data from the third order regression;

  (4) refers to data from the fourth order regression.

From the first and second order data, calculate $t(2)$, relating to c_i, as

$$t(2) = \sqrt{\frac{s_{SSR}^2(2) - s_{SSR}^2(1)}{s_{MSE}(2)}} \tag{5}$$

From the second and third order data, calculate $t(3)$, relating to d_i, as

$$t(3) = \sqrt{\frac{s_{SSR}^2(3) - s_{SSR}^2(2)}{s_{MSE}(3)}} \tag{6}$$