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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.

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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

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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.

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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

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)

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s_{SSE}^{2}	residual sum of squares (SSE)
s_{SSR}^{2}	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
$s(x_{\mathrm{c,WRC}})$	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 $R_{\mathrm{wr},i}$ and calibration line based on the single point method of the WRM only
t	reduced variable of the t-distribution
$x_{\mathrm{c,wrm}}$	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
$x_{\mathrm{L,wr}}$	lowest mole fraction in the working range
$x_{\mathrm{U,wr}}$	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

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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.

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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.

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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.

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

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

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

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

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

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

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

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

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

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

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In the acceptance of the instrument carry out a test for the determination of the third order data using a significance test between third and fourth order:

$$t(4) = \sqrt{\frac{s_{\mathrm{SSR}}^2(4) - s_{\mathrm{SSR}}^2(3)}{s_{\mathrm{MSE}}(4)}}$$

If the fourth order is significant, the system is unsuitable for the application.

NOTE The uncertainty of the relative response factor K, compared to the uncertainty of the reference component, is considered negligible. [See equations (13) and (15)](K_i compared to $R_{\mathrm{rrf},i}$).

5.1.4.4 Comparison

Compare each calculated value of t with the critical values (annex A) at its associated number of degrees of freedom. Calculate the number of degrees of freedom using the following equation:

$$\nu = n - (m + 1)$$

NOTE For example with seven CRMs each analysed 5 times, $n = 5 \times 7 = 35$, for $t(1)$ $\nu = 35 - (1 + 1) = 33$, for $t(2)$ $\nu = 35 - (2 + 1) = 32$, for $t(3)$ $\nu = 31$.

If the calculated value of t is less than the critical value (with the same ν), the coefficient is not significant (at a significance level of 95 %). If the calculated value of t is greater than the critical value, the coefficient is significant (at a significance level of 95 %).

Select the most appropriate order which includes an intercept term as follows:

- if $t(3)$ is significant, select the third order response function;
- if $t(3)$ is not significant and $t(2)$ is significant, select the second order response function;
- if $t(3)$ and $t(2)$ are not significant and $t(1)$ is significant, select the first order response function;
- if $t(3)$, $t(2)$ and $t(1)$ are not significant, do not continue with this procedure as there is no suitable relationship between the mole fraction and the response.

At this stage, consider the significance of the intercept term. From the selected response function, check the 95 % confidence interval of the intercept. If this interval includes zero, then the intercept can be set to zero and removed from the response function. Repeat the regression analysis for the selected order and for any lower orders. Use the same procedure as described above without the intercept ($a_i = 0$). The coefficients calculated by this process are identified as b_{0i}, c_{0i} and d_{0i}.

Calculate $t_0(1)$, relating to b_{0i}, with the appropriate $s_{\mathrm{SSR},0}^2$ (sum of squares due to zero intercept regression) and $s_{\mathrm{MSE},0}$ (residual mean square due to zero intercept), using the following equations:

$$t_0(1) = \sqrt{\frac{s_{\mathrm{SSR},0}^2(1)}{s_{\mathrm{MSE},0}(1)}} \qquad (7)$$

If a higher order response function has been selected with a zero intercept, then use the zero intercept data to calculate $t_0(2)$ [and $t_0(3)$]. Compare each calculated value of t with the critical values (annex A) at its associated number of degrees of freedom. The number of degrees of freedom is calculated as follows:

$$\nu = n - m$$

Select the most appropriate order with zero intercept term as follows:

- if $t_0(3)$ is significant, select the third order response function;
- if $t_0(3)$ is not significant and $t_0(2)$ is significant, select the second order response function;

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— if $t_0(3)$ and $t_0(2)$ are not significant and $t_0(1)$ is significant, select the first order response function;

— if $t_0(3)$, $t_0(2)$ and $t_0(1)$ are not significant, do not continue with this procedure as there is no suitable relationship between the mole fraction and the response.

5.2 Step 2: Selection of the response functions to be used in practice

5.2.1 General remarks

The response functions selected in step 1 (see 5.1) are the optimal relationships between mole fraction and response. However, it may be necessary to select another response function when the computer program of the gas chromatograph is not capable of handling third order functions or functions with an intercept. In this case, a first order equation without an intercept has to be used. This approach is usually called the single point calibration method. When there is a difference between the optimal function and the first order equation without an intercept function, it is obvious that additional uncertainty may be introduced.

The two methods, namely method A using the optimal function and method B using single point calibration, are different in terms of calculation of the uncertainty and in the way calibrations are dealt with by the gas chromatograph. Annex B describes how data from a typical test result are handled using method A and method B.

5.2.2 Method A

Calculate the desired response functions using CRMs and the coefficients of the response functions. The routine calibration, using a WRM, updates the response function coefficients. Possible additional uncertainty (resulting from other response functions than the optimal ones) shall be taken into account in the standard calculations. It is sufficient to calculate the response functions which are needed in practice.

5.2.3 Method B

5.2.3.1 General assumptions

Calibrate the gas chromatograph using a WRM. This implies the use of a linear calibration (first order regression) without an intercept. This procedure does not update a calibration based on CRMs but stands on its own; an additional calculation step is needed to take into account the possible additional uncertainty ($s_{\text{wrm},i}$).

For this calculation the following assumptions are made:

— the optimal response functions have already been calculated using step 1 (see 5.1);

— the mole fractions of the components in the WRM are within the working range of the components in the process gas (centre of the range, if possible);

— the response on the WRM is known ($R_{\text{wrm},i}$);

— the working ranges of the components in the process gas are within the application range of the respective part of ISO 6974;

— the mole fractions of the components in the process gas have a more or less normal distribution with the mole fraction of the WRM as the average.

5.2.3.2 Calculations

Calculate the derivative of the optimal response functions towards the response of the gas chromatograph (R_i) as follows:

a) optimal response function determined by method A is:

$$x_i = a_i + b_i R_i + c_i R_i^2 + d_i R_i^3$$

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b) using single point calibration, differentiate the optimal response function using the following equation:

$$x_i' = b_i + 2c_iR_i + 3d_iR_i^2$$

c) calculate x_i' at $R_{\mathrm{wrm},i}$ (average of two analyses at least) using the following equation:

$$x_i'(\mathrm{wrm}) = b_i + 2c_iR_{\mathrm{wrm},i} + 3d_iR_{\mathrm{wrm},i}^2$$

d) calculate the response factor based on the WRM using the following equation:

$$R_{\mathrm{f,wrm},i} = \frac{x_{\mathrm{wrm},i}}{R_{\mathrm{wrm},i}} \tag{8}$$

e) calculate T_i by subtracting $R_{\mathrm{f,wrm},i}$ from $x_i'(\mathrm{wrm})$ using the following equation:

$$T_i = x_i'(\mathrm{wrm}) - R_{\mathrm{f,wrm},i} \tag{9}$$

NOTE T_i is the difference in the slope between the tangent of the optimal response function in $R_{\mathrm{wrm},i}$ and calibration line based on the single point method of the WRM only. The working ranges of the components in the process gas should be known so as to calculate the extra uncertainty. Divide the working ranges by 4 to calculate the component standard deviations, as follows:

$$s_{\mathrm{wr},i} = \frac{x_{\mathrm{U,wr},i} - x_{\mathrm{L,wr},i}}{4} \tag{10}$$

Moreover multiply $s_{\mathrm{wr},i}$ by T_i to calculate the standard deviation caused by using the WRM calibration line conforming with method B as follows:

$$s_{\mathrm{B},i} = T_i \cdot s_{\mathrm{wr},i} \tag{11}$$

NOTE $s_{\mathrm{B},i}$ is used in the calculation of the component mole fraction uncertainties in step 5 (see 5.5).

Caution — When step 1 consists only of replicates of one CRM at mole fraction levels (nearly) similar to those of the sample to be analysed, then the optimal response functions (step 1) are not really known and the extra calculations for method B cannot be carried out ($s_{\mathrm{B},i} = 0$, by definition). In this case, no estimate can be made using a (possible) calibration line conforming to method B and there is a risk of making systematic errors without knowing. This risk shall, in this case, be decreased by limiting the deviation between the composition of the calibration gas and the composition of the sample as shown in Table 1. In step 5, $s_{\mathrm{B},i}$ is then zero.

Table 1 — Allowed tolerances

Sample component mole fraction %	**Calibration gas mixture** deviation of component mole fraction % relative to sample mole fraction
0,001 to 0,1	± 100
0,1 to 1	± 50
1 to 10	± 10
10 to 50	± 5
50 to 100	± 3

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5.3 Step 3: Routine calibration with a working-reference gas mixture

Carry out routine calibration (daily, weekly, etc.) of the gas chromatograph normally using a working-reference gas mixture (WRM). The composition of the WRM shall be within the working range of each component and shall contain all the direct components. It is recommended to perform the calibration with the WRM at least in duplicate.

5.4 Step 4: Calculation of non-normalized component mole fractions

5.4.1 Method A

Calculate the non-normalized mole fraction of the direct components in the sample as follows:

$$x^*_{\mathrm{mc},i} = \frac{x_{\mathrm{c,wrm},i}}{\hat{x}_{\mathrm{wrm},i}} \times \hat{x}_{\mathrm{mc},i} \qquad (12)$$

Calculate the non-normalized mole fraction of the indirect components in the sample as follows:

$$x^*_{\mathrm{rrf},i} = K_i \times \frac{R_{\mathrm{rrf},i}}{R_{\mathrm{mc,ref}}} \times x^*_{\mathrm{mc,ref}} = K_i \times \frac{R_{\mathrm{rrf},i}}{R_{\mathrm{mc,ref}}} \times \frac{x_{\mathrm{c,wrm,ref}}}{\hat{x}_{\mathrm{wrm,ref}}} \times \hat{x}_{\mathrm{mc,ref}} \qquad (13)$$

NOTE Relative response factors, K, for TCD and FID detectors are given for information in annex C.

5.4.2 Method B

Calculate the non-normalized mole fraction of the direct components in the sample as follows:

$$x^*_{\mathrm{mc},i} = \frac{x_{\mathrm{c,wrm},i}}{R_{\mathrm{wrm},i}} \times R_{\mathrm{mc},i} \qquad (14)$$

Calculate the non-normalized mole fraction of the indirect components in the sample as follows:

$$x^*_{\mathrm{rrf},i} = K_i \times \frac{R_{\mathrm{rrf},i}}{R_{\mathrm{mc,ref}}} \times x^*_{\mathrm{mc,ref}} = K_i \times \frac{x_{\mathrm{c,wrm,ref}}}{R_{\mathrm{wrm,ref}}} \times R_{\mathrm{rrf},i} \qquad (15)$$

NOTE Relative response factors, K, for TCD and FID detectors are given for information in annex C.

5.5 Step 5: Calculation of non-normalized component standard deviations

5.5.1 General

Calculate the standard deviation of the component mole fraction for each of the direct and indirect components.

5.5.2 Direct components

5.5.2.1 Standard deviation

Calculate the standard deviation of the non-normalized mole fraction of the direct components in the sample by differentiating equation (12) or (14). This method is the standard method for error propagation. Detailed information about this method can be found in literature on this subject (see reference [5] in the Bibliography).

NOTE In equation (12) there are three sources of error for the non-normalized mole fraction of the direct component (x^*_{mc}). Normally, for two of these three sources of error, the contribution of uncertainty to the measurement of the mole fraction of a component in the sample is calculated. It is assumed that the contribution of the uncertainty to the mole fraction measurement of the components in the WRM [$s(x_{\mathrm{wrm}})$] is negligible. If this contribution is not negligible (for example, if the mole fractions in the WRM are based on analysis instead of gravimetrical preparation), then equations (17) or (19) should preferably be used to calculate this uncertainty.

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5.5.2.2 Uncertainty determination for method A

Calculate the uncertainty based on the standard method for error propagation of the non-normalized direct components as follows:

$$s(\overset{*}{x}_{\mathrm{mc},i}) = \overset{*}{x}_{\mathrm{mc},i} \times \sqrt{\left[\frac{s(\hat{x}_{\mathrm{mc},i})}{\hat{x}_{\mathrm{mc},i}}\right]^2 + \left[\frac{s(\hat{x}_{\mathrm{wrm},i})}{\hat{x}_{\mathrm{wrm},i}}\right]^2} \qquad (16)$$

In equation (16) various values determined during the regression (step 1 or step 2) and during the calibration with the CRM (step 3) are necessary. Calculate the uncertainty based on the mole fractions of the components in the WRM using the following equation:

$$s(\overset{*}{x}_{\mathrm{mc},i}) = \overset{*}{x}_{\mathrm{mc},i} \times \sqrt{\left[\frac{s(\overset{*}{x}_{\mathrm{mc},i})}{\overset{*}{x}_{\mathrm{mc},i}}\right]^2 + \left[\frac{s(x_{\mathrm{c,wrm},i})}{x_{\mathrm{c,wrm},i}}\right]^2} \qquad (17)$$

5.5.2.3 Uncertainty determination for method B

Calculate the uncertainty based on the standard method for error propagation of the non-normalized direct components as follows:

$$s(\overset{*}{x}_{\mathrm{mc},i}) = \sqrt{\frac{s_{\mathrm{MSE},i} \times (h_{\mathrm{wrm}} + h_{\mathrm{S}})}{h_{\mathrm{wrm}} \times h_{\mathrm{S}}}} \qquad (18)$$

The s_{MSE} value, used in equation (18), is derived from step 1, and is used as an overall approximation of the measurement error. The number of replicates of the sample (h_{S}) is, for example in the case of a laboratory gas chromatograph, two or three and in case of a field gas chromatograph, one (by definition). Calculate the uncertainty based on the mole fractions of the components in the WRM using the following equation:

$$s(\overset{*}{x}_{\mathrm{mc},i}) = \overset{*}{x}_{\mathrm{mc},i} \times \sqrt{\left[\frac{s(\overset{*}{x}_{\mathrm{mc},i})}{\overset{*}{x}_{\mathrm{mc},i}}\right]^2 + \left[\frac{s(x_{\mathrm{c,wrm},i})}{x_{\mathrm{c,wrm},i}}\right]^2} \qquad (19)$$

Calculate the uncertainty introduced by using a single point calibration method using the following equation:

$$s(\overset{*}{x}_{\mathrm{mc},i}) = \sqrt{s(\overset{*}{x}_{\mathrm{mc},i})^2 + s_{\mathrm{B},i}^2} \qquad (20)$$

5.5.3 Indirect components

5.5.3.1 General

The calculation of the mole fractions of the indirect components involves the use of a reference component (or bridge component). As can be seen in equation (13) or (15), this involves the use of extra sources of error in the calculation.

5.5.3.2 Method A

For method A, account the uncertainty for the sources of error of the indirect components in the sample as follows:

$$s(\overset{*}{x}_{\mathrm{rrf},i}) = \overset{*}{x}_{\mathrm{rrf},i} \times \sqrt{\left[\frac{s(\hat{x}_{\mathrm{mc,ref}})}{\hat{x}_{\mathrm{mc,ref}}}\right]^2 + \left[\frac{s(\hat{x}_{\mathrm{WRM,ref}})}{\hat{x}_{\mathrm{WRM,ref}}}\right]^2 + \left[\frac{s(R_{\mathrm{rrf},i})}{R_{\mathrm{rrf},i}}\right]^2 + \left[\frac{s(R_{\mathrm{mc,ref}})}{R_{\mathrm{mc,ref}}}\right]^2} \qquad (21)$$

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Take into account the additional uncertainty based on the mole fractions of the components in the WRM as follows:

$$s(x^*_{\mathrm{rrf},i}) = x^*_{\mathrm{rrf},i} \times \sqrt{\left[\frac{s(x^*_{\mathrm{rrf},i})}{x^*_{\mathrm{rrf},i}}\right]^2 + \left[\frac{s(x_{\mathrm{c,wrm},i})}{x_{\mathrm{c,wrm},i}}\right]^2} \qquad (22)$$

5.5.3.3 Method B

For method B, account the uncertainty for the sources of error in the mole fractions of the indirect components in the sample as follows:

$$s(x^*_{\mathrm{rrf},i}) = \sqrt{\frac{s_{\mathrm{MSE,ref}} \times (h_{\mathrm{wrm}} + h_{\mathrm{s}})}{h_{\mathrm{wrm}} \times h_{\mathrm{s}}}} \qquad (23)$$

Derive the s_{MSE} value, used in equation (23), from step 1, and use this as an overall approximation of the measurement error. The number of replicates of the sample (h_{s}) is, for example in the case of a laboratory gas chromatograph, two or three and in case of a field gas chromatograph, one (by definition).

Take into account the additional uncertainty based on the mole fractions of the components in the WRM as follows:

$$s(x^*_{\mathrm{rrf},i}) = x^*_{\mathrm{rrf},i} \times \sqrt{\left[\frac{s(x^*_{\mathrm{rrf},i})}{x^*_{\mathrm{rrf},i}}\right]^2 + \left[\frac{s(x_{\mathrm{c,wrm},i})}{x_{\mathrm{c,wrm},i}}\right]^2} \qquad (24)$$

Take into account the uncertainty introduced by using a single point calibration method as follows:

$$s(x^*_{\mathrm{rrf},i}) = \sqrt{s(x^*_{\mathrm{rrf},i})^2 + s^2_{\mathrm{B,ref}}} \qquad (25)$$

5.6 Step 6: Calculation of normalized component mole fractions

In the calculation of the normalized mole fractions, the mole fractions of the “other components” (with a fixed mole fraction) are also needed. It is assumed that the total amount of these components in the sample is small compared to the rest of the (direct and indirect) components.

Normalization of the results is allowed if the sum of the mole fractions of the non-normalized component mole fractions is no less than 0,98 or greater than 1,02. Calculate the fraction of the normalized components using the following equation:

$$x_i = \frac{x_i^*}{\sum\limits_{w=1}^{q} x_w^*} \times (1 - x_{\mathrm{oc}}) \qquad (26)$$

5.7 Step 7: Calculation of normalized component standard deviations

Calculate the normalized component standard deviations of the normalized components using the following equations.

$$s(x_i) = x_i \times \sqrt{\frac{1 - 2x_i^*}{x_i^{*2}} \times s(x_i^*)^2 + \sum_{w=1}^{q} s(x_w^*)^2} \qquad (27)$$

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At the right side of equation (27), the sum of all the squared standard deviations (variances) of the non-normalized component mole fractions (direct + indirect components) is calculated. Equation (27) is an approximation and is based on the assumption that the sum of the non-normalized mole fractions is close to 1.

NOTE The (summed) mole fraction of the other components (x_{oc}) is, in most cases, very small when compared to the rest of the components. Therefore the standard deviation of the other components (x_{oc}) is not taken into account in the calculation of the standard deviation of the normalized components. This would make the calculations much more complicated without having any significant impact on the end result.

5.8 Step 8: Calculation of uncertainty and repeatability of the results

5.8.1 Absolute uncertainty

Approximate the absolute uncertainty, $U_{\text{abs}}(x_i)$, of the normalized components using the following equations.

$$U_{\text{abs}}(x_i) = t \times s(x_i) \tag{28}$$

t can be obtained from the Table A.1 in annex A. The number of degrees of freedom of this t is derived from step 1 [$n - (m + 1)$ in case of a response function with intercept, and $n - m$ in case of a response function without intercept].

5.8.2 Relative uncertainty

Calculate the relative uncertainty $U_{\text{rel}}(x_i)$, expressed as a percentage, of the normalized components using the following equation:

$$U_{\text{rel}}(x_i) = \frac{U_{\text{abs}}(x_i)}{x_i} \times 100 \tag{29}$$

5.9 Relationship between ISO 6974-2 and ISO 6976

5.9.1 General

In ISO 6976, data are needed to calculate the listed physical properties and their repeatability. In this subclause, a link is established between the output of this part of ISO 6974 and ISO 6976.

5.9.2 Non-normalized mole fraction

Calculate the repeatability of the standard deviations of the non-normalized components mole fractions as follows:

$$r_i^* = 2\sqrt{2} \times s(x_i^*)$$

where

$$\Delta x_i^* = r_i^*$$

5.9.3 Normalized mole fraction

Calculate the repeatability of the normalized components mole fractions as follows:

$$r_i = 2\sqrt{2} \times s(x_i)$$

where

x_i is the normalized mole fraction

$$\Delta x_i = r_i$$

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Annex A
(informative)

Critical values of *t*

The critical values of *t* are given for confidence levels of 95 % and 99 % in Table A.1.

Table A.1 — Critical values of *t*

Degrees of freedom	**Confidence level**	
	95 %	99 %
1	12,7	63,7
2	4,30	9,92
3	3,18	5,84
4	2,78	4,60
5	2,57	4,03
6	2,45	3,71
7	2,36	3,50
8	2,31	3,36
9	2,26	3,25
10	2,23	3,17
11	2,20	3,11
12	2,18	3,05
13	2,16	3,01
14	2,14	2,98
15	2,13	2,95
16	2,12	2,92
17	2,11	2,90
18	2,10	2,88
19	2,09	2,86
20	2,09	2,85
∞	1,96	2,58

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Annex B
(informative)

Example

This annex gives, as an example, an overview of experimental results obtained with a gas chromatograph. Data from analyses are presented in Table B.1 and treatment of the results following the steps outlined in clause 5 are presented in Tables B.2 to B.10.

Table B.1 — Raw data from analyses using certified reference gas mixtures (CRM) (triplicate analysis)

	Methane, CRM						
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	65,146	85,776	75,602	88,766	79,758	70,301	95,203
Responses	165 798,87	214 424,77	190 392,92	221 549,75	200 286,27	177 903,69	236 194,26
	165 979,54	214 555,59	190 208,11	221 426,74	200 304,79	177 911,01	236 139,76
	165 981,30	214 285,16	190 246,59	221 133,67	200 070,49	177 783,43	236 314,58
	Ethane, CRM						
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	5,702	3,439	10,894	0,595	8,374	7,380	1,451
Responses	23 570,03	14 283,97	44 673,11	2 502,28	34 442,71	30 387,47	6 044,86
	23 585,87	14 295,91	44 659,86	2 496,92	34 428,37	30 389,68	6 044,94
	23 590,53	14 275,36	44 625,63	2 494,49	34 403,68	30 378,11	6 048,77
	Propane, CRM						
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	3,927	3,422	0,081	2,291	0,820	2,872	0,899
Responses	20 659,79	18 044,84	439,66	12 152,91	4 269,36	15 084,82	4 791,53
	20 668,98	18 064,06	434,65	12 154,09	4 267,50	15 133,59	4 795,68
	20 680,61	18 041,95	434,00	12 132,08	4 266,81	15 081,18	4 828,73
	2-Methylpropane, CRM						
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	0,033	0,144	0,230	0,366	0,472	0,592	0,558
Responses	212,41	923,47	1 460,75	2 304,16	2 958,62	3 681,85	3 515,96
	214,33	925,21	1 454,15	2 321,25	2 944,19	3 665,56	3 519,30
	214,28	924,62	1 455,57	2 294,51	2 940,71	3 680,96	3 521,76

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Table B.1 *(continued)*

***n*-Butane, CRM**							
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	0,030	0,143	0,235	0,348	0,460	0,685	0,621
Responses	198,80	873,20	1 460,75	2 187,50	2 842,89	4 298,82	3 826,17
	202,53	874,69	1 453,74	2 160,36	2 876,33	4 273,51	3 828,50
	202,37	872,91	1 456,10	2 181,44	2 872,86	4 298,56	3 828,75
Nitrogen, CRM							
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	17,605	2,481	12,733	5,751	4,326	8,852	0,301
Responses	53 439,93	7 757,14	38 806,68	17 839,91	13 432,12	27 199,58	993,44
	53 471,20	7 760,39	38 767,16	17 831,05	13 425,94	27 231,83	992,75
	53 475,91	7 756,20	38 780,51	17 819,08	13 417,57	27 219,39	994,79
Carbon dioxide, CRM							
	Gas 1	**Gas 2**	**Gas 3**	**Gas 4**	**Gas 5**	**Gas 6**	**Gas 7**
Mole fraction (%)	7,558	4,595	0,225	1,883	5,791	9,317	0,967
Responses	27 318,70	16 645,62	836,95	6 837,86	20 938,43	33 587,92	3 515,53
	27 337,69	16 658,36	834,69	6 834,00	20 939,91	33 598,91	3 513,75
	27 348,80	16 634,59	835,18	6 829,18	20 919,43	33 586,73	3 516,45
Working-reference gas mixture (duplicate analyses)							
Component	**N_2**	**CO_2**	**CH_4**	**C_2H_6**	**C_3H_8**	***iso*-C_4H_{10}**	***n*-C_4H_{10}**
Mole fraction (%)	13,703	1,049	82,568	2,099	0,431	0,068	0,082
Responses	41 139,33	3 814,33	205 395,02	12 101,09	2 276,10	440,22	513,29
	41 139,42	3 814,36	205 395,22	12 101,14	2 276,13	440,24	513,31
Sample (duplicate analysis)							
Component	**N_2**	**CO_2**	**CH_4**	**C_2H_6**	**C_3H_8**	***iso*-C_4H_{10}**	***n*-C_4H_{10}**
Responses	40 831,46	3 808,56	205 856,65	11 975,91	2 285,85	426,39	529,00
	40 823,92	3 807,52	205 934,98	11 977,43	2 286,06	426,93	529,01
Component	***neo*-C_5H_{12}**	***iso*-C_5H_{12}**	***n*-C_5H_{12}**	**C_{6+}**			
Responses	54,74	144,81	140,46	553,32			
	54,43	144,87	140,31	557,18			

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Step 1: Regression analysis (see 5.1.4)

The response function for carbon dioxide has been selected as the example for calculations. Calculations for the other components can be made in a similar way.

A computer program has been used to fit the first, second and third order response functions (including the intercept). The results of these fits are given in Table B.2 (mole fractions have been divided by 100 to be expressed as a percentage).

Table B.2 — Fits to response function

Order	s_{SSR}^2	s_{MSE}
First	0,021 492 884	$7{,}228\,87 \times 10^{-9}$
Second	0,021 492 970	$2{,}849\,30 \times 10^{-9}$
Third	0,021 492 985	$2{,}181\,36 \times 10^{-9}$

Step 2: Selection of the response function (see 5.1.4)

The t value calculated for each order of polynomial function is given in Table B.3.

Table B.3 — Criteria for choice of the response function

Order	calculated t value	ν	critical t value
First	1 724,297	19	2,09
Second	5,494	18	2,10
Third	2,622	17	2,11

Conclusion: The third order term is significant ($t(3)$ > critical t value), the most appropriate model at this stage is the third order response function.

Verification of the correct function chosen

Test of the intercept of the third order response function:

Intercept = $-7{,}541 \times 10^{-5} \pm 6{,}343 \times 10^{-5}$

95 % confidence interval = $-1{,}388 \times 10^{-4} \leqslant -7{,}541 \times 10^{-5} \leqslant -1{,}198 \times 10^{-5}$

The 95 % confidence interval does not include zero. Therefore, the intercept is significant.

Conclusion: For carbon dioxide, the third order model with intercept is selected.

The optimal response function for each of the other components is calculated for the other components in the CRMs.

Table B.4 — The optimal response functions for the other components in the CRMs

Component	Order	Intercept?	a_i	b_i	c_i	d_i
Methane	3	yes	$-4{,}126 \times 10^{-1}$	$9{,}745 \times 10^{-6}$	$-2{,}783 \times 10^{-11}$	$4{,}670 \times 10^{-17}$
Ethane	3	no	—	$2{,}382 \times 10^{-6}$	$1{,}968 \times 10^{-12}$	$-1{,}512 \times 10^{-17}$
Propane	1	no	—	$1{,}897 \times 10^{-6}$	—	—
iso-Butane	1	yes	$-3{,}337 \times 10^{-5}$	$1{,}607 \times 10^{-6}$	—	—
n-Butane	1	no	—	$1{,}607 \times 10^{-6}$	—	—
Nitrogen	3	no	—	$3{,}155 \times 10^{-6}$	$4{,}919 \times 10^{-12}$	$-4{,}377 \times 10^{-17}$
Carbon dioxide	3	yes	$-7{,}541 \times 10^{-5}$	$2{,}775 \times 10^{-6}$	$-1{,}063 \times 10^{-12}$	$3{,}201 \times 10^{-17}$

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The relative response factor (K) used for the back-flush measured C_{6+} component is estimated to be 0,59 in this example.

Method A: The response functions used will be the same as the optimal response functions calculated in step 1. In practice, when method A is followed and other response functions are used, the desired response functions have to be fitted to the CRM data. The rest of procedure of method A is exactly the same, independent of the type of response functions used in practice.

No extra calculations are needed, the relevant information is obtained from step 1.

Method B: The response function used will be first order without the intercept, and the extra uncertainty due to using a “non-optimal” response function will be calculated.

Example: Calculation of carbon dioxide

— Optimal response function determined using method A:

$$x_{CO_2} = -7{,}541 \times 10^{-5} + 2{,}775 \times 10^{-6} R_{CO_2} - 1{,}063 \times 10^{-12} R_{CO_2}^2 + 3{,}201 \times 10^{-17} R_{CO_2}^3$$

— Using single point calibration (method B), differentiate the optimal response function as follows:

$$x'_{CO_2} = 2{,}775 \times 10^{-6} - 2{,}126 \times 10^{-12} R_{CO_2} + 9{,}603 \times 10^{-17} R_{CO_2}^2$$

— Response of the WRM for carbon dioxide: $R_{CO_2} = 3\,814{,}345$ (average of the two analyses). Thus:

$$x'_{CO_2} = 2{,}775 \times 10^{-6} - 2{,}126 \times 10^{-12} \times 3\,814{,}345 + 9{,}603 \times 10^{-17} \times (3\,814{,}345)^2 = 2{,}768\,3 \times 10^{-6}$$

— Response factor based on the WRM: $R_{f,wr,CO_2} = 0{,}010\,49/3814{,}345 = 2{,}750\,1 \times 10^{-6}$

$$T_{CO_2} = x'_{wr,CO_2}(\mathrm{wr}) - R_{f,wr,CO_2} = 2{,}768\,3 \times 10^{-6} - 2{,}750\,1 \times 10^{-6} = 1{,}820\,0 \times 10^{-8}$$

— The working range for carbon dioxide is for example (at a certain location where this particular gas chromatograph is located):

$x_{L,wr,CO_2} = 0{,}005$ mole fraction

$x_{U,wr,CO_2} = 0{,}020$ mole fraction

Thus $s_{wr,CO_2} = (x_{U,wr,CO_2} - x_{L,wr,CO_2}) / 4 = (0{,}020 - 0{,}005) / 4 = 0{,}003\,75$ mole fraction

— The extra standard deviation (using method B) is therefore:

$s_{wrm,CO_2} = T_{CO_2} \times s_{wr,CO_2} = 1{,}820\,0 \times 10^{-8} * 0{,}003\,75 = 6{,}825 \times 10^{-11}$ mole fraction

— For the other components in the CRM see Table B.5

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Table B.5 — Calculation for other components in the CRM

Component	T_i	$x_{\text{L,wr},i}$ mole fraction	$x_{\text{U,wr},i}$ mole fraction	$s_{\text{B},i}$ mole fraction
Methane	$1{,}979\,0 \times 10^{-6}$	0,80	0,84	$1{,}979\,0 \times 10^{-8}$
Ethane	$6{,}690\,5 \times 10^{-7}$	0,01	0,03	$3{,}345\,3 \times 10^{-9}$
Propane	$3{,}420\,0 \times 10^{-9}$	0,002	0,006	$3{,}420\,0 \times 10^{-12}$
iso-Butane	$6{,}235\,0 \times 10^{-8}$	0,000 5	0,000 6	$6{,}235\,0 \times 10^{-12}$
n-Butane	$9{,}490\,0 \times 10^{-9}$	0,000 6	0,001	$9{,}490\,0 \times 10^{-13}$
Nitrogen	$-4{,}761\,4 \times 10^{-8}$	0,12	0,14	$-2{,}380\,7 \times 10^{-10}$
Carbon dioxide	$1{,}820\,0 \times 10^{-8}$	0,005	0,02	$6{,}825\,0 \times 10^{-11}$

NOTE The standard deviations given in this table are to be used in step 5.

Step 3: (see 5.3)

Two analyses have been performed using the WRM.

Step 4: (see 5.4)

For the calculation of the non-normalized mole fractions, the average value of the responses of the components in the sample and the WRM have been taken for the rest of the calculations.

Method A

Direct component (CO_2):

$\hat{x}_{\text{mc,CO}_2}$ = $1{,}047\,8 \times 10^{-2}$ mole fraction

$x^{*}_{\text{mc,CO}_2}$ = $0{,}010\,49 / 0{,}010\,495 \times 1{,}047\,8 \times 10^{-2}$ = 0,010 473 mole fraction or 1,0473 % (mole fraction expressed as a percentage)

Indirect component (*neo*-C_5H_{12}, C_3 as reference):

$\hat{x}_{\text{mc,C}_3\text{H}_8}$ = $1{,}871\,9 \times 10^{-5}$ % (mole fraction expressed as a percentage)

$x^{*}_{\text{rrf},neo\text{-C}_5\text{H}_{12}}$ = 0,007 753 % (mole fraction expressed as a percentage)

Method B

Direct component (CO_2):

$x^{*}_{\text{mc,CO}_2}$ = $1{,}047\,27 \times 10^{-2}$ mole fraction or 1,047 3 % (mole fraction expressed as a percentage)

Indirect component (*neo*-C_5H_{12}, C_3 as reference):

$x^{*}_{\text{rrf},neo\text{-C}_5\text{H}_{12}}$ = $7{,}752\,1 \times 10^{-5}$ mole fraction or 0,007 752 % (mole fraction expressed as a percentage)

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