INTERNATIONAL STANDARD

ISO 6974-2

Second edition
2012-05-15

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

Part 2:
Uncertainty calculations

Gaz naturel — Détermination de la composition et de l'incertitude associée par chromatographie en phase gazeuse — Partie 2: Calculs d'incertitude

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 6974-2 was prepared by Technical Committee ISO/TC 193, *Natural Gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition of ISO 6974-2, together with ISO 6974-1:2012, cancels and replaces ISO 6974-1:2000 and ISO 6974-2:2001, which have been technically revised.

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

- *Part 1: General guidelines and calculation of composition*
- *Part 2: Uncertainty calculations*
- *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* C_1 *to* C_8 *hydrocarbons using three capillary columns*

Future subsequent parts of ISO 6974 are planned.

Introduction

ISO 6974 describes methods of analysis of natural gas and methods for calculating component mole fractions and uncertainties. ISO 6974 (all parts) is intended for the measurement of H_2, He, O_2, N_2, CO_2 and hydrocarbons, either as individual components or as a group, for example all hydrocarbons above C_5, defined as C_{6+}. This approach is suitable for a range of end applications, including calibrating gas mixtures and providing natural gas composition and uncertainty data to be used in the calculation of calorific value and other additive physical properties of the gas. Details of these end applications are provided in ISO 6974-3 and subsequent parts of ISO 6974.

ISO 6974-1 gives guidelines for calculating the mole composition of natural gas, determined using one of the gas chromatographic methods described in ISO 6974-3 and subsequent parts of ISO 6974. ISO 6974-1 also describes all the essential steps for setting up an analysis, including outlining the structure of the analysis, defining the working ranges and establishing the analytical procedure.

This part of ISO 6974 describes the steps required to calculate the uncertainty of the component mole fractions of natural gas determined using gas chromatography.

ISO 6974-3 and subsequent parts of ISO 6974 describe different gas chromatographic methods. These methods cover both daily practice in the laboratory and on-line field applications. ISO 6974-1:2012, Annex A, provides a comparison of the characteristics of the analytical methods described in ISO 6974-3 and subsequent parts of ISO 6974.

It is intended that this part of ISO 6974 be used in conjunction with ISO 6974-1 and a method of analysis, e.g. ISO 6974-3 or subsequent parts of ISO 6974.

ISO 6974-1:2012, 5.5, describes the conventional normalization approach for calculating processed mole fractions from raw mole fractions. When conventional normalization is used for multiple operation methods without bridging, the uncertainties of the calculated mole fractions will be conservative. If a more accurate assessment of uncertainty is required, an alternative approach to normalization, using the generalized least squares (GLS) method, can be used; this is described in ISO 6974-1:2012, Annex B. Further alternative approaches are available for calculating processed mole fractions, including methane-by-difference (see ISO 6974-1:2012, Annex C) and data harmonization (see Reference [1]).

INTERNATIONAL STANDARD **ISO 6974-2:2012(E)**

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

Part 2:
Uncertainty calculations

1 Scope

This part of ISO 6974 describes the process required to determine the uncertainty associated with the mole fraction for each component from a natural gas analysis in accordance with ISO 6974-1.

2 Normative references

The following referenced documents are indispensable for the application 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 6974-1:2012, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6974-1 apply.

4 Symbols

4.1 Symbols

b_z	parameters of the regression function ($z = 0$, 1, 2 or 3)
$\bar{b}_z$	mean parameters of the regression function (in “mean normalization” method)
C_i	sensitivity coefficient
k	coverage factor
K	relative response factor with respect to the reference component
n_i	total number of components (direct plus indirect, but excluding “other components”)
n_j	total number of gas standards or mixtures
n_l	total number of injections (and therefore total number of responses)
s	standard deviation
T	total mole fraction of all raw components

$u(\ldots)$	standard uncertainty (of the quantity in parentheses)
$U(\ldots)$	expanded uncertainty (of the quantity in parentheses)
x	normalized mole fraction
x^*	raw mole fraction
x'	mole fraction calculated using the methane-by-difference approach [Annex A]
$\hat{x}$	adjusted mole fraction [Annex C]
y	instrumental response of the specified analyte
$\bar{y}$	mean instrumental response (in “mean normalization” method)
$\hat{y}$	adjusted instrumental response [Annex C]
Y	instrumental response [Annex C]
α	intercept of a first-order calibration function [Annex C]
β	gradient of a first-order calibration function [Annex C]
γ	gradient of the calibration curve [Annex C]
$\bar{\delta}$	mean of the distribution of non-linearity errors

4.2 Subscripts

cal	calibration [Annex A]
i	component
ind	components or groups of components to be analysed by indirect measurement
j	gas standard/mixture
l	injection
oc	other components
p, q	indices defining a regression coefficient
ref	reference (component or pressure)
s	index defining a component
wms	working measurement standard

5 Calculation of uncertainty

5.1 General considerations

The process of setting up a gas chromatograph for the analysis of natural gas consists of the steps outlined in the flowcharts in Figures 1 and 2.

Steps 1 to 8 are covered in ISO 6974-1. This part of ISO 6974 covers steps 9 and 10.

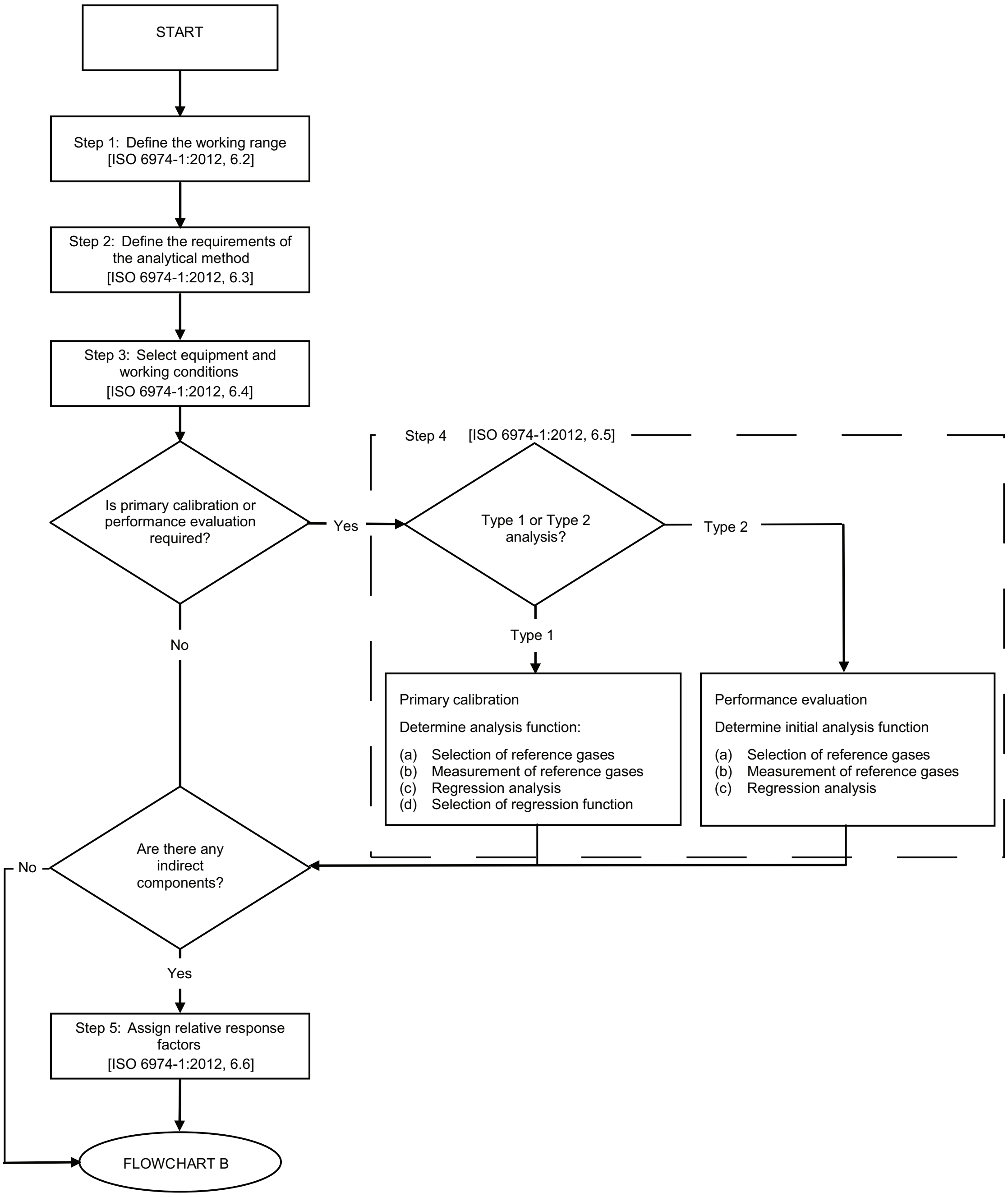

Figure 1 — Procedure for determining mole fraction and uncertainty — Steps 1 to 5

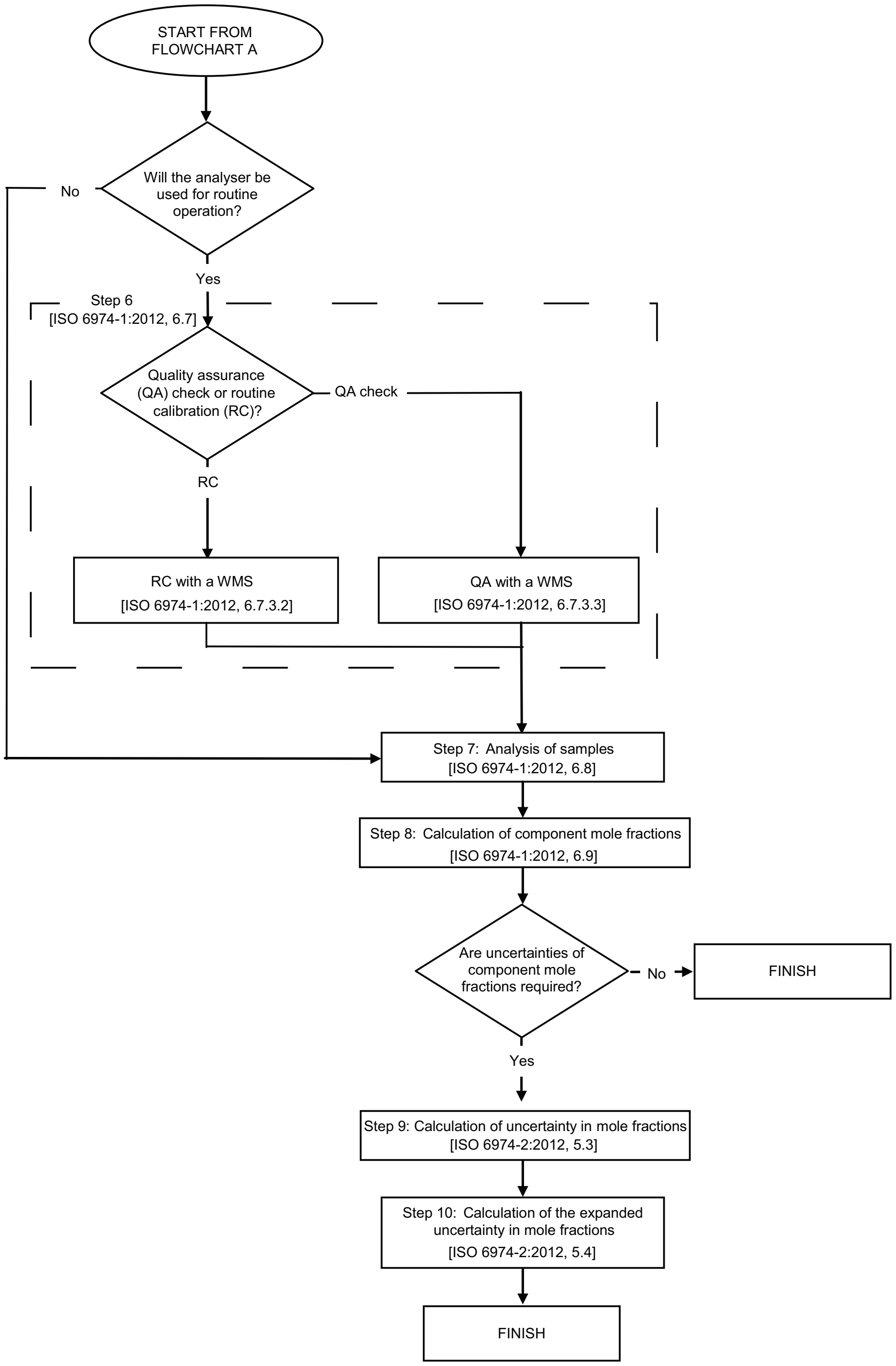

Figure 2 — Procedure for determining mole fraction and uncertainty — Steps 6 to 10

5.2 Principles

Uncertainties associated with the component mole fractions shall be calculated in accordance with ISO/IEC Guide 98-3.

For Type 1 analyses in accordance with ISO 6974-1, the uncertainty calculation includes random and systematic uncertainties from three main sources: uncertainty of the certified reference mixtures, uncertainty of analysis and uncertainty of the data fitting procedure.

For Type 2 analyses in accordance with ISO 6974-1, the uncertainty calculation includes both random elements and systematic errors introduced by the assumption of a linear response through the origin, the systematic errors being calculated from the results of the initial performance evaluation.

Subclause 5.3 describes methods for estimating the uncertainties of processed mole fractions calculated from raw mole fractions using the conventional normalization method. Annex A provides a method for use when the methane-by-difference approach (see ISO 6974-1:2012, Annex C) is employed.

ISO 6974-1 recommends the use of the generalized least squares (GLS) approach for calculation of the processed mole fraction. However, in some circumstances, an alternative approach using ordinary least squares may be acceptable and calculation of uncertainty in processed mole fractions in this situation is described in Annex C.

5.3 Step 9 — Calculation of uncertainty of mole fractions

5.3.1 Determining the equations to be used

5.3.1.1 General considerations

The equations to be used in this step for calculating the uncertainty of mole fractions are given in 5.3.2 and 5.3.3. The equations to be used should be determined by following the three-stage process described in 5.3.1.2 to 5.3.1.4.

The following points should be taken into consideration when selecting the equations to be used.

a) When using the “mean normalization” method (see 5.3.2), the following are calculated in turn for each analyte:
    1) mean peak analyser response from all runs;
    2) raw mole fraction;
    3) normalized mole fraction.
b) When using the “run-by-run normalization” method (see 5.3.3), the following are calculated in turn for each analyte:
    1) raw mole fraction for each run;
    2) normalized mole fraction for each run;
    3) mean normalized mole fraction.

5.3.1.2 Stage 1

Calculate the uncertainty of the raw mole fraction for components determined *directly* by using the appropriate equation selected from Table 1.

Table 1 — Selecting the equation for calculating the uncertainty of the raw mole fraction for components determined directly

Normalization method	**Equation**		
	Type 1 analysis	**Type 2 analysis**	
		Linearity errors *not* corrected	**Linearity errors corrected**
Mean	Equation (1)	Equation (2)	Equation (3)
Run-by-run	Equation (12)	Equation (13)	Equation (14)

5.3.1.3 Stage 2

Calculate the uncertainty of the raw mole fraction for any additional components determined *indirectly* by using the appropriate equation selected from Table 2.

Table 2 — Selecting the equation for calculating the uncertainty of the raw mole fraction for components determined indirectly

Normalization method	**Equation (Type 1 or Type 2 analysis)**
Mean	Equation (4)
Run-by-run	Equation (15)

5.3.1.4 Stage 3

Calculate the uncertainty of the normalized mole fraction for all components by using the appropriate equation selected from Table 3.

Table 3 — Selecting the equation for calculating the uncertainty of the normalized mole fraction for all components

Normalization method	**Equation (Type 1 or Type 2 analysis)**
Mean	Equation (5)
Run-by-run	Equation (16)

5.3.2 Calculation of uncertainty of component mole fractions — Mean normalization method

5.3.2.1 General considerations

The mean normalization method is used in 5.3.2.2 to 5.3.2.4 to calculate the uncertainty of the component mole fractions determined in accordance with ISO 6974-1:2012, 6.9.2.

5.3.2.2 Uncertainty of raw mole fractions

For Type 1 analyses in accordance with ISO 6974-1, calculate the uncertainty of raw mole fractions using Equation (1):

$$u^2\left(x_i^*\right) = \sum_{p=0}^{p=3}\sum_{q=0}^{q=3}\left[C_i(x_i^*,\overline{b_{p,i}})C_i(x_i^*,\overline{b_{q,i}})u\left(\overline{b_{p,i}},\overline{b_{q,i}}\right)\right] + \left[C_i(x_i^*,\overline{y_i})\right]^2 u^2\left(\overline{y_i}\right) \tag{1}$$

For Type 2 analyses in accordance with ISO 6974-1, calculate the uncertainty of raw mole fractions using Equation (2):

$$u^2\left(x_i^*\right) = \left(x_i^*\right)^2 \left\{\left[\frac{u\left(\overline{b_{1,i}}\right)}{\overline{b_{1,i}}}\right]^2 + \left[\frac{u\left(\overline{y_i}\right)}{\overline{y_i}}\right]^2\right\} \tag{2}$$

For Type 2 analyses in accordance with ISO 6974-1, if mean raw mole fractions are corrected for non-linearity errors associated with the assumed analyser response (see ISO 6974-1:2012, 6.9.4), then additional terms are included in Equation (2) to allow for uncertainty in correction term $\delta\left(x_i^*\right)$, giving Equation (3).

NOTE 1 This approach is consistent with ISO/IEC Guide 98-3:2008, F.2.4.5.

$$u^2\left(x_i^*\right) = \left(x_i^*\right)^2 \left\{\left[\frac{u\left(\overline{b_{1,i}}\right)}{\overline{b_{1,i}}}\right]^2 + \left[\frac{u\left(\overline{y_i}\right)}{\overline{y_i}}\right]^2 + \frac{\overline{u^2\left[\delta\left(x_i^*\right)\right]} + u^2\left(\overline{\delta_i}\right) + \overline{\delta_i}^2}{n_l}\right\} \tag{3}$$

The final term in Equation (3), $\overline{\delta_i}^2$, is included only if mean mole fractions remain uncorrected (see ISO 6974-1:2012, 6.9.4).

$\overline{u^2\left[\delta\left(x_i^*\right)\right]}$ is the mean variance of the correction terms over the analytical range of the analyser and $u^2\left(\overline{\delta_i}\right)$ is the variance of the mean correction term.

NOTE 2 This approach is consistent with ISO/IEC Guide 98-3:2008, F.2.4.5.

Using Equation (4), calculate the uncertainty of raw mole fractions of any indirect components from the uncertainty of the raw mole fraction of the reference component determined using Equations (1) to (3):

$$u^2\left(x_{\text{ind},i}^*\right) = \left(x_{\text{ind},i}^*\right)^2 \left\{\left[\frac{u\left(x_{\text{ref}}^*\right)}{x_{\text{ref}}^*}\right]^2 + \left[\frac{u\left(\overline{y_{\text{ind},i}}\right)}{\overline{y_{\text{ind},i}}}\right]^2 + \left[\frac{u\left(\overline{y_{\text{ref}}}\right)}{\overline{y_{\text{ref}}}}\right]^2 + \frac{\left[\frac{u\left(K_i\right)}{K_i}\right]^2}{n_l}\right\} \tag{4}$$

5.3.2.3 Uncertainty of normalized mole fraction

Calculate the uncertainty of the normalized mole fraction using Equation (5):

$$u^2\left(x_i\right) = \sum_{s=1}^{s=n_i}\left\{\left[C_i\left(x_i,x_s^*\right)\right]^2 u^2\left(x_s^*\right)\right\} + \left[C_i\left(x_i,x_{\text{oc}}\right)\right]^2 u^2\left(x_{\text{oc}}\right) \tag{5}$$

5.3.2.4 Input data

a) $u\left(\overline{y_i}\right)$ are estimated from the standard deviation, s, of the n_l responses to the unknown sample, using Equation (6):

$$u\left(\overline{y_i}\right) = \frac{s\left(y_{i,l}\right)}{\sqrt{n_l}} \tag{6}$$

If a multiple operation method with bridging is used, estimate $u\left(\overline{y_i}\right)$ for each appropriate component from the standard error of the mean of the set of n_l responses derived using ISO 6974-1:2012, Equation (8).

The use of the mean and standard error of the mean as estimators of the desired statistics is based on the assumption that the observations of responses are uncorrelated with time. The use of very large numbers of repeat measurements may render this assumption unjustified and should therefore be avoided (see ISO/IEC Guide 98-3:2008, 4.2.7).

b) $u\left(\overline{b_{p,i}}, \overline{b_{q,i}}\right)$ are estimated for Type 1 analyses in accordance with ISO 6974-1 as the values of $\frac{u\left(b_{p,i}, b_{q,i}\right)}{\sqrt{n_l}}$ obtained during the determination of the analysis function, using the generalized least squares (GLS) method.

The use of a WMS to scale the calibration curve during a Type 1 analysis [see ISO 6974-1:2012, Equation (5)] is likely to result in additional uncertainty. Care should be taken to account for this.

c) $u^2\left(\overline{b_{1,i}}\right)$ are estimated for Type 2 analyses in accordance with ISO 6974-1 from the uncertainties of the mean responses to the WMS combined with the uncertainties of the mole fractions of the WMS, using Equation (7):

$$u^2\left(\overline{b_{1,i}}\right) = \frac{\overline{b_{1,i}}^{\,2} \left\{ \left[\frac{u\left(\overline{y_{i,\text{wms}}}\right)}{\overline{y_{i,\text{wms}}}} \right]^2 + \left[\frac{u\left(x_{i,\text{wms}}\right)}{x_{i,\text{wms}}} \right]^2 \right\}}{n_l} \tag{7}$$

d) The sensitivity coefficients for the raw mole fraction with respect to the mean response to the unknown sample $C_i(x_i^*, \overline{y_i})$ are derived from ISO 6974-1:2012, Equation (9):

$$C_i(x_i^*, \overline{y_i}) = \frac{\partial x_i^*}{\partial \overline{y_i}} = \sum_{p=0}^{p=3} \left[p \cdot \overline{b_{p,i}} \left(\overline{y_i}\right)^{p-1} \right] \tag{8}$$

e) The sensitivity coefficients for the raw mole fraction with respect to the coefficients of the analysis function $C_i(x_i^*, \overline{b_{p,i}})$ are derived from ISO 6974-1:2012, Equation (9):

$$C_i(x_i^*, \overline{b_{p,i}}) = \frac{\partial x_i^*}{\partial \overline{b_{p,i}}} = \left(\overline{y_i}\right)^p \tag{9}$$

f) The sensitivity coefficients for mole fractions with respect to raw mole fractions are derived from ISO 6974-1:2012, Equation (11):

$$C_i(x_i, x_s^*) = \frac{\partial x_i}{\partial x_s^*} = \frac{T - x_i^*}{T^2}\left(1 - x_{\text{oc}}\right) \qquad \text{(when } i = s\text{)}$$

$$C_i(x_i, x_s^*) = \frac{\partial x_i}{\partial x_s^*} = \frac{-x_i^*}{T^2}\left(1 - x_{\text{oc}}\right) \qquad \text{(when } i \neq s\text{)} \tag{10}$$

where T is the so-called “unnormalized total”, $\sum_{i=1}^{n_i} x_i^*$.

g) The sensitivity coefficients for mole fractions with respect to mole fractions of the “other components” (see ISO 6974-2:2012, 3.4) are derived from ISO 6974-1:2012, Equation (11):

$$C_i(x_i, x_{\text{oc}}) = \frac{\partial x_i}{\partial x_{\text{oc}}} = -\frac{x_i^*}{T} \tag{11}$$

h) Values of $u\left(K_i\right)$ for flame ionization detectors (FIDs) and thermal conductivity detectors (TCDs) are specified in Annex B.

5.3.3 Calculation of uncertainty of component mole fractions — Run-by-run normalization method

5.3.3.1 General considerations

The run-by-run normalization method is used in 5.3.3.2 to 5.3.3.4 to calculate the uncertainty of the component mole fractions determined in accordance with ISO 6974-1:2012, 6.9.3.

5.3.3.2 Uncertainty of raw mole fraction

For Type 1 analyses in accordance with ISO 6974-1, calculate the uncertainty of raw mole fractions using Equation (12):

$$u^2\left(x_{i,l}^*\right)=\sum_{p=0}^{p=3}\sum_{q=0}^{q=3}\left[C_i(x_{i,l}^*,b_{p,i,l})C_i(x_{i,l}^*,b_{q,i,l})u\left(b_{p,i,l},b_{q,i,l}\right)\right]+\left[C_i(x_{i,l}^*,y_{i,l})\right]^2 u^2\left(y_{i,l}\right) \tag{12}$$

For Type 2 analyses in accordance with ISO 6974-1, calculate the uncertainty of raw mole fractions using Equation (13):

$$u^2\left(x_{i,l}^*\right)=\left(x_{i,l}^*\right)^2\left\{\left[\frac{u\left(b_{1,i,l}\right)}{b_{1,i,l}}\right]^2+\left[\frac{u\left(y_{i,l}\right)}{y_{i,l}}\right]^2\right\} \tag{13}$$

As in 5.3.2.2, for Type 2 analyses in accordance with ISO 6974-1, if raw mole fractions are corrected for non-linearity errors associated with the assumed analyser response (see ISO 6974-1:2012, 6.9.4), then additional terms are included in Equation (13) to allow for the uncertainty of correction term $\delta\left(x_i^*\right)$, giving Equation (14):

$$u^2\left(x_{i,l}^*\right)=\left(x_{i,l}^*\right)^2\left\{\left[\frac{u\left(b_{1,i,l}\right)}{b_{1,i,l}}\right]^2+\left[\frac{u\left(y_{i,l}\right)}{y_{i,l}}\right]^2+\overline{u^2\left[\delta\left(x_i^*\right)\right]}+u^2\left(\overline{\delta}_i\right)+\overline{\delta}_i^{\,2}\right\} \tag{14}$$

The final term in Equation (14), $\overline{\delta}_i^{\,2}$, is included only if raw mole fractions are left uncorrected (see ISO 6974-1:2012, 6.9.4).

Using Equation (15), calculate the uncertainty of the raw mole fraction of any indirect components from the uncertainty of the raw mole fraction of the reference component determined using Equations (12) to (14):

$$u^2\left(x_{\text{ind},i}^*\right)=\left(x_{\text{ind},i}^*\right)^2\left\{\left[\frac{u\left(x_{\text{ref},l}^*\right)}{x_{\text{ref},l}^*}\right]^2+\left[\frac{u\left(y_{\text{ind},i,l}\right)}{y_{\text{ind},i,l}}\right]^2+\left[\frac{u\left(y_{\text{ref},l}\right)}{y_{\text{ref},l}}\right]^2+\left[\frac{u\left(K_i\right)}{K_i}\right]^2\right\} \tag{15}$$

5.3.3.3 Uncertainty of normalized mole fraction

Calculate the uncertainty of the normalized mole fraction using Equation (16):

$$u^2\left(\overline{x_i}\right)=\frac{\sum_{l=1}^{l=n_l}\left[\sum_{s=1}^{s=n_i}\left\{\left[C_i(x_{i,l},x_{s,l}^*)\right]^2 u^2\left(x_{s,l}^*\right)\right\}+\left[C_i(x_{i,l},x_{\text{oc}})\right]^2 u^2\left(x_{\text{oc}}\right)\right]}{n_l^2} \tag{16}$$

5.3.3.4 Additional input data

a) $u\left(y_{i,l}\right)$ are estimated from the standard deviations, s, of the l responses to the sample. If a multiple operation method with bridging is used, estimate $u\left(y_{i,l}\right)$, for each appropriate component, from the standard deviation of the set of n_l responses derived using ISO 6974-1:2012, Equation (12).

b) $u\left(b_{p,i,l},b_{q,i,l}\right)$ are estimated for Type 1 analyses in accordance with ISO 6974-1 as the values of $u\left(b_{p,i},b_{q,i}\right)$ obtained during the determination of the analysis function using the generalized least squares (GLS) method.

The use of a WMS to scale the calibration curve during a Type 1 analysis [see ISO 6974-1:2012, Equation (5)] is likely to result in additional uncertainty. Care should be taken to account for this.

c) $u^2\left(b_{1,i,l}\right)$ are estimated for Type 2 analyses in accordance with ISO 6974-1 from the uncertainties of the mean responses to the WMS combined with the uncertainties of the mole fractions of the WMS, using Equation (17):

$$u^2\left(b_{1,i,l}\right)=b_{1,i,l}^2\left[\left(\frac{u\left(\overline{y_{i,\text{wms}}}\right)}{\overline{y_{i,\text{wms}}}}\right)^2+\left(\frac{u\left(x_{i,\text{wms}}\right)}{x_{i,\text{wms}}}\right)^2\right] \tag{17}$$

d) The sensitivity coefficients for the raw mole fraction with respect to the response to the unknown sample $C_i(x_{i,l}^*,y_{i,l})$ are derived from ISO 6974-1:2012, Equation (13):

$$C_i(x_{i,l}^*,y_{i,l})=\frac{\partial x_{i,l}^*}{\partial y_{i,l}}=\sum_{p=0}^{p=3}\left[p\cdot b_{p,i,l}\left(y_{i,l}\right)^{p-1}\right] \tag{18}$$

e) The sensitivity coefficients of the raw mole fraction with respect to the coefficients of the analysis function $C_i(x_{i,l}^*,b_{p,i,l})$ are derived from ISO 6974-1:2012, Equation (13):

$$C_i(x_{i,l}^*,b_{p,i,l})=\frac{\partial x_{i,l}^*}{\partial b_{p,i,l}}=\left(y_{i,l}\right)^p \tag{19}$$

f) The sensitivity coefficients for the mole fraction with respect to the raw mole fraction are derived from ISO 6974-1:2012, Equation (11):

$$C_i(x_{i,l},x_{s,l}^*)=\frac{\partial x_{i,l}}{\partial x_{s,l}^*}=\frac{T_i-x_{i,l}^*}{T_l^2}\left(1-x_{\text{oc}}\right) \qquad \text{(when } i=s\text{)}$$

$$C_i(x_{i,l},x_{s,l}^*)=\frac{\partial x_{i,l}}{\partial x_{s,l}^*}=\frac{-x_{i,l}^*}{T_l^2}\left(1-x_{\text{oc}}\right) \qquad \text{(when } i\neq s\text{)} \tag{20}$$

g) The sensitivity coefficients for the mole fractions with respect to the mole fractions of the “other components” (see ISO 6974-2:2012, 3.4) are derived from ISO 6974-1:2012, Equation (15):

$$C_i(x_{i,l},x_{\text{oc}})=\frac{\partial x_{i,l}}{\partial x_{\text{oc}}}=\frac{x_{i,l}^*}{T_l} \tag{21}$$

5.4 Step 10 — Calculation of the expanded uncertainty of mole fractions

Calculate the expanded uncertainty, $U(x_i)$, of the normalized components by multiplying $u(x_i)$ by an appropriate coverage factor using Equation (22):

$$U\left(x_i\right) = k \times u\left(x_i\right) \tag{22}$$

NOTE A coverage factor of $k = 2$, providing a level of confidence of approximately 95 %, is usually used.

Annex A
(informative)

Calculation of processed component uncertainties for the methane-by-difference approach

A.1 General considerations

This annex describes a procedure for calculating the uncertainties of processed component mole fractions determined using the methane-by-difference approach described in ISO 6974-1:2012, Annex C.

A.2 Calculation of methane-by-difference component uncertainties

For all components including methane, the standard uncertainty of a mole fraction x'_i is calculated using Equation (A.1):

$$u\left(x'_i\right)=\sqrt{s^2\left(x'_i\right)+u_{\text{cal}}^2\left(x'_i\right)} \tag{A.1}$$

where

$s(x'_i)$ is the standard deviation of replicate processed (methane-by-difference) mole fractions at level x'_i;

$u_{\text{cal}}(x'_i)$ is the calibration uncertainty at level x'_i.

For components other than methane, the calibration uncertainty $u_{\text{cal}}(x'_i)$ is determined in accordance with ISO 6974-1:2012, 6.5 (step 4; see Figure 1).

For methane, the calibration uncertainty is calculated using Equation (A.2):

$$u_{\text{cal}}\left(x'_1\right)=\sqrt{\sum_{i=2}^{n_i}u_{\text{cal}}^2\left(x'_i\right)} \tag{A.2}$$

Equation (A.1) applies to a mole fraction obtained from a single analysis. If the mole fractions are mean values of n_l replicates, the standard uncertainty is given by Equation (A.3):

$$u\left(x'_i\right)=\sqrt{\frac{s^2\left(x'_i\right)}{n_l}+u_{\text{cal}}^2\left(x'_i\right)} \tag{A.3}$$

Annex B
(normative)

Uncertainties of relative response factors

B.1 Uncertainties of relative response factors for flame ionization detectors (FIDs)

The relative standard uncertainties of the relative response factors, as calculated for an FID and given in ISO 6974-1:2012, Table D.1, shall be taken to be equal to 2 %[2]. Alternative figures may be used if determined by thoroughly validated experimental procedures.

NOTE The method for determining the relative response factors for an FID is given in ISO 6974-1:2012, D.1.

B.2 Uncertainties of relative response factors for thermal conductivity detectors (TCDs)

The relative standard uncertainties of the relative response factors, as calculated for a TCD and given in ISO 6974-1:2012, Table D.2, shall be taken to be equal to 10 %[2]. Alternative figures may be used if determined by thoroughly validated experimental procedures.

NOTE The method for determining the relative response factors for a TCD is given in ISO 6974-1:2012, D.2.

Annex C
(informative)

Alternative calculation of the uncertainty of the value of the unknown

This annex provides an alternative procedure[3] to the generalized least squares approach (see ISO 6974-1:2012, 6.5.5). The approach described in this annex has the benefit of being a more straightforward procedure with which to carry out the calculations. In order to maintain the simplicity of this alternative approach, it can only be applied when the analysis and calibration functions can be approximated in a first-order form.

Consider a set of data of points (x_i, y_i) forming a first-order calibration curve where x_i is the mole fraction of each standard and y_i the instrumental response. The equation for a first-order calibration function is given by Equation (C.1):

$$y_i = \beta x_i + \alpha \tag{C.1}$$

where α and β are the intercept and gradient of the line respectively. In this case, the intercept and the gradient are highly correlated.

This alternative approach reduces the data to a set of points expressed with respect to the centroid ($\bar{x}, \bar{y}$), where $\bar{x}$ and $\bar{y}$ are the mean values of x and y.

The calibration curve can now be expressed as given in Equation (C.2):

$$\left(y_i - \bar{y}\right) = \gamma\left(x_i - \bar{x}\right) \tag{C.2}$$

where γ is the gradient of the calibration function.

Consider the measurement of an "unknown" standard producing an instrumental response of Y. The mole fraction of the unknown ($\hat{x}$) can be expressed as the linear first-order function given in Equation (C.3):

$$\hat{x} = \frac{\left(Y - \bar{y}\right)}{\gamma} + \bar{x} \tag{C.3}$$

NOTE The parameters of the analysis function in ISO 6974-1:2012, Equation (2), b_0 and b_1, are related to the parameters in Equation (C.3) by $b_0 = \bar{x} - \bar{y}/\gamma$ and $b_1 = 1/\gamma$.

The covariances cov($\bar{y},\bar{x}$) and cov(γ, $\bar{x}$) are both zero. In accordance with ISO/IEC Guide 98-3, the uncertainty of the mole fraction given by Equation (C.3) is calculated using Equation (C.4):

$$u\left(\hat{x}\right)^2 = u\left(\bar{x}\right)^2 + \frac{1}{\gamma^2}\left[\left(\hat{x} - \bar{x}\right)^2 u\left(\gamma\right)^2 + u\left(Y\right)^2 + u\left(\bar{y}\right)^2\right] \tag{C.4}$$

The mole fraction $\bar{x}$ is defined as given by Equation (C.5):

$$\bar{x} = \frac{1}{n_j}\sum_i x_i \tag{C.5}$$

where n_j is the number of standards measured.

If the uncertainties $u(x)$ are uncorrelated, the standard error of the estimated mean is given by Equation (C.6):

$$u(\bar{x})^2 = \frac{1}{{n_j}^2} \sum_i u(x_i)^2 \tag{C.6}$$

When all the uncertainties are equal to $u(x)$, this simplifies to Equation (C.7):

$$u(\bar{x})^2 = \frac{u(x)^2}{n_j} \tag{C.7}$$

Similar expressions can be generated for $u(\bar{y})$ and $u(Y)$, as given in Equations (C.8) and (C.9) respectively:

$$u(\bar{y})^2 = \frac{u(y)^2}{n_l} \tag{C.8}$$

$$u(Y)^2 = \frac{u(y)^2}{n_l} \tag{C.9}$$

where n_l is the number of measurements of each standard.

Incorporating Equations (C.7), (C.8) and (C.9) into (C.4) gives Equation (C.10):

$$u(\hat{x})^2 = \frac{u(x)^2}{n_j} + \frac{u(y)^2}{\gamma^2}\left(\frac{1}{n_j} + \frac{1}{n_l}\right) + \frac{u(\gamma)^2}{\gamma^2}(\hat{x} - \bar{x})^2 \tag{C.10}$$

This equation can be used to evaluate the uncertainty of the calculated value of the unknown from knowledge of the uncertainty of the standards [$u(x)$], the uncertainty of the analysis [$u(y)$] and the uncertainty of the gradient of the calibration curve [$u(\gamma)$]. This can be calculated from an ordinary least squares fit of the analytical data that follow the relationship given by Equation (C.2).

Bibliography

[1] VARGHA, G., MILTON, M., COX, M. and KAMVISSIS, S., Harmonisation of Coupled Calibration Curves to Reduce Correlated Effects in the Analysis of Natural gas by Gas Chromatography, *J. Chromatogr. A.*, 2005, 1062, pp. 239-245

[2] TONG, H.Y. and KARASEK, F.W., Flame Ionisation Detector Response Factors for Compound Classes in Quantitative Analysis of Complex Organic Mixtures, *Anal. Chem.*, 1984, 56, 2124-2128

[3] DRAPER, N.R. and SMITH, H., *Applied Regression Analysis*, 3rd edition, Wiley, New York, 1998

[4] ISO Guide 31, *Reference materials — Contents of certificates and labels*

[5] ISO Guide 34, *General requirements for the competence of reference material producers*

[6] ISO Guide 35, *Reference materials — General and statistical principles for certification*

[7] ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

[8] 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*

[9] 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*

[10] 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*

[11] 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* C_1 *to* C_8 *hydrocarbons using three capillary columns*

[12] ISO 10715, *Natural gas — Sampling guidelines*

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