INTERNATIONAL STANDARD

ISO 6975

Second edition
1997-04-01

Natural gas — Extended analysis — Gas-chromatographic method

Gaz naturel — Analyse étendue — Méthode par chromatographie en phase gazeuse

Reference number
ISO 6975:1997(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
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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.

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.

International Standard ISO 6975 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition cancels and replaces the first edition (ISO 6975:1986), which has been technically revised.

Annexes A to D of this International Standard are for information only.

Introduction

This International Standard describes the specifications that an accurate method for the complete and extended analysis of natural gas shall fulfil.

The analytical methods involve injection of natural gas on to packed or open tubular (capillary) columns in one or more gas chromatographs. The components coming off the columns are detected by thermal-conductivity detector (TCD) or flame ionization detector (FID).

Compared to other analytical methods, the extended gas-chromatographic analysis supplies considerable knowledge of the individual components in the natural-gas mixture. This allows quantitative measurement of particular components in the C_{6+} fraction and calculation of physical properties. Although the higher hydrocarbons influence physical properties such as calorific values and density by less than 0,3 % and 0,004 %, respectively, knowledge of them is required for evaluation of the pseudo-values for the C_{6+} fraction.

In addition, vapour phase equilibrium calculations often require detailed composition data, especially of hydrocarbons with carbon numbers higher than 6.

The simultaneous determination of benzene and other aromatics is needed for gas consumers using natural gas as a chemical feedstock since these components can interfere in some processes.

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Natural gas — Extended analysis — Gas-chromatographic method

1 Scope

This International Standard describes the specifications for the quantitative analysis of the following components of natural gas:

- helium
- hydrogen
- argon
- oxygen
- nitrogen
- carbon dioxide
- saturated hydrocarbons from C_1 to C_5
- hydrocarbon fractions from C_6 upwards
- aromatic compounds as benzene and toluene

The gas-chromatographic methods determine the components in the following ranges:

oxygen:	0,001 % (*n*/*n*)	to	0,5 % (*n*/*n*)
helium:	0,001 % (*n*/*n*)	to	0,5 % (*n*/*n*)
hydrogen:	0,001 % (*n*/*n*)	to	0,5 % (*n*/*n*)
argon:	0,001 % (*n*/*n*)	to	0,5 % (*n*/*n*)
nitrogen:	0,001 % (*n*/*n*)	to	40 % (*n*/*n*)
carbon dioxide:	0,001 % (*n*/*n*)	to	40 % (*n*/*n*)
methane:	50 % (*n*/*n*)	to	100 % (*n*/*n*)
ethane:	0,02 % (*n*/*n*)	to	15 % (*n*/*n*)
propane:	0,001 % (*n*/*n*)	to	5 % (*n*/*n*)

higher hydrocarbons: The method can measure hydrocarbon components from 10^{-6} (*n*/*n*) up to their maximum concentration, which is compatible with the requirement that the gas is free from hydrocarbon condensate at any pressure in the range 1×10^2 kPa to 7×10^3 kPa.

This method is not intended for the determination of oxygen compounds (water vapour, methanol, glycols) or sulfur compounds.

It is not possible to make unambiguous identifications of hydrocarbons above C_6. Even where "spiking" a gas mixture with known components shows where they elute, it cannot be stated with certainty that such a component is the only one with that retention time. Unidentified components are classified according to the carbon number which the analysis indicates to be appropriate. While this is a necessary simplification, it does allow a reasonable quantitative value to be obtained.

This method is intended for use in situations where the hexanes plus compositional breakdown and/or the complete analysis is desired.

The method is not intended for dense phase gases whose pressure exceeds the cricondebar (critical condensation pressure), or for gas samples containing any measurable hydrocarbon condensate, liquid water or process fluid such as methanol or glycols (see ISO 6570-1 and ISO 10715).

Gases which have been treated for transmission are unlikely to contain detectable levels of hydrocarbons above C_{12}. Samples taken from nearer the well head, before the gas has reached gas treatment plants, may contain hydrocarbons to C_{16} or above.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

ISO 6142:1981, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6143:1981, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

ISO 6326-1:1989, *Natural gas — Determination of sulfur compounds — Part 1: General introduction.*

ISO 6326-2:1981, *Gas analysis — Determination of sulfur compounds in natural gas — Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds.*

ISO 6326-3:1989, *Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry.*

ISO 6326-4:1994, *Natural gas — Determination of sulfur compounds — Part 4: Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants.*

ISO 6326-5:1989, *Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method.*

ISO 6570-1:1983, *Natural gas — Determination of potential hydrocarbon liquid content — Part 1: Principles and general requirements.*

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

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[1] To be published. (Revision, in parts, of ISO 6974:1984)

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

ISO 6974-3:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, inert gases and hydrocarbons up to* C_8.

ISO 6974-4:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and hydrocarbons* (C_1 *up to* C_5 *and* C_{6+}) *for a laboratory and on-line measuring system.*

ISO 6974-5:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and hydrocarbons* (C_1 *up to* C_5 *and* C_{6+}) *for a laboratory and on-line process application.*

ISO 10715:1997, *Natural gas — Sampling guidelines.*

ISO 14111:1997, *Natural gas — Guidelines for traceability in analysis.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 resolution: Gas-chromatographic resolution is a characteristic of the separation of two adjacent peaks and is measured as twice the distance between the maxima of the named peaks divided by the sum of the intercepts on the baseline made by tangents drawn to the peaks at half their height (see figure 1). The resolution R_{AB} may be expressed by the following equation:

$$R_{AB} = 2 \times \frac{d_R(B) - d_R(A)}{w(B) + w(A)}$$

where

$d_R(A)$ and $d_R(B)$ are the retention distances of the eluted components A and B;

$w(A)$ and $w(B)$ are the widths of the respective peaks at their base.

3.2 main components: The nitrogen, carbon dioxide and saturated hydrocarbons from methane to n-pentane present in a natural-gas sample.

3.3 associated components: The helium, hydrogen, argon and oxygen present in a natural-gas sample.

3.4 trace components: The hydrocarbons and/or groups of hydrocarbons from n-pentane upwards present in a natural-gas sample.

3.5 other components: Those components for which this method is not intended, such as oxygen compounds (water vapour, methanol, glycol) and sulfur compounds.

3.6 response: The response is the output signal for a component that is measured as peak area or peak height (more often as peak area).

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[2] To be published. (Revision, in parts, of ISO 6974:1984)

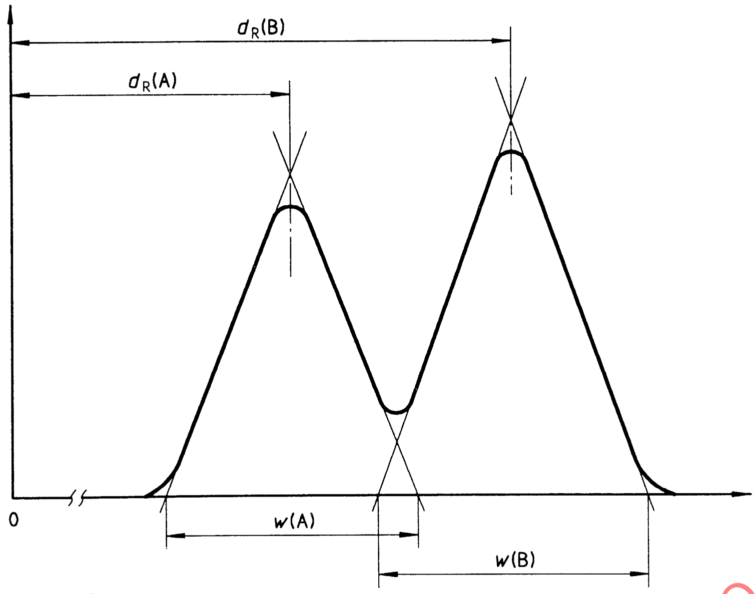

Figure 1 — Resolution of two adjacent peaks

3.7 reference component: The component present in the working-reference gas mixture against which the relative response factors of sample components not present in the working-reference gas mixture are defined.

3.8 relative response factor (for an FID)**:** The relative response factor K_i is calculated as the ratio of the carbon number of the reference component to the carbon number of a particular sample component. Thus if the reference component is *n*-butane, then the relative response factor for C_7 components in the sample (heptane isomers, methylcyclohexane, toluene, etc.) is calculated as

$$K_i = \frac{4}{7} = 0{,}571$$

3.9 concentration of a group of components: The concentration of a group of components is the sum of the concentrations of the normal hydrocarbon components and their isomers. The response of the group is the sum of the responses of these components. The relative response of the group is equal to the relative response of the normal alkane of the group. The group is named according to the normal alkane of the group.

4 Principle

The components to be determined in a gaseous sample are physically separated by gas chromatography and compared with calibration data obtained under the same set of conditions.

The main components are separated using a packed or open tubular column in a gas chromatograph and detected by TCD. An FID may be used additionally.

The analytical system used separates oxygen from nitrogen to check air contamination in the sample.

The hydrocarbons from propane upwards are separated using an open tubular column in a gas chromatograph and detected by FID. The method assumes that the response of an FID to hydrocarbons is proportional to the carbon number. Hence, components not present in the calibration gas are quantified by means of knowledge of their carbon number.

Associated components can be determined by following special gas-chromatographic techniques (see e.g. the various parts of ISO 6974).

Identification of hydrocarbons is made by linear retention index calculation. The retention index RI_i of a component i is calculated as

$$\mathrm{RI}_i = 100 \times \frac{t_i - t_x}{t_{(x+1)} - t_x} + 100x$$

where

t_i is the retention time of component i;

t_x is the retention time of an appropriate n-alkane of carbon number x;

$t_{(x+1)}$ is the retention time of an n-alkane of carbon number $(x + 1)$.

This method of calculation was described by Hayes and Pitzer[3] (see annex D) and is true only for temperature-programmed analysis.

A list of retention indices is given in annex C.

The retention indices should be seen as indications rather than definite values. They are more valuable in indicating the difference Δ(RI) between compounds.

5 Analysis and analytical requirements

5.1 Apparatus and materials

5.1.1 Analytical system

The analytical system shall consist of a gas-chromatographic unit and an integrator and data reduction system.

The gas-chromatographic unit may consist of one or more gas chromatographs capable of isothermal and/or temperature-programmed operation and equipped with a TCD and/or an FID and a sample transfer and introduction system.

Each gas chromatograph shall be connected to an integrator.

5.1.2 Reference gas mixtures

5.1.2.1 Certified-reference gas mixtures (CRMs)

Certified-reference gas mixtures are used for the determination of the response curves of the measuring system. CRMs can be binary or multicomponent mixtures and shall be prepared gravimetrically in accordance with ISO 6142 or certified and validated by comparison with primary-standard gas mixtures (PSMs) of closely related composition (see ISO 6143).

The composition of the CRM shall be traceable to the composition of the PSM whenever available (see ISO 14111).

In the hierarchy of reference materials, this type of gas mixture corresponds to the certified reference material.

5.1.2.2 Working-reference gas mixtures (WRMs)

These mixtures are used as working standards for the regular calibration of the measuring system. WRMs can be binary or multicomponent mixtures and shall be prepared gravimetrically in accordance with ISO 6142 or certified and validated by comparison with CRMs of closely related composition (see ISO 6143).

The composition of the WRM shall be traceable to the composition of the PSM whenever available (see ISO 14111).

The concentration of trace components will be calculated with the aid of a reference component, so the WRM need only contain main components.

For the determination of the main components, a WRM containing nitrogen, carbon dioxide and normal hydrocarbons from methane to *n*-butane as a minimum is required. A second WRM containing helium, argon, hydrogen and oxygen is also required for the determination of the associated components. In both mixtures, methane shall be the complementary gas.

Optionally, a single gas mixture containing all the above-mentioned components can be used.

For safety reasons, regulations may require that a WRM containing oxygen be prepared with an inert complementary gas.

The concentration of each component in the WRM shall be within the tolerances given in table 1 relative to those expected in the sample gas.

Table 1 — Tolerance between concentrations of components in the WRM and sample

Actual component concentration in sample % (*n*/*n*)	**Derivation of component concentration in WRM** (% relative to sample concentration)
up to 0,1	± 100
0,1 to 1	± 50
1 to 10	± 10
10 to 50	± 5
50 to 100	± 3

5.1.2.3 Control gas

A control gas is a high-pressure gas mixture of known composition containing all the components present in the working-reference gas mixture. A control gas can be either a sample gas with a composition determined in accordance with ISO 6143 or a multicomponent mixture prepared in accordance with ISO 6142.

A control gas is used for the determination of the mean (μ) and standard deviation (σ) of the concentrations of the components detected.

5.2 Structure of the analysis

The analysis takes into account the following components:

x_{mc}: main and associated components determined by using response curves, single-point calibration or a reference component;

x_{bc}: trace components determined by using a reference component;

x_{oc}: other components that are measured by using other methodologies (see e.g. the various parts of ISO 6326).

The summation of the concentrations, in % (*n*/*n*), is defined as 100:

$$x_{mc} + x_{bc} + x_{oc} = 100$$

5.3 Resolution

5.3.1 Main components

The resolution between two adjacent peaks for each component from nitrogen to 2-methylpropane shall not be less than 2.

The resolution between two adjacent peaks for each component from 2-methylpropane to *n*-pentane shall not be less than 4.

In the event that a valve switching is performed in multicolumn analysis, the resolution between the peak of the component eluted before switching the valve and the peak of the component that would be eluted without the valve switching shall not be less than 4.

As oxygen is detected only to check air contamination of the sample gas, the resolution between the peaks of oxygen and nitrogen shall not be less than 1,5.

5.3.2 Trace components

The column used for trace components shall also be capable of separating some of the main components, i.e. hydrocarbons from C_3 to C_5.

To achieve satisfactory separation of light aromatics and cycloparaffins, the column shall be capable of the following resolution:

> The ratio of the height of the ethane peak to the height of the valley between ethane and propane shall not be less than 1 500:1. For this measurement, the sample shall contain approximately 3 % (*n*/*n*) of ethane.
>
> The resolution between 2-methylpropane and *n*-butane shall not be less than 4.
>
> The resolution between *n*-pentane and *n*-hexane shall not be less than 15.
>
> The resolution between *n*-octane and *n*-nonane shall not be less than 30.

NOTE — If such measurements are made from recorder charts, different conditions from those normally chosen to display the chromatogram will be necessary. Thus two analyses at very different attenuations will be needed to measure the valley between ethane and propane and the peak height of ethane.

5.3.3 Associated components

The resolution between two adjacent peaks shall not be less than 1,5.

6 Procedures

6.1 Setting up the analytical system

Set up all the analytical system in accordance with the manufacturer's instructions and the analytical methods chosen.

The sample cylinder and transfer line shall be heated sufficiently to avoid condensation and sorption of higher hydrocarbons in the sampling system. The sample cylinder and transfer line shall be heated to at least 10 K above the sampling temperature. Special precautions shall be taken at any spot in the system where pressure reduction occurs.

NOTE — The temperature of a natural gas will drop by approximately 0,005 K per kilopascal of pressure reduction.

6.2 Injection

Purge the sample valve slowly with the gas to be analysed, using at least 20 times the volume of the valve and associated pipework.

Stop the purge to allow the gas to reach the temperature of the valve and ambient pressure, then inject. The working-reference gas mixture shall be injected in the same way.

NOTE — It is also possible to introduce the sample into a previously evacuated sample loop and allow it to equilibrate to ambient pressure before injection.

7 Calibration and control charts

7.1 Calibration

Main components, except C_4 and C_5 hydrocarbons, shall be analysed using multi-level calibration.

C_4 and C_5 hydrocarbons can be analysed either using single-point calibration or using relative FID response factors.

Trace components shall be analysed using relative FID response factors. The concentration of the reference component shall be less than 1 % (n/n).

Associated components shall be analysed using single-point calibration.

7.1.1 Multi-level calibration (determination of response curve)

With multi-level calibration, the response curve for the detector over the range to be analysed is determined. This is done with at least seven calibration points for each component, distributed equally over the range. These seven points shall be determined using at least seven certified-reference gas mixtures as described in 5.1.2.1.

The response curve can be determined for each component as described in annex A.

NOTES

1 Using seven calibration points for each component enables fourth-order detector behaviour to be confirmed with a high sensitivity. Third-order behaviour mostly indicates a defective detector.

2 When determining a multi-level response curve, it is preferable that the ambient pressure is constant for the whole of the calibration cycle since the amount injected is directly proportional to the ambient pressure. One way of avoiding problems is to record the ambient pressure at each injection of calibration gas and then correct the measured response to standard pressure using the following equation:

$$R_{c,st} = R_c \times \frac{p_{st}}{p_c}$$

where

$R_{c,st}$ is the response corrected to standard pressure;

R_c is the measured response;

p_c is the ambient pressure, in kilopascals;

p_{st} is standard atmospheric pressure (101,325 kPa).

7.1.2 Single-point calibration (determination of response curve)

Single-point calibration is used on the assumption that the detector behaviour intercepts the origin and is linear over a small range around the point at which the chromatograph is calibrated.

7.2 Regular calibration

Carry out regular calibration using a WRM as described in 5.1.2.2. Do this by injecting, in accordance with the procedures given in 6.2, the WRM twice and taking the mean result to adjust the response curve.

For the calibration interval, see 7.3.

7.3 Control charts

Inspection of the calibration data (see 7.1 and 7.2) can give an indication as to whether the equipment and the method is working satisfactorily. However, the determination of the response curve is intended to define the instrument response to the components present in the WRM, and it is therefore inappropriate to use this same data to test the method. A cylinder of control gas of known composition, as described in 5.1.2.3, typical of the natural gases for which the method is to be used, is required.

Carry out a control gas analysis with each batch of sample. Its composition is unvarying and so the results of this analysis can be used as an indication as to whether the method is no longer working satisfactorily or recalibration is necessary, or both. Before first use, analyse the control gas, using the method and WRM as specified, sufficient times (at least 10) for precision data to be calculated. For each component in the control gas, calculate the mean concentration and its standard deviation. These values should be typical of those that would be expected for this control gas on subsequent occasions.

Assuming that the analytical results for the control gas follow a normal distribution, 68,3 % of any set of repeat results should fall within ± 1 standard deviation of the mean value, 95,4 % should fall within ± 2 standard deviations and 99,7 % should fall within ± 3 standard deviations. In other words, while the system is behaving normally, an individual result obtained on the control gas would fall outside ± 3 standard deviations on only 3 occasions out of 1 000. This is sufficiently rare for such a result to be regarded as representing a real change either in the method or in the determination of the response curve, which requires remedial action to be taken (the control gas is assumed to be stable, and not giving rise to false readings). Any individual result may fall outside ± 2 standard deviations on 1 occasion in 20. Such a result should be seen as a warning, not requiring action unless the next result also exceeds this limit.

7.4 Use of control charts

Construct, for each component in the control gas, a control chart with the mean value for the component and concentrations representing the mean ± 2 standard deviations and the mean ± 3 standard deviations marked on the y-axis. Draw lines parallel to the x-axis from these points. Each time the control gas is analysed, plot the value using the x-axis as the time scale.

If it is known that the standard deviation for a component varies with concentration, and that the range of concentrations likely to be encountered is sufficiently wide for these variations to be significant, it may be advisable to have two control charts for such a component, representing the system behaviour towards test gases of different compositions.

Compare the plotted values from each analysis of the control gas with the mean value and the ± 2 standard deviation lines and ± 3 standard deviation lines. Figure 2 shows a typical example for nitrogen at around 2,5 %. This shows relatively little scatter around the mean value, and gives reassurance that the measurement of this component is satisfactory.

If individual results fall outside the warning limits (± 2 standard deviations) more than just occasionally, this can indicate that

— either there is a systematic tendency for results to be too high or too low (provided that only the upper or the lower warning limit has been crossed),

— or the random error for measurement of that component has increased (if both limits are crossed randomly).

Figure 3 shows a control chart for carbon dioxide. Results for the first few days remain close to the mean, but the plot then shows a clear drift downwards. Although the – 3 standard deviation limit has not been exceeded, this clearly suggests that some systematic error is present, allowing underestimation of the carbon dioxide.

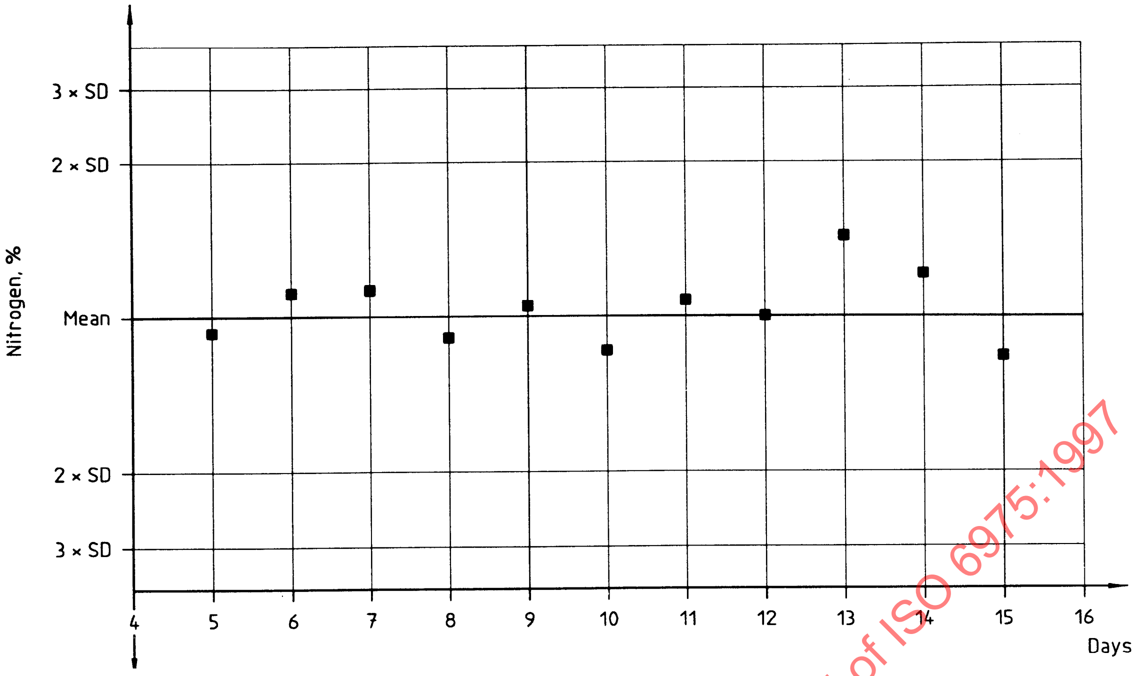

Figure 2 — Example of a control chart for nitrogen

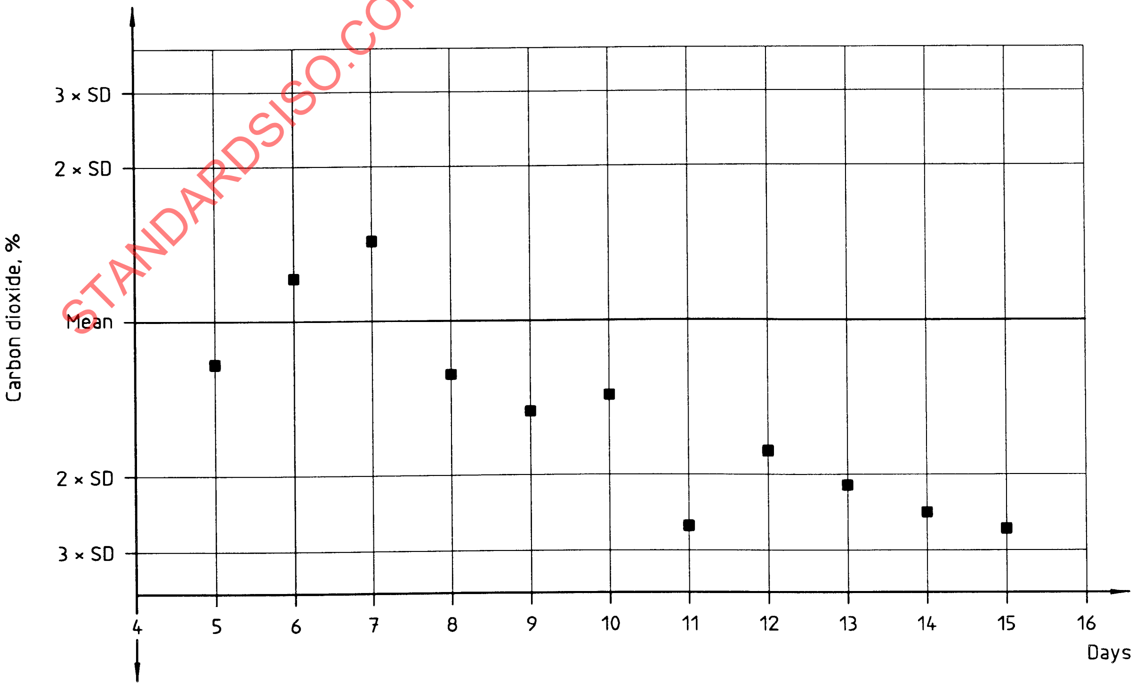

Figure 3 — Example of a control chart for carbon dioxide

Figure 4 illustrates an increased random error. Days 5 to 8 appear normal, but from days 9 to 13 much greater but non-systematic variations occur. Once again, no single result exceeds ± 3 standard deviations, but some attention to the method is clearly required.

The initial control limits selected are the result of a single repeatability measurement made before the chart is drawn. More information becomes available as the chart is used, and it is reasonable to redraw these limits after 25 or 50 data points have been collected. This assumes, of course, that the method has remained stable, as in figure 2. Do not use data which clearly indicate some fault to revise the control limits.

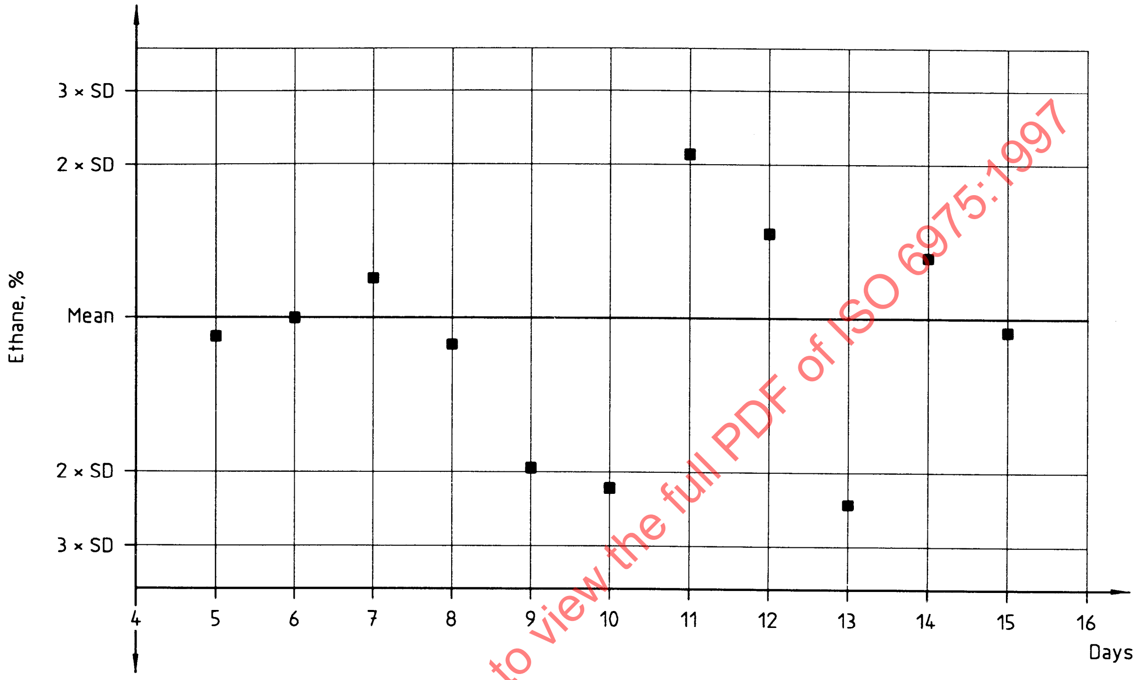

Figure 4 — Example of a control chart for ethane

8 Calculations

8.1 Uncorrected concentrations

8.1.1 Main components

Calculate the uncorrected concentration $x_{i\text{s}}$, in % (n/n), of each of the main components in the sample using the following equation:

$$x_{i\text{s}} = \frac{a_i R_{i\text{s}}^3 + b_i R_{i\text{s}}^2 + c_i R_{i\text{s}} + d_i}{a_i R_{i\text{ws}}^3 + b_i R_{i\text{ws}}^2 + c_i R_{i\text{ws}} + d_i} \times x_{i\text{ws}} \qquad \ldots (1)$$

where

a_i, b_i, c_i and d_i are constants for the ith component;

$R_{i\text{s}}$ is the response for the ith component in the sample;

$R_{i\text{ws}}$ is the response for the ith component in the WRS;

$x_{i\text{ws}}$ is the uncorrected concentration, in % (n/n), of the ith component in the WRS.

NOTE — If C_4 and C_5 hydrocarbons are determined using single-point calibration and equation (1), the values of a_i, b_i and d_i are zero, while the value of c_i is 1.

8.1.2 Trace components

Calculate the uncorrected concentrations x_{is}, in % (n/n), of each trace components in the sample using the following equation:

$$x_{is} = K_{\text{bc}i} \times \frac{a_{\text{bc}} R_{is}^3 + b_{\text{bc}} R_{is}^2 + c_{\text{bc}} R_{is} + d_{\text{bc}}}{a_{\text{bc}} R_{\text{bcws}}^3 + b_{\text{bc}} R_{\text{bcws}}^2 + c_{\text{bc}} R_{\text{bcws}} + d_{\text{bc}}} \times x_{\text{bcws}} \qquad \ldots (2)$$

where

a_{bc}, b_{bc}, c_{bc} and d_{bc} are constants for the reference component;

$K_{\text{bc}i}$ is the relative response factor for the reference and ith components;

R_{is} is the response for the ith component in the sample;

R_{bcws} is the response for the reference component in the WRS;

x_{bcws} is the uncorrected concentration, in % (n/n), of the reference component in the WRS.

NOTE — If the reference component is different from propane, the values of a_{bc}, b_{bc} and d_{bc} are zero, while the value of c_{bc} is 1.

8.1.3 Associated components

Calculate the uncorrected concentration x_{is}, in % (n/n), of each of the associated components in the sample using the following equation:

$$x_{is} = \frac{R_{is}}{R_{i\text{ws}}} \times x_{i\text{ws}}$$

where

R_{is} is the response for the ith component in the sample;

$R_{i\text{ws}}$ is the response for the ith component in the WRS;

$x_{i\text{ws}}$ is the uncorrected concentration, in % (n/n), of the ith component in the WRS.

8.1.4 Other components

This method is not intended for the determination of oxygen compounds (water vapour, methanol, glycol) or sulfur compounds but, if the content of such compounds is known from other methods, their total concentration x_{oc}, in % (n/n), shall be calculated using the equation:

$$x_{\text{oc}} = \sum_{j=1}^{m} x_{j\text{oc}}$$

where

$x_{j\text{oc}}$ is the concentration, in % (n/n), of the jth component;

m is the number of components taken into account.

8.2 Correction

If the sum of all concentrations of the components detected is between 99 % (n/n) and 101 % (n/n), correct the results to 100 %. If it is not, re-analyse.

Carry out the correction as follows:

$$x_i^* = \frac{x_{is}}{\sum_{i=1}^{k} x_{is}} \times (100 - x_{ocs})$$

where

x_i^* is the corrected concentration, in % (n/n), of the ith component;

x_{is} is the uncorrected concentration, in % (n/n), of the ith component in the sample;

x_{ocs} is the uncorrected total concentration, in % (n/n), of the other components in the sample;

k is the number of components detected.

9 Precision

The analytical method chosen shall have a precision, calculated in accordance with ISO 5725-1, at least as good as the following:

9.1 Main components

The results presented are based on the analysis by twelve laboratories calculated in accordance with ISO 5725-1.

$$\log_{10} r = -0{,}680\,02 \times \log_{10} x - 0{,}159\,95$$

$$\log_{10} R = -0{,}582\,83 \times \log_{10} x + 0{,}751\,622\,2$$

where

r is the relative repeatability;

R is the relative reproducibility;

x is the component concentration, in % (n/n).

9.2 Trace components

The results presented are based on the analysis by six laboratories calculated in accordance with ISO 5725-1.

$$\ln r = 0{,}680 \times \ln x - 4{,}238$$

$$\ln R = 0{,}625 \times \ln x - 3{,}022$$

where

r is the repeatability, in % (n/n);

R is the reproducibility, in % (n/n);

x is the component concentration, in % (n/n).

10 Test report

The test report shall include at least the following information:

a) a reference to this International Standard;

b) all information necessary for complete identification of the sample, for example:

- the date of sampling,
- the place in the pipeline system at which the sample was taken;

c) the sampling method used (including the size and type of material of the high-pressure cylinder used);

d) a complete list of all components determined or detected;

e) if possible, the precision of the determined concentrations of the components of the sample, including the number of determinations;

f) details of any deviation from the procedure specified;

g) any unusual features noted during the determination (i.e. in the chromatogram).

Annex A
(informative)

Determination of the response curves for the main components in a sample

A.1 General

To determine a response curve, results are needed at a number of different main-component concentrations. The number of concentrations needed depends on the order of the best-fit response curve. The minimum number of concentrations needed is the same as the number of constants (see below) in the polynomial equation of the best-fit response curve. However, a few extra concentrations are advisable because in most cases the order of the response curve is unknown beforehand, and a limited number of additional concentrations will decrease the influence of measurement error on the curves. Therefore, analysis at seven concentrations is advised.

These concentrations should be equally spaced across the specified working range of each component. The lowest concentration should be slightly below the lowest concentration in the working range, the highest concentration should be slightly above the highest concentration in the working range.

The following polynomials can be used to determine the best-fit curve:

$X_i = b_{i,1}R_i$ (first order through the origin)

$X_i = b_{i,0} + b_{i,1}R_i$ (first order)

$X_i = b_{i,0} + b_{i,1}R_i + b_{i,2}R_i^2$ (second order)

$X_i = b_{i,0} + b_{i,1}R_i + b_{i,2}R_i^2 + b_{i,3}R_i^3$ (third order)

where

X_i is the concentration of the ith component in the CRM;

R_i is the response for the ith component, expressed in counts;

$b_{i,0}$ to $b_{i,3}$ are the constants for the ith component.

A.2 Number of analyses

Each of the CRMs containing the main components is analysed at least twice on the gas chromatograph.

A.3 Calculation (fitting) of the response curves

To calculate, for each of the main components, the constants in the four response curve polynomials given in clause A.1, a certain amount of matrix algebra is needed. For this reason, a computer with appropriate software is needed. The calculations in matrix algebra notation are given in brief detail only. The method described can be found in practically any book on linear regression, so that an exhaustive introduction is not necessary here.

After analysing the CRMs, the following set of equations can be set up:

$$X_{i,1} = b_{i,0} + b_{i,1}R_1 + b_{i,2}R_1{}^2 + \ \ldots \ + b_{i,m}R_1{}^m + e_{i,1}$$

$$X_{i,2} = b_{i,0} + b_{i,1}R_2 + b_{i,2}R_2{}^2 + \ \ldots \ + b_{i,m}R_2{}^m + e_{i,2}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$X_{i,n} = b_{i,0} + b_{i,1}R_n + b_{i,2}R_n{}^2 + \ \ldots \ + b_{i,m}R_n{}^m + e_{i,n}$$

where

n is the total number of analyses (if seven CRMs are analysed, $n = 2 \times 7 = 14$);

m is the order of the response curve equation (for a second-order equation, $m = 2$);

$e_{i,1}$ to $e_{i,n}$ are residuals, i.e. the differences between the actual concentration of the ith component of the CRM and the concentration of the ith component calculated from the response curve after determination of the b-values).

or, expressed in matrix terms:

$$\vec{X}_i = R_{\mathrm{CRM},i} \times \vec{b}_i + \vec{e}_i$$

where

$\vec{X}_i$ is a vector containing the concentrations of the main CRM components:

$$\vec{X}_i = \begin{bmatrix} X_{i,1} \\ X_{i,2} \\ \cdots \\ X_{i,n} \end{bmatrix}$$

$R_{\mathrm{CRM},i}$ is a matrix containing the responses for the ith component in each CRM in accordance with the response curve for the ith component:

$$R_{\mathrm{CRM},i} = \begin{bmatrix} 1 \ R_{i,1} \ R_{i,1}^2 \cdots R_{i,1}^m \\ 1 \ R_{i,2} \ R_{i,2}^2 \cdots R_{i,2}^m \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ 1 \ R_{i,n} \ R_{i,n}^2 \cdots R_{i,n}^m \end{bmatrix}$$

$\vec{b}_i$ is a vector containing the polynomial constants for the ith component:

$$\vec{b}_i = \begin{bmatrix} b_{i,0} \\ b_{i,1} \\ b_{i,2} \\ \cdots \\ b_{i,m} \end{bmatrix}$$

The vector containing the polynomial constants is calculated as follows:

$$\vec{b}_i = (R_{\mathrm{CRM},i}^{\mathrm{T}} \times R_{\mathrm{CRM},i})^{-1} \times R_{\mathrm{CRM},i}^{\mathrm{T}} \times \vec{X}_i$$

where

$R_{\mathrm{CRM},i}^{\mathrm{T}}$ is the transpose of the R-matrix for the ith component;

$(\ \ )^{-1}$ indicates the inverse of the matrix inside the brackets.

NOTE — See annex B for further details on the elements of the matrices used.

The concentration of the ith component is calculated from the equation

$$\hat{X}_i = R_{\mathrm{CRM},i} \times \vec{b}_i$$

where

$\hat{X}_i$ is a vector containing the calculated concentrations for the ith component.

The vector $\vec{e}_i$ containing residuals is calculated as follows:

$$\vec{e}_i = \vec{X}_i - \hat{X}_i = \vec{X}_i - R_{\mathrm{CRM},i} \times \vec{b}_i$$

When the matrix notation is transformed back to the original polynomial equations, the concentration of any component can be calculated from one of the following four equations:

$$\hat{X}_i = b_1 R_i$$

$$\hat{X}_i = b_0 + b_1 R_i$$

$$\hat{X}_i = b_0 + b_1 R_i + b_2 R_i^2$$

$$\hat{X}_i = b_0 + b_1 R_i + b_2 R_i^2 + b_3 R_i^3$$

A.4 Choice of the right order for the response curve equation

After calculating the four possible response curve polynomials for each of the main components, a choice has to be made as to which of the curves is most appropriate to each of the components. This decision is based on limited use of statistics.

First, the variance S_e^2 of the residuals of the four polynomials is calculated from the equation

$$S_e^2 = \frac{\sum_{i=1}^{n} (X_i - \hat{X}_i)^2}{n - p}$$

where

n is the total number of analyses (for seven CRMs analysed, $n = 2 \times 7 = 14$);

m is the order of the response curve equation;

p is the number of polynomial constants in the response curve equation ($= m + 1$);

X_i is the actual concentration of the ith component in the CRM;

$\hat{X}_i$ is the calculated concentration of the ith component in the CRM.

The value of S_e^2 is a measure of the overall repeatability of the gas-chromatographic method when the right order has been chosen for the response curve equation.

For each of the four response curve equations, the variance of the residuals, or the residual mean square, is calculated as follows:

$$S_{e'_1}^2 = \frac{\sum_{i=1}^{n} (X_i - \hat{X}_i)^2}{n - 1} \qquad \text{(first order through the origin)}$$

$$S_{e_1}^2 = \frac{\sum_{i=1}^{n} (X_i - \hat{X}_i)^2}{n-2} \qquad \text{(first order)}$$

$$S_{e_2}^2 = \frac{\sum_{i=1}^{n} (X_i - \hat{X}_i)^2}{n-3} \qquad \text{(second order)}$$

$$S_{e_3}^2 = \frac{\sum_{i=1}^{n} (X_i - \hat{X}_i)^2}{n-4} \qquad \text{(third order)}$$

The difference SS_d between the residual variances for the second- and third-order response curves is first calculated as follows:

$$SS_{\mathrm{d}_{3-2}} = \left| (n-4) \times S_{e_3}^2 - (n-3) \times S_{e_2}^2 \right|$$

with one degree of freedom (df = 1).

A test is then made as to whether the difference in variances deviates significantly from the variance of the third-order response curve as follows:

$$F_\mathrm{cal} = \frac{SS_{\mathrm{d}_{3-2}} / (4-3)}{S_{e_3}^2}$$

The calculated F-value (F_cal) is compared with the value from table A.1 for $F_{0,05,\,1,\,n-4}$ (0,05 means test at the 5 % level; 1 is the number of degrees of freedom of the numerator; n–4 is the number of degrees of freedom of the denominator).

— If $F_\mathrm{cal} \leqslant F$, then the third-order response curve is not significantly better than the second-order response curve, and the test is repeated with the next pair of curves (see below).

— If $F_\mathrm{cal} > F$, then the third-order response curve is significantly better than the second-order response curve, and the third-order response curve is used as the calibration line.

If the third-order response curve is not significantly better than the second-order response curve, then the following test is carried out to determine whether the second-order response curve is better than the first-order response curve. For this purpose, the difference SS_d between the residual variances for the first- and second-order response curves is calculated as follows:

$$SS_{\mathrm{d}_{2-1}} = \left| (n-3) \times S_{e_2}^2 - (n-2) \times S_{e_1}^2 \right|$$

A new F-value is then calculated from the equation

$$F_\mathrm{cal} = \frac{SS_{\mathrm{d}_{2-1}} / (3-2)}{S_{e_2}^2}$$

The calculated F-value (F_cal) is compared with the value from table A.1 for $F_{0,05,\,1,\,n-3}$.

— If $F_\mathrm{cal} \leqslant F$, then the second-order response curve is not significantly better than the first-order response curve, and the test is repeated with the next set of curves.

— If $F_\mathrm{cal} > F$, then the second-order response curve is significantly better than the first-order response curve, and the second-order response curve is used as the calibration line.

Table A.1 — F-table

Critical points at 5 % level

$F_{0,05,\,\mathrm{df1},\,\mathrm{df2}}$ where df1 = 1

df2	F
1	161
2	18,5
3	10,1
4	7,71
5	6,61
6	5,99
7	5,59
8	5,32
9	5,12
10	4,96
11	4,84
12	4,75
13	4,67
14	4,60
15	4,54
16	4,49
17	4,45
18	4,41
19	4,38
20	4,35
30	4,17
40	4,08
60	4,00
120	3,92
∞	3,84

A.5 Calculation of the variance and covariance of the curves

The variance and covariance are determined using the following covariance matrices:

For a straight line through the origin:

$$s_{b_1}^2 = \frac{s_{e_1}^2}{\sum\limits_{i=1}^{n} R_i^2}$$

For a first-order polynomial:

$$\begin{pmatrix} s_{b_1}^2 & r_{b_1 b_0} \\ r_{b_1 b_0} & s_{b_0}^2 \end{pmatrix} = \begin{pmatrix} \sum\limits_{i=1}^{n} R_i^2 & \sum\limits_{i=1}^{n} R_i \\ \sum\limits_{i=1}^{n} R_i & n \end{pmatrix}^{-1} \times s_{e_1}^2$$

For a second-order polynomial:

$$\begin{pmatrix} S_{b_2}^2 & r_{b_2 b_1} & r_{b_2 b_0} \\ r_{b_2 b_1} & S_{b_1}^2 & r_{b_1 b_0} \\ r_{b_2 b_1} & r_{b_1 b_0} & S_{b_0}^2 \end{pmatrix} = \begin{pmatrix} \sum_{i=1}^{n} R_i^4 & \sum_{i=1}^{n} R_i^3 & \sum_{i=1}^{n} R_i^2 \\ \sum_{i=1}^{n} R_i^3 & \sum_{i=1}^{n} R_i^2 & \sum_{i=1}^{n} R_i \\ \sum_{i=1}^{n} R_i^2 & \sum_{i=1}^{n} R_i & n \end{pmatrix}^{-1} \times S_{e_2}^2$$

For a third-order polynomial:

$$\begin{pmatrix} S_{b_3}^2 & r_{b_3 b_2} & r_{b_3 b_1} & r_{b_3 b_0} \\ r_{b_3 b_2} & S_{b_2}^2 & r_{b_2 b_1} & r_{b_2 b_0} \\ r_{b_3 b_1} & r_{b_2 b_1} & S_{b_1}^2 & r_{b_1 b_0} \\ r_{b_3 b_0} & r_{b_2 b_0} & r_{b_1 b_0} & S_{b_0}^2 \end{pmatrix} = \begin{pmatrix} \sum_{i=1}^{n} R_i^6 & \sum_{i=1}^{n} R_i^5 & \sum_{i=1}^{n} R_i^4 & \sum_{i=1}^{n} R_i^3 \\ \sum_{i=1}^{n} R_i^5 & \sum_{i=1}^{n} R_i^4 & \sum_{i=1}^{n} R_i^3 & \sum_{i=1}^{n} R_i^2 \\ \sum_{i=1}^{n} R_i^4 & \sum_{i=1}^{n} R_i^3 & \sum_{i=1}^{n} R_i^2 & \sum_{i=1}^{n} R_i \\ \sum_{i=1}^{n} R_i^3 & \sum_{i=1}^{n} R_i^2 & \sum_{i=1}^{n} R_i & n \end{pmatrix}^{-1} \times S_{e_3}^2$$

Annex B

(informative)

Further details on the matrices used in annex A

$$[b_1] = \left[\sum R_i^2\right]^{-1} \times \left[\sum (R_i \times X_i)\right]$$

$$\begin{bmatrix} b_0 \\ b_1 \end{bmatrix} = \begin{bmatrix} n & \sum R_i \\ \sum R_i & \sum R_i^2 \end{bmatrix}^{-1} \times \begin{bmatrix} \sum X_i \\ \sum (R_i \times X_i) \end{bmatrix}$$

$$\begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} n & \sum R_i & \sum R_i^2 \\ \sum R_i & \sum R_i^2 & \sum R_i^3 \\ \sum R_i^2 & \sum R_i^3 & \sum R_i^4 \end{bmatrix}^{-1} \times \begin{bmatrix} \sum X_i \\ \sum (R_i \times X_i) \\ \sum (R_i^2 \times X_i) \end{bmatrix}$$

$$\begin{bmatrix} b_0 \\ b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} n & \sum R_i & \sum R_i^2 & \sum R_i^3 \\ \sum R_i & \sum R_i^2 & \sum R_i^3 & \sum R_i^4 \\ \sum R_i^2 & \sum R_i^3 & \sum R_i^4 & \sum R_i^5 \\ \sum R_i^3 & \sum R_i^4 & \sum R_i^5 & \sum R_i^6 \end{bmatrix}^{-1} \times \begin{bmatrix} \sum X_i \\ \sum (R_i \times X_i) \\ \sum (R_i^2 \times X_i) \\ \sum (R_i^3 \times X_i) \end{bmatrix}$$