
**Natural gas — Gas chromatographic
requirements for hydrocarbon dewpoint
calculation**

*Gaz naturel — Exigences relatives à la chromatographie en phase
gazeuse pour le calcul du point de rosée hydrocarbures*

STANDARDSISO.COM : Click to view the full PDF of ISO 23874:2006



PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 23874:2006

© ISO 2006

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword	iv
1 Scope	1
2 Normative references	1
3 Principle	2
4 Materials	2
5 Apparatus	2
6 Performance requirements	3
7 Sampling	3
8 Analytical procedure	4
9 Methods of test	7
10 Uncertainty in composition	9
11 Calculation of dewpoint temperature	9
12 Analytical uncertainty contribution to dewpoint temperature	9
Annex A (informative) Typical analytical conditions for C₅ to C₁₂ analysis	10
Annex B (informative) Validation of fraction data	12
Annex C (informative) Precision of area ratio	16
Annex D (informative) Recommendations on sample calibration gas introduction	20
Annex E (informative) Calculation of fraction quantities, boiling points and component uncertainties	22
Bibliography	26

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 23874 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

STANDARDSISO.COM : Click to view the full PDF of ISO 23874:2006

Natural gas — Gas chromatographic requirements for hydrocarbon dewpoint calculation

1 Scope

This International Standard describes the performance requirements for analysis of treated natural gas of transmission or pipeline quality in sufficient detail so that the hydrocarbon dewpoint temperature can be calculated using an appropriate equation of state. It can be applied to gases that have maximum dewpoint temperatures (cricondentherms) between 0 °C and – 50 °C. The pressures at which these maximum dewpoint temperatures are calculated are in the range 2 MPa (20 bar) to 5 MPa (50 bar). Major components are measured using ISO 6974 (all parts) and the ranges of components that can be measured are as defined in ISO 6974-1. The procedure given in this International Standard covers the measurement of hydrocarbons in the range C₅ to C₁₂. *n*-Pentane, which is quantitatively measured using ISO 6974 (all parts), is used as a bridge component and all C₆ and higher hydrocarbons are measured relative to *n*-pentane.

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

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

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 C₈ using two packed columns*

ISO 6974-4, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line measuring system using two columns*

ISO 6974-5, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line process application using three columns*

ISO 6974-6, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C₁ to C₈ hydrocarbons using three capillary columns*

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

ISO 10715, *Natural gas — Sampling guidelines*

3 Principle

For hydrocarbon gas mixtures such as natural gas, the phase boundary or dewpoint line distinguishing single-phase gas from gas-liquid mixtures is a complex function of pressure, temperature and composition. For a given composition, the pressure at which the dewpoint temperature is at a maximum is intermediate between those found in transmission and distribution operations. The analysis shall be comprehensive for inert components and for hydrocarbons up to C_{12} . It is not necessary to measure helium, hydrogen, water and sulfur compounds unless any of these is present at greater than 0,01 mole fraction.

The analysis shall be performed in two parts. Major components (nitrogen, carbon dioxide and hydrocarbons from C_1 to C_5) shall be analysed according to ISO 6974 (all parts). Higher hydrocarbons (C_5 to C_{12}) shall be analysed to satisfy the requirements given in this International Standard. This allows the traceability of measurements according to ISO 6974 (all parts) to be extended to the higher hydrocarbons.

It is not possible to identify all the measured higher hydrocarbons, nor is it possible to obtain a reference gas mixture that contains more than a few representatives of the higher hydrocarbons. The analytical data are, therefore, handled with a number of simplifying assumptions.

- Unidentified components are allocated a carbon number or molar mass according to their positions in the chromatogram with respect to identified n -alkanes.
- Alkanes of carbon number 7 and above are summed by carbon number and treated as fractions for input to the dewpoint calculation.
- Average boiling points and densities of fractions are calculated from the individual boiling points and quantities of the components that comprise them; individual-component boiling points are calculated by interpolation between the bracketing n -alkanes [1].
- Sample components are quantified by comparison with n -pentane, which has been measured according to ISO 6974 (all parts), using relative response factors based on their allocated carbon numbers.

NOTE When using ISO 6974 (all parts), n -pentane can be measured as a direct component that is also present in the calibration-gas mixture, or as an indirect component using a response factor relative to a different component (for example, n -butane) in the calibration gas mixture. In either case, the uncertainty on the quantity of n -pentane can be calculated according to ISO 6974-2.

4 Materials

4.1 Certified-reference gas mixture for major components (CRM1), such as is required for ISO 6974 (all parts).

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

4.2 Certified-reference gas mixture, for higher hydrocarbons (CRM2), containing as a minimum, n -pentane, n -hexane, benzene, cyclohexane, n -heptane, toluene, methylcyclohexane and n -octane. Ideally, the CRM2 should also contain n -nonane, n -decane, n -undecane and n -dodecane in methane.

The mole fractions of components in CRM2 shall be chosen to be appropriate for the application, provided that the mixture is stable and free from the possibility of condensation in transport, storage and in use.

5 Apparatus

5.1 Measurement system for major components, comprised of a sample introduction and transfer unit, a separation unit, a detection unit, an integrator and a data reduction system, capable of meeting the analytical requirements described in 6.1.

ISO 6974 (all parts) describes equipment suitable for this part of the analysis.

5.2 Measurement system for higher hydrocarbons, comprised of a sample-introduction and transfer unit, a separation unit, a detection unit, an integrator and a data-reduction system, capable of meeting the analytical requirements described in 6.2.

Annex A describes a system that has been shown to be suitable. The user is responsible for demonstrating in each case that his/her chosen system is also suitable.

6 Performance requirements

6.1 Major components

The system for measurement of major components shall have performance as described in ISO 6974 (all parts).

6.2 Higher hydrocarbons

The system for measurement of higher hydrocarbons shall satisfy the following requirements:

- be capable of measuring alkanes up to and including *n*-dodecane;
- be capable of measuring individual alkanes at a concentration of 0,000 000 1 mole fraction (0,1 ppm¹⁾ or less;
- be able to distinguish and measure benzene, toluene, cyclohexane and methylcyclohexane as individual components;
- use a detection system that can, at least in principle, measure all hydrocarbons in the range C₅ to C₁₂;
- use a detection system that has a predictable response to hydrocarbons based on mass or carbon content, such that unidentified components of known molar mass or carbon number can be measured relative to other known components in the sample or in the calibration gas;

NOTE 1 It is most likely that the detection system is a flame ionization detector (FID).

- use a separation procedure such that the boiling points of unidentified components can be calculated by interpolation between those of known *n*-alkanes.

NOTE 2 Increasing the column temperature at a constant rate throughout the analysis (linear temperature programming) allows such interpolation.

NOTE 3 Annex A describes a configuration that has been found to be suitable for the requirements of 6.2.

7 Sampling

Carry out representative sampling in such a way that the sample represents the gas, particularly the higher hydrocarbons, at the time of sampling. Sampling and sample transfer shall be performed in accordance with ISO 10715.

1) ppm is a deprecated unit.

8 Analytical procedure

8.1 Major components

Follow the procedure specified in ISO 6974 (all parts).

8.2 Higher hydrocarbons

The analytical procedure consists of the following steps. All of these steps shall be carried out when the method is first introduced, and some of them when changes in equipment cause historical measurement data to be no longer valid. For normal use, steps may be left out provided that the procedures and equipment remain under statistical control.

8.2.1 Step 1 — Precision

Since quantitative information is derived by comparing the response of unknown components with that of *n*-pentane, which has been measured according to ISO 6974 (all parts), the precision information of interest is that of the ratio of component responses to that of *n*-pentane.

- Perform a number of repeat analyses on a typical natural gas and, for each analysis, calculate the ratio of the area of each peak to the area of *n*-pentane. For each peak, calculate the mean and the standard deviation of the ratios from all analyses.
- Where component data are to be summed into fractions or groups (see 9.3), calculate the ratio of the total peak area for that fraction or group to the area of *n*-pentane. For each fraction, calculate the mean and the standard deviation of the ratios.
- Convert both sets of mean and standard deviation data into natural logarithms, plot the natural logarithm of the standard deviation, $\ln s$, as a function of natural logarithm of the area ratio, $\ln R_A$, and perform a first-order regression analysis on the data. Annex C shows a worked example.
- Calculate the 95 % confidence limits for the regression line and plot these on the same graph. Select values of a and b in Equation (1) by trial and error such that

$$\ln s = a + b \times \ln R_A \quad (1)$$

results in a straight line that closely approximates to the upper 95 % confidence line (see Annex C). This line now defines the precision of measurement, as given in Equation (2):

$$s = \exp(a + b \times \ln R_A) \quad (2)$$

- This standard deviation is used as the standard uncertainty for each peak or fraction.

8.2.2 Step 2 — Relative response factors

When using a flame ionization detector, relative response factors, F_{RR} , are claimed to be proportional to carbon number. Under most circumstances this is true, but variations from ideal operating conditions can cause this assumption to be false, and so it is necessary that it be checked. This is all the more necessary for other types of detector. The procedure below uses the known composition of CRM2 to check the relative response factors. The most likely outcome is that the factors are directly related to carbon number, but the uncertainty with which this is validated shall be taken into account in the overall uncertainty calculation. Since *n*-pentane is the reference component, the response factor is conveniently expressed as a relative carbon response factor, $F_{RR,C}$, to that of *n*-pentane.

- Perform a number (not less than 5) of repeat analyses using CRM2. Measure the mean peak area response for each component and the equivalent standard deviations.

- Calculate the relative carbon response factor for each component, i , as given in Equation (3):

$$F_{RR,Ci} = \frac{5 \times \bar{A}_i \times c_{k,nC5}}{N \times \bar{A}_{nC5} \times c_{k,i}} \quad (3)$$

where

- \bar{A}_i is the average peak area of component i ;
- \bar{A}_{nC5} is the average peak area of n -C5;
- $c_{k,i}$ is the known concentration of component i ;
- $c_{k,nC5}$ is the known concentration of n -C5;
- N is the carbon number of component i ;
- 5 is the carbon number of n -C5 (n -pentane).

Equation (3) can also be expressed using area ratios, as given in Equation (4):

$$F_{RR,Ci} = \frac{5 \times \bar{R}_{A,i:nC5} \times c_{k,nC5}}{N \times c_{k,i}} \quad (4)$$

where $\bar{R}_{A,i:nC5}$ is the average peak area ratio of component i to n -C5. $F_{RR,C}$ values should be very close to 1.

- Calculate the average relative carbon response factor for each component, and the standard deviation of this value. The uncertainty of the $F_{RR,C}$ uses these standard deviation values and the uncertainties of the composition data for CRM2. The overall uncertainty of the $F_{RR,C}$ is calculated from the averages of the individual component values.

8.2.3 Step 3 — Validation of fraction data

Inert gases and individual hydrocarbons up to hexane can be measured unambiguously and used in the calculation software. Beyond this, n -alkanes up to C_{12} , benzene, toluene, cyclohexane and methylcyclohexane can be identified, but other hydrocarbons, in general, cannot be clearly identified and measured because of the large amount of overlap that occurs between isomers and the lack of reliable retention data. Even if individual isomers can be identified, it is unlikely that their critical properties, which are necessary for the calculation, are tabulated in the software.

Components that are measured but unidentified are summed into fractions or carbon number groups. Thus all components eluting after n -C₆ up to and including n -C₇, with the exceptions of benzene and cyclohexane, are summed as the C_7 fraction (FR7). The average boiling point and specific gravity of this summed group are calculated (see 9.3.2) and used by the software to calculate appropriate critical properties for the fraction. Two checks are made at this stage to ensure that the fraction data are as close an approximation as possible and to estimate the uncertainties involved. These are

- to compare attributed and “true” boiling points,
- to show that linear interpolation is valid.

8.2.3.1 Boiling-point comparison

The *n*-alkanes are easily distinguished in the separation and their properties are well known. They are, therefore, used as the basis for checking boiling point data. From an existing and comprehensive analysis, calculate the C₇ to C₁₂ fraction quantities, where measurable, according to 9.3.1. Identify these fractions as the equivalent *n*-alkanes and calculate the dewpoint on this basis. Now rename the C₇ group as the fraction, FR7, rather than *n*-C₇, and give it a boiling point and specific gravity that are those of the *n*-alkane. Recalculate the dewpoint.

This fraction dewpoint is likely to be slightly different from the *n*-alkane dewpoint. Adjust the boiling point value until the dewpoint agrees with that from the *n*-alkane. This adjusted boiling point, $T_{BP,a}$, provides the best fit when comparing the fraction property with that of the *n*-alkane. Repeat this substitution for each *n*-alkane individually, and note the adjusted boiling point in each case. Include the C₆ fraction and *n*-C₆. Even though the C₆ components are likely to be measured individually, the adjusted boiling point of *n*-C₆ is required for the calculation of the C₇ fraction properties in 9.3.2.

Having defined these adjusted boiling points (which can, in some cases, coincide with the "true" values), now define all carbon-number groups as fractions with these adjusted boiling points in each case. Recalculate the dewpoint. The difference between this last dewpoint value and that found when all groups are treated as *n*-alkanes is taken as the uncertainty value.

NOTE Annex B shows an example of such calculations.

8.2.3.2 Interpolation

Fraction boiling points are calculated on the assumption that the boiling points of individual unidentified components can be calculated by linear interpolation between the values for the bracketing *n*-alkanes. This is checked by using known data for *n*-alkanes. The boiling point of *n*-C₈ is calculated by interpolation between the known values (adjusted boiling points) for *n*-C₇ and *n*-C₉ and compared with the adjusted boiling point for *n*-C₈ found in 8.2.3.1. The calculated boiling point of the *n*-alkane is calculated as given in Equation (5):

$$T_{BP,cal,n-C_x} = T_{BP,a,n-C_{x-1}} + \frac{(t_{R,n-C_x} - t_{R,n-C_{x-1}}) \times (T_{BP,a,n-C_{x+1}} - T_{BP,a,n-C_{x-1}})}{(t_{R,n-C_{x+1}} - t_{R,n-C_{x-1}})} \quad (5)$$

where

$t_{R,i}$ is the retention time of component *i* in the sample;

$T_{BP,a,n-C_i}$ is the adjusted boiling point of *n*-alkane *i* in the sample.

The same is applied to other *n*-alkanes where interpolation is possible. For each *n*-alkane, the difference between the calculated boiling point and the adjusted boiling point from 8.2.3.1 is recorded. The boiling point uncertainty arising from interpolation is calculated as the mean of the absolute values of the differences between the calculated and adjusted boiling points for *n*-C₈, *n*-C₉, *n*-C₁₀ and *n*-C₁₁.

The sensitivity of the calculated dewpoint to these boiling point uncertainties is now determined. The analytical data used in 8.2.3.1 are used again but with fraction boiling-point data based on the adjusted boiling points for *n*-alkanes calculated as in 9.3.2. The dewpoint temperature is calculated from this analysis. Each fraction boiling point is then incremented by the boiling-point uncertainty calculated above and the dewpoint recalculated. The difference between the two dewpoint values is the uncertainty associated with interpolation.

NOTE Annex B shows an example of such calculations.

8.2.4 Step 4 — Sample introduction

Introduce the sample in accordance with 9.1.

8.2.5 Step 5 — Calculation of the composition

Calculate the composition of individual components and of fractions in accordance with 9.2.

8.2.6 Step 6 — Calculation of the composition uncertainty

Calculate the uncertainty of the composition in accordance with Clause 10.

9 Methods of test

9.1 Introduction of a typical sample of natural gas

To minimize surfaces on which higher hydrocarbons can be adsorbed, the connection to the sample cylinder can consist of a metering valve or needle valve fitted with low-dead-volume tubing. If this is not available, use a low-internal-volume pressure regulator with a stainless steel diaphragm and with no plastics material in contact with the sample gas.

If the temperature of the gas in the pipeline from which the sample was taken is known, ensure that the cylinder and the connecting tubing up to the pressure-reduction device or needle valve is heated to at least 10 °C above the gas temperature. The cylinder should be heated (if necessary) for not less than 4 h before use. The connecting tubing need only be heated at the time of use. Downstream of the pressure-reduction device or needle valve the gas is close to atmospheric pressure and heating is not necessary.

Purge the sample valve and connecting tubing with a low flow (about 10 ml/min) of sample gas for 5 min to 10 min. The volume flowed shall be at least 20 times the volume of the sample loop and connecting tubing. Inject the sample. If the analyser has provision to stop the sample flow before injection, then a means shall be provided to vent the gas to a by-pass line when using a needle valve or metering valve to control sample flow. If repeat analyses are going to be made, continue to flow the sample through the sample loop and connecting tubing while the analysis is proceeding.

NOTE Annex D shows examples of connections that have proved to be satisfactory.

9.2 Calculation of the composition

Components are measured relative to the peak for *n*-pentane. The quantity of *n*-pentane is derived from analysis in accordance with ISO 6974 (see 8.1). The quantity of each component, c_i , is calculated in accordance with Equation (6):

$$c_i = \frac{5 \times R_i \times c_{n-C5} \times F_{RR,C,i,n-C5}}{N \times R_{n-C5}} \quad (6)$$

where

R_i is the instrument response to component *i* in the sample;

R_{n-C5} is the instrument response to *n*-pentane in the sample;

c_{n-C5} is the quantity of *n*-pentane in the sample, determined according to ISO 6974;

$F_{RR,C,i,n-C5}$ is the relative carbon response factor of component *i* to that of *n*-pentane;

N is the carbon number of component *i*.

9.3 Calculation of fraction quantities and properties

Other than the *n*-alkanes, benzene, toluene, cyclohexane and methyl cyclohexane, most peaks measured in the C₇ to C₁₂ part of the chromatogram are unidentified. They can be accounted for by using the widely

accepted assumption that (with the exception of aromatics and some cycloalkanes) all components eluting between the n -alkanes $n-C_x$ and $n-C_{x+1}$ are iso-alkanes of carbon number $x + 1$. This means that the same carbon number can be applied to those components as is used for $n-C_{x+1}$, and so quantitative values can be derived for unidentified components.

These unidentified components are summed as fractions by carbon number. Such fractions can be input into an equation of state used for dewpoint calculation, alongside individual identified components. Critical properties for individual components are available in the equation of state database, whereas those for fractions can be calculated from the average boiling points and densities of the fractions.

9.3.1 Calculation of fraction quantities

Individual peaks measured in the chromatogram are calculated according to 9.2, with the appropriate carbon-number values selected as described in 9.3. The calculated quantities for unidentified peaks that elute from immediately after $n-C_x$ up to and including $n-C_{x+1}$ are summed and the total allocated to fraction $x + 1$. Any peaks that are separately identified in this region, such as benzene and cyclohexane in the C_7 fraction, and toluene and methyl cyclohexane in the C_8 fraction, are not included in this summation, since they are accounted for individually.

NOTE Annex E shows a worked example of such a calculation.

9.3.2 Calculation of fraction properties

If the separation uses a linear temperature programme, then the boiling points of unidentified components can be inferred by linear interpolation between the values for the bracketing n -alkanes. Thus, the boiling point, $T_{BP,y}$, of a component y , which elutes between $n-C_x$ and $n-C_{x+1}$, is calculated by Equation (7).

$$T_{BP,y} = T_{BP,n-C_x} + \frac{(t_{R,y} - t_{R,n-C_x}) \times (T_{BP,n-C_{x+1}} - T_{BP,n-C_x})}{(t_{R,n-C_{x+1}} - t_{R,n-C_x})} \quad (7)$$

where

- $t_{R,y}$ is the retention time of component y ;
- $t_{R,n-C_x}$ is the retention time of the n -alkane $n-C_x$;
- $t_{R,n-C_{x+1}}$ is the retention time of the n -alkane $n-C_{x+1}$;
- $T_{BP,n-C_x}$ is the boiling point of the n -alkane $n-C_x$;
- $T_{BP,n-C_{x+1}}$ is the boiling point of the n -alkane $n-C_{x+1}$.

The boiling point of the fraction, $T_{BP,FR}$, is then found by weighting the quantity of each component in the group by its boiling point, summing the total and dividing by the total quantity, according to Equation (8):

$$T_{BP,FR} = \frac{\sum (R_i \times T_{BP,i})}{\sum t_{R,i}} \quad (8)$$

The fraction density can be taken to be identical to that of the n -alkane within that fraction, since densities vary little among isomers.

NOTE 1 Calculated component concentrations can be used in Equation (8) in place of instrument responses, but can be more subject to rounding errors.

NOTE 2 Annex E shows a worked example of such a calculation.

10 Uncertainty in composition

From Equation (6), the combined uncertainty, $u_c(c_i)$, of the concentration, c_i , of component, i , is calculated using Equation (9):

$$\frac{u_c^2(c_i)}{c_i^2} = \frac{u^2\left(\frac{t_{R,i}}{t_{R,n-C5}}\right)}{\left(\frac{t_{R,i}}{t_{R,n-C5}}\right)^2} + \frac{u^2(c_{n-C5})}{c_{n-C5}^2} + \frac{u^2(F_{RR,C,i,n-C5})}{F_{RR,C,i,n-C5}^2} \quad (9)$$

The first term uses the precision of the area ratios, as described in 8.2.1. The second term uses the uncertainty of the n -pentane content, as calculated using ISO 6974 (all parts). The third term uses the uncertainty of the relative carbon response factor, $F_{RR,C}$, as described in 8.2.2. The expanded uncertainty, $U_c(c_i)$, is determined by multiplying the combined standard uncertainty, $u_c(c_i)$, by an appropriate k factor.

NOTE Annex E shows a worked example of such a calculation.

11 Calculation of dewpoint temperature

The composition is described as a mixture of individually measured components, including all those measured using ISO 6974 (all parts), and fractions or groups where components have been summed by carbon number. This combination is entered into a suitable equation of state, in which the dewpoint temperature at one or more defined pressures can be calculated. Alternatively, the cricondenbar or cricondentherm may be calculated directly, or the temperature at which, at a selected pressure, a defined amount of condensate is formed.

When entering data for fractions rather than for individual components, it is necessary to include the average boiling points and densities with the quantity.

12 Analytical uncertainty contribution to dewpoint temperature

The equation of state has an uncertainty associated with its use; these considerations are outside the scope of this International Standard. However, it is possible to estimate the contribution made by the uncertainty on composition to the dewpoint temperature uncertainty, although this does not account for all the uncertainty of the result.

Equations of state use iterative numerical methods, which are not amenable to an analytical approach in the way that Equation (9) is derived from Equation (6). For example, a solution is to use a Monte Carlo method in which a large number of compositions, based on the measured value but adjusted according to the known composition uncertainties, are separately entered into the equation of state and the variation in the calculated dewpoint temperatures is noted.

Compositions are created using a random-number generator set up to develop a normal distribution, with, for each component, a mean that is the measured value, and a standard deviation that is the analytical uncertainty. Each composition produces a dewpoint temperature, the mean and standard deviation of these temperature values are calculated. This standard deviation can be taken to be the uncertainty contribution arising from the analytical uncertainty.

This does not take into account uncertainties associated with the use of fractions, as described in 8.2.3. The different uncertainty contributions due to the analytical procedure, to the use of fractions and to the equation of state (if known), shall be quoted individually.

Annex A (informative)

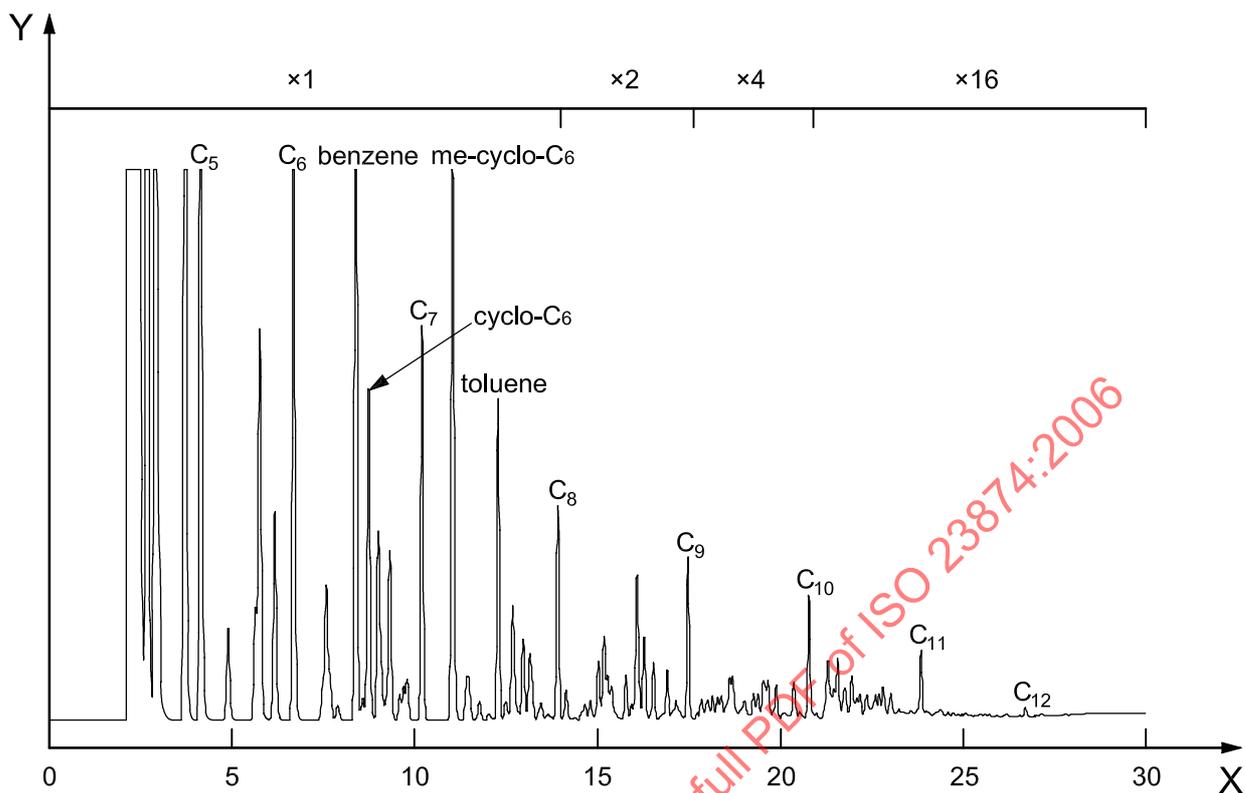
Typical analytical conditions for C₅ to C₁₂ analysis

Typical conditions for the C₅ to C₁₂ analysis are as given below:

Column:	30 m × 0,53 mm id	
Coating:	CP-Sil 5 film 2 µm thick	
Temperature:	Initial temperature	35 °C
	Initial time	3,5 min
	Ramp rate 1	6 °C/min
	Final temperature 1	200 °C
	Final time 1	0 min
	(Ramp rate 2	20 °C/min
	Final temperature 2	225 °C
	Final time 2	4 min)
Carrier gas:	Helium	
Flowrate:	6,5 ml/min at 35 °C	
Split flow:	10,5 ml/min	
Sampling valve temperature:	100 °C	
Sample loop volume:	1 ml	
Detector:	Flame ionization	
Detector temperature:	230 °C	
Auxiliary helium flow:	22 ml/min	
Hydrogen flow:	31,5 ml/min	
Air flow:	440 ml/min	

NOTE Ramp rate 2, final temperature 2 and final time 2 are not part of the analytical cycle. They are included to ensure that the baseline for the next analysis is not contaminated by residual column bleed.

A typical chromatogram is shown in Figure A.1.



Key

- X retention time, expressed in minutes
- Y relative response

Figure A.1 — Example of a typical chromatogram

Annex B (informative)

Validation of fraction data

The average boiling points calculated for fractions are used by the software to compute the equivalent critical properties for the fractions which are then used in the dewpoint calculation. The suitability of this use of calculated boiling points is tested by using a composition where the carbon number groups are first entered as *n*-alkanes and then as fractions with boiling points equivalent to those of the *n*-alkanes. This approach overestimates the dewpoint temperature, since the *n*-alkanes have the highest boiling point of the isomers at any particular carbon number; but the comparison is still valid.

The composition is shown in Table B.1.

Table B.1 — Composition

Component	mole %
Nitrogen	0,803
Carbon dioxide	2,981
Methane	85,730
Ethane	7,567
Propane	2,189
<i>i</i> -Butane	0,182
<i>n</i> -Butane	0,364
neo-Pentane	0,000 0
<i>i</i> -Pentane	0,060 9
<i>n</i> -Pentane	0,067 7
2,2-di-me-C4	0,001 0
2,3-di-me-C4	0,003 7
2-me-C5	0,009 7
3-me-C5	0,004 7
<i>n</i> -C6	0,012 1
Benzene	0,003 9
cyclo-C6	0,003 6
FR7	0,009 1
Toluene	0,001 2
me-cyclo-C6	0,001 8
FR8	0,001 3
FR9	0,000 5
FR10	0,000 1
FR11	9,43E-06
FR12	5,27E-07

The composition is adjusted by summing the C_6 alkanes under the title $n-C_6$ and by changing FR7 to FR12 into $n-C_7$ to $n-C_{12}$, respectively. When this composition is used to calculate dewpoint, the appropriate critical data for the n -alkanes are used by the software. Each n -alkane in turn is then denominated as a fraction, and the boiling point and specific gravity of the n -alkane are applied to it. The dewpoint calculation is repeated. If the second calculation differs from the first, then the boiling point that was used does not apparently generate sufficiently similar critical properties. Alternative boiling points are tested until the calculated dewpoint agrees sufficiently closely with the original n -alkane calculation.

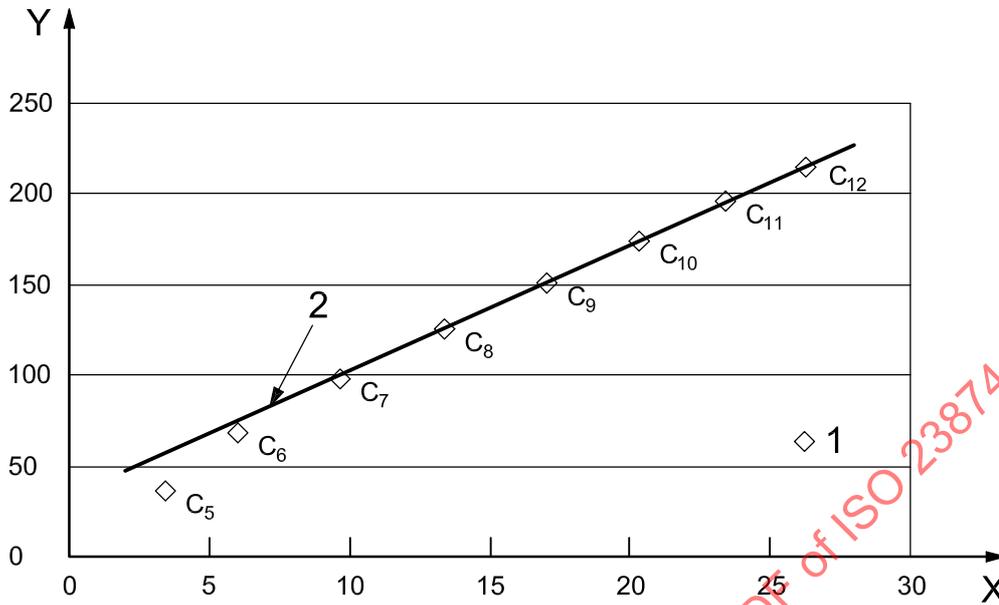
Table B.2 shows the results for each carbon number group in turn and for all components.

Table B.2 — Calculated dewpoints at 3,5 MPa (35 bar)

Sample	“True” boiling point	Dewpoint	Model boiling point	Dewpoint
Original	—	—	—	– 10,49
$n-C_6$ as a fraction	68,46	– 10,74	71,00	– 10,49
$n-C_7$ as a fraction	98,55	– 10,59	99,70	– 10,47
$n-C_8$ as a fraction	125,36	– 10,57	127,00	– 10,48
$n-C_9$ as a fraction	150,63	– 10,62	152,40	– 10,48
$n-C_{10}$ as a fraction	173,96	– 10,48	173,96	– 10,48
$n-C_{11}$ as a fraction	195,51	– 10,51	196,50	– 10,49
$n-C_{12}$ as a fraction	214,97	– 10,50	216,00	– 10,49
All as fractions	—	—	—	– 10,39

As can be seen, when all n -alkanes are given a modified fraction boiling point, there is a small residual error of 0,10 °C.

Interpolation of boiling-point data assumes a linear relationship between boiling points and retention times. Figure B.1 shows the results when using an analytical procedure similar to that in Annex A.



Key

- X retention time, expressed in minutes
- Y boiling point, expressed in degrees Celsius
- 1 data point identified by carbon number
- 2 fitted line

Figure B.1 — Relationship between *n*-alkane boiling points and retention times

Figure B.1 includes a best-estimate straight line drawn through the points for the higher *n*-alkanes. This indicates that the C₈ to C₁₂ *n*-alkanes do show a linear relationship, that C₇ has very similar behaviour, and that C₅ and C₆ deviate significantly. This is caused by the initial isothermal period, which has a significant effect on lighter components but little on the heavier ones. It also justifies measuring the C₆ isomers individually rather than as a fraction.

Uncertainties associated with interpolation are assessed by comparing the calculated boiling points of *n*-alkanes using Equation (5) with the adjusted boiling points derived in 8.2.3.1. Table B.3 shows the outcome.

Table B.3 — Comparison of boiling points

Component	Adjusted boiling point	Interpolated boiling point	Error
<i>n</i> -C ₆	71,00	62,73	- 8,27
<i>n</i> -C ₇	100,10	98,36	- 1,74
<i>n</i> -C ₈	127,00	127,03	0,03
<i>n</i> -C ₉	152,40	151,43	- 0,97
<i>n</i> -C ₁₀	173,96	175,28	1,32
<i>n</i> -C ₁₁	196,50	195,80	- 0,70

The mean of the absolute values for C_8 to C_{11} is $0,75\text{ }^{\circ}\text{C}$. The errors for $n\text{-}C_6$ and $n\text{-}C_7$ are significantly higher than this value but these are relative to the projected straight line in Figure B.1. When boiling points are calculated for the unidentified C_7 alkanes, the interpolation occurs between the adjusted boiling points of $n\text{-}C_6$ and $n\text{-}C_7$, not between values inferred from the straight line. The value based on C_8 to C_{11} is the best estimate of interpolation error.

Having established a typical boiling-point uncertainty, the effect on the calculated dewpoint temperature can be derived. A normal dewpoint calculation is performed and then compared with the one for which the values of the fraction boiling points are increased by $0,75\text{ }^{\circ}\text{C}$ throughout. Table B.4 shows the result.

Table B.4 — Effect of boiling-point errors on dewpoint temperatures

Pressure MPa (bar)	Dewpoint (normal)	Dewpoint (+ error)	Difference
0,5 (5)	– 30,05	– 29,73	0,32
1,0 (10)	– 22,85	– 22,56	0,29
1,5 (15)	– 18,95	– 18,70	0,25
2,0 (20)	– 16,57	– 16,33	0,24
2,5 (25)	– 15,10	– 14,88	0,22
3,0 (30)	– 14,28	– 14,08	0,20
3,5 (35)	– 13,96	– 13,77	0,19
4,0 (40)	– 14,06	– 13,89	0,17
4,5 (45)	– 14,55	– 14,40	0,15
5,0 (50)	– 15,43	– 15,28	0,15
5,5 (55)	– 16,70	– 16,57	0,13
6,0 (60)	– 18,45	– 18,33	0,12
6,5 (65)	– 20,82	– 20,71	0,11
7,0 (70)	– 24,15	– 24,05	0,10
mean error	—	—	0,19

The mean value of $0,19\text{ }^{\circ}\text{C}$ coincides with the value at the highest dewpoint temperature, at $3,5\text{ MPa}$ (35 bar). Combining this with the $0,10\text{ }^{\circ}\text{C}$ error from boiling point estimation gives a total of $0,29\text{ }^{\circ}\text{C}$. Allowing a total uncertainty of $0,5\text{ }^{\circ}\text{C}$ for fraction effects leaves a comfortable margin.

Annex C (informative)

Precision of area ratio

For an illustrative analysis, Table C.1 lists the peaks measured, the means, standard deviations and relative standard deviations of the ratios of peak areas to that of *n*-pentane, and the natural logarithms of the means and standard deviations of the area ratios.

Table C.1 — Component data

Component	Area ratios to <i>n</i> -C ₅			Area ratios	
	Mean	Standard deviation	Relative standard deviation %	Natural logarithm of the mean	Natural logarithm of the standard deviation
<i>n</i> -C ₅	1	0	0,00	—	—
2,2-di-me-C ₄	0,122 838	0,000 160	0,13	– 2,10	– 8,74
2,3-di-me-C ₄	0,075 513	0,001 342	1,78	– 2,58	– 6,61
2-me-C ₅	0,373 544	0,001 125	0,30	– 0,98	– 6,79
3-me-C ₅	0,207 924	0,000 166	0,08	– 1,57	– 8,71
<i>n</i> -C ₆	0,492 807	0,000 180	0,04	– 0,71	– 8,62
C ₇ (a) ^a	0,030 047	0,000 277	0,92	– 3,50	– 8,19
C ₇ (b)	0,022 051	0,000 048	0,22	– 3,81	– 9,95
C ₇ (c)	0,026 011	0,000 321	1,24	– 3,65	– 8,04
C ₇ (d)	0,011 231	0,000 046	0,41	– 4,49	– 9,98
Benzene	0,004 394	0,000 115	2,62	– 5,43	– 9,07
C ₇ (e)	0,015 291	0,000 142	0,93	– 4,18	– 8,86
cyC ₆	0,093 074	0,000 187	0,20	– 2,37	– 8,58
C ₇ (f)	0,120 672	0,000 093	0,08	– 2,11	– 9,29
C ₇ (g)	0,104 495	0,000 136	0,13	– 2,26	– 8,90
C ₇ (h)	0,014 378	0,000 046	0,32	– 4,24	– 9,98
<i>n</i> -C ₇	0,155 427	0,000 137	0,09	– 1,86	– 8,89
me-cycC ₆	0,075 853	0,000 163	0,22	– 2,58	– 8,72
C ₈ (a)	0,015 573	0,000 026	0,17	– 4,16	– 10,54
C ₈ (b)	0,003 958	0,000 008	0,19	– 5,53	– 11,78
C ₈ (c)	0,000 322	0,000 017	5,37	– 8,04	– 10,97
C ₈ (d)	0,000 322	0,000 015	4,64	– 8,04	– 11,11
Toluene	0,001 689	0,000 047	2,81	– 6,38	– 9,96
C ₈ (e)	0,003 262	0,000 005	0,16	– 5,73	– 12,14

Table C.1 (continued)

Component	Area ratios to $n-C_5$			Area ratios	
	Mean	Standard deviation	Relative standard deviation %	Natural logarithm of the mean	Natural logarithm of the standard deviation
$C_8(f)$	0,024 304	0,000 065	0,27	- 3,72	- 9,64
$C_8(g)$	0,016 720	0,000 043	0,26	- 4,09	- 10,05
$C_8(h)$	0,003 751	0,000 015	0,39	- 5,59	- 11,13
$C_8(i)$	0,002 815	0,000 027	0,97	- 5,87	- 10,51
$C_8(j)$	0,000 854	0,000 041	4,75	- 7,07	- 10,11
$n-C_8$	0,022 363	0,000 080	0,36	- 3,80	- 9,44
$C_9(a)$	0,000 544	0,000 037	6,75	- 7,52	- 10,21
$C_9(b)$	0,000 980	0,000 003	0,30	- 6,93	- 12,73
$C_9(c)$	0,001 057	0,000 013	1,22	- 6,85	- 11,26
$C_9(d)$	0,001 686	0,000 017	0,98	- 6,39	- 11,01
$C_9(e)$	0,001 927	0,000 030	1,57	- 6,25	- 10,41
$C_9(f)$	0,001 570	0,000 011	0,68	- 6,46	- 11,45
$C_9(g)$	0,001 576	0,000 031	1,94	- 6,45	- 10,39
$C_9(h)$	0,000 408	0,000 012	2,86	- 7,80	- 11,36
$C_9(i)$	0,001 523	0,000 022	1,45	- 6,49	- 10,72
$C_9(j)$	0,003 175	0,000 030	0,93	- 5,75	- 10,43
$C_9(k)$	0,002 043	0,000 016	0,80	- 6,19	- 11,02
$C_9(l)$	0,000 157	0,000 017	10,75	- 8,76	- 10,99
$C_9(m)$	0,000 206	0,000 007	3,50	- 8,49	- 11,84
$n-C_9$	0,003 630	0,000 049	1,36	- 5,62	- 9,92
$C_{10}(a)$	0,000 102	0,000 005	5,14	- 9,19	- 12,16
$C_{10}(b)$	0,000 115	0,000 010	8,64	- 9,07	- 11,52
$C_{10}(c)$	0,000 196	0,000 013	6,63	- 8,54	- 11,25
$C_{10}(d)$	0,000 171	0,000 009	5,19	- 8,67	- 11,63
$C_{10}(e)$	0,000 114	0,000 012	10,52	- 9,08	- 11,33
$C_{10}(f)$	0,000 166	0,000 010	5,81	- 8,71	- 11,55
$C_{10}(g)$	0,000 263	0,000 053	20,00	- 8,24	- 9,85
$C_{10}(h)$	0,000 235	0,000 012	5,11	- 8,36	- 11,33
$C_{10}(i)$	0,000 149	0,000 014	9,40	- 8,81	- 11,18
$C_{10}(j)$	0,000 154	0,000 011	7,34	- 8,78	- 11,39
$C_{10}(k)$	0,000 147	0,000 007	4,49	- 8,82	- 11,93
$C_{10}(l)$	0,000 292	0,000 005	1,69	- 8,14	- 12,22

Table C.1 (continued)

Component	Area ratios to $n-C_5$			Area ratios	
	Mean	Standard deviation	Relative standard deviation %	Natural logarithm of the mean	Natural logarithm of the standard deviation
C ₁₀ (m)	0,000 190	0,000 007	3,67	- 8,57	- 11,87
C ₁₀ (n)	0,000 136	0,000 008	5,78	- 8,90	- 11,75
C ₁₀ (o)	0,000 192	0,000 015	7,66	- 8,56	- 11,12
$n-C_{10}$	0,000 589	0,000 012	2,06	- 7,44	- 11,32
C ₁₁ (a)	0,000 093	0,000 004	3,98	- 9,28	- 12,51
C ₁₁ (b)	0,000 181	0,000 012	6,64	- 8,62	- 11,33
C ₁₁ (c)	0,000 048	0,000 004	7,51	- 9,95	- 12,53
C ₁₁ (d)	0,000 051	0,000 006	11,69	- 9,88	- 12,02
$n-C_{11}$	0,000 141	0,000 004	2,68	- 8,87	- 12,49
C ₁₂ (a)	0,000 222	0,000 023	10,43	- 8,41	- 10,67
$n-C_{12}$	0	0	—	—	—
FR6 ^b	1,272 627	0,000 986	0,08	0,24	- 6,92
FR7	0,499 603	0,000 175	0,03	- 0,69	- 8,65
FR8	0,094 243	0,000 167	0,18	- 2,36	- 8,70
FR9	0,020 481	0,000 148	0,72	- 3,89	- 8,82
FR10	0,002 672	0,000 144	5,38	- 5,92	- 8,85
FR11	0,000 141	0,000 004	2,68	- 8,87	- 12,49
FR12	0,000 222	0,000 023	10,43	- 8,41	- 10,67

^a C₇(a), C₇(b), etc., are unidentified C₇ components.

^b FR6, FR7, etc., are the fractions or groups which are the sum of all the C₆ alkanes, all the C₇ alkanes, etc. Individual C₆ alkanes are identified, so either the individuals or FR6 can be used, but not both.

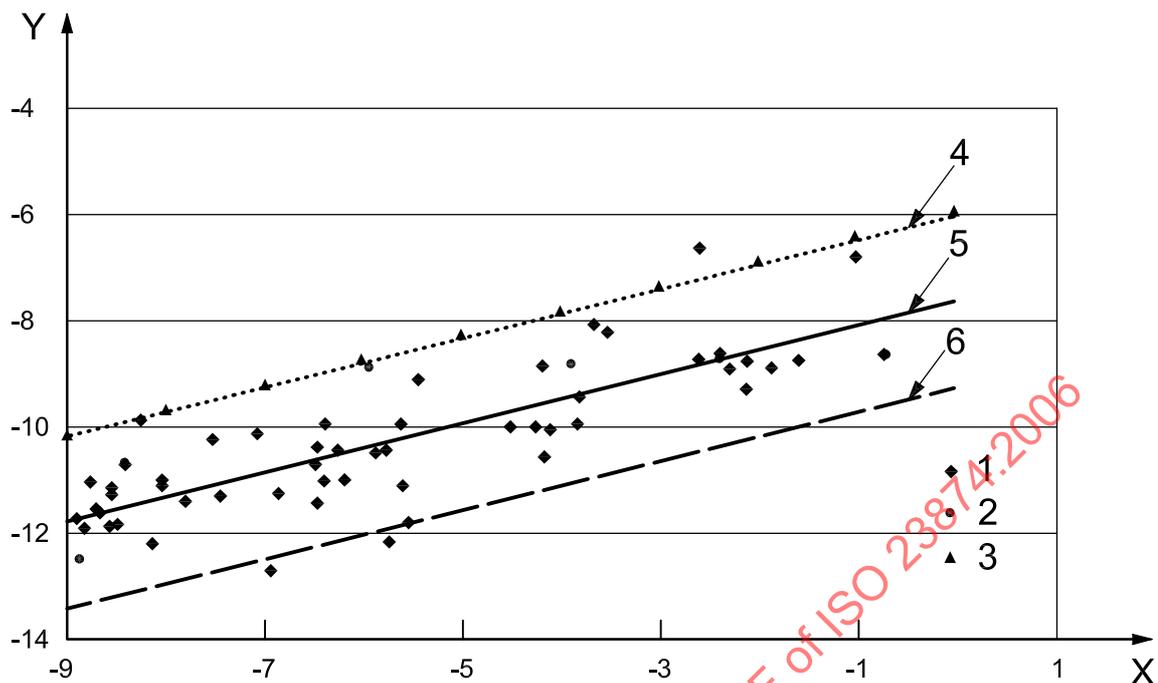
The logarithms of the means and standard deviations of the area ratios are plotted in Figure C.1, where the individual peaks and the fractions or groups are separately identified. Regression analysis shows that the relationship between the standard deviation, s , and the mean peak area ratio, \bar{R}_{Am} , is described by Equation (C.1):

$$\ln s = - 7,618 9 + 0,461 9 \times \ln \bar{R}_{Am} \tag{C.1}$$

This regression line is also shown in Figure C.1. The 95 % confidence limits for the regression line have been calculated and are also plotted in the figure. These limits show little curvature and so the upper limit, which is the criterion that should be used, can be closely approximated by a straight line given by Equation (C.2):

$$\ln s = - 5,9 + 0,47 \times \ln \bar{R}_{Am} \tag{C.2}$$

and is also shown in Figure C.1.

**Key**

- X natural logarithm of the area ratio
 Y natural logarithm of the standard deviation ratio
- 1 data points for individual compounds
 2 data points for groups of compounds
 3 limit
 4 upper 95 %
 5 regression line
 6 lower 95 %

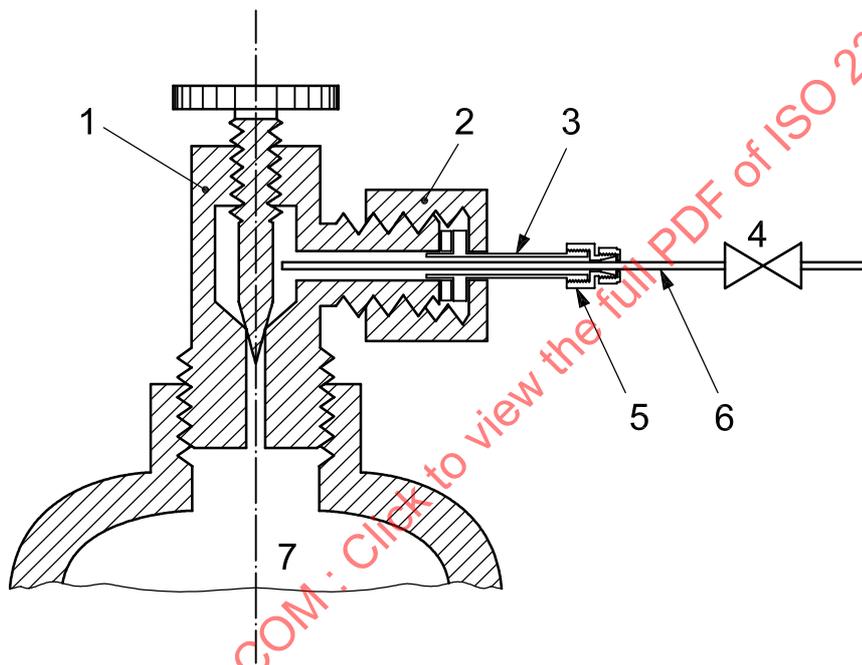
Figure C.1 — Relationship between standard deviations and means of peak area ratios

Annex D
(informative)

Recommendations on sample calibration gas introduction

Trace levels of higher hydrocarbons in both calibration gases and samples are easily adsorbed onto surfaces in pressure-reduction equipment and transfer lines. This is a reversible process and so representative sample transfer can be achieved with sufficient purging. "Sufficient" can, however, be excessive if the quantity of sample is limited, and it is beneficial to limit adsorption possibilities to save both time and sample amount.

Figure D.1 shows a configuration that has been shown to be satisfactory.



Key

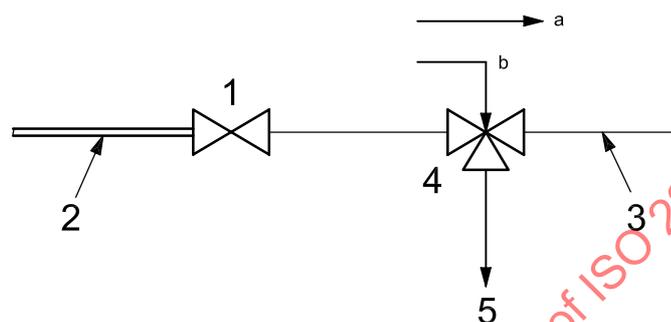
- 1 cylinder valve
- 2 nut
- 3 stem
- 4 needle valve
- 5 0,32 cm (1/8 in) outside diameter (od) tubing fitting drilled through
- 6 0,32 cm (1/8 in) od tubing
- 7 cylinder

Figure D.1 — Cylinder outlet arrangement

Typical cylinder-outlet nut and stem are used, chosen to suit the cylinder type. The stem is terminated with a female stud coupling that has a 0,32 cm (1/8 in) od compression fitting. The coupling is drilled through so that the tubing can slide through the fitting and down the cylinder stem. The tubing should preferably be internally treated to minimize adsorption problems.

With the nut tightened onto the cylinder outlet, the tubing is slid through the fitting until it is felt to contact the interior of the cylinder valve. The tubing is withdrawn by a small amount (about 1 mm) and the compression fitting tightened. A high-quality needle valve suitable for the maximum cylinder pressure is attached to the outlet of the 0,32 cm (1/8 in) tubing and further tubing fitted from the outlet of the needle valve to the sampling valve on the chromatograph. This may be 0,32 cm (1/8 in) or 0,16 cm (1/16 in) tubing, depending on the distance required.

If the chromatograph is fitted with a means for stopping the sample flow before injection, it is necessary to take care to prevent pressure build-up as gas continues to flow through the needle valve into a closed system. Figure D.2 shows a pipework layout that avoids this problem.



Key

- 1 needle valve
- 2 0,32 cm (1/8 in) od tubing from cylinder
- 3 0,16 cm (1/16 in) od tubing to GC valve
- 4 3-way valve
- 5 vent
- a Position 1.
- b Position 2.

Figure D.2 — Sample stop flow

With all connections secure, the cylinder valve is opened and the needle valve adjusted to give the desired purge flow. This would typically be 5 ml/min to 10 ml/min. It can be advisable to start with a higher purge rate (50 ml/min to 60 ml/min) for 1 min or 2 min to clear the cylinder outlet. Once the flow has been set to the normal purge rate, it should be maintained for the number of analyses required. This maintains the equilibrium between hydrocarbons in the gas phase and those that are inevitably adsorbed on the surfaces of the tubing and valves.

The three-way valve allows gas to continue to flow through the gas-sampling valve or to be diverted to vent, shutting off the flow to the chromatograph. Flow should be restored through the gas sampling valve as soon as possible after injection so that the surfaces downstream of the three-way valve are kept equilibrated.