

Natural gas — Performance evaluation for on-line analytical systems

The European Standard EN ISO 10723:2002 has the status of a British Standard

ICS 75.060

Committees responsible for this British Standard

The preparation of this British Standard was entrusted to Technical Committee PTI/15, Natural gas and gas analysis, upon which the following bodies were represented:

AEA Technology
British Compressed Gases Association
British Gas plc
Combustion Engineering Association
Department of Trade and Industry (Oil and Gas Office)
Department of Trade and Industry (National Physical Laboratory)
Department of Transport
GAMBICA (BEAMA Ltd.)
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Contents

	Page
Committees responsible	Inside front cover
National foreword	i
Introduction	ii
Method	
1 Scope	1
2 Normative references	1
3 Principle	2
4 Suitability of analytical systems	2
5 Test gases	3
6 Test procedures	5
7 Evaluation of results	14
Annexes	
A (informative) Example of application using chromatography	16
B (informative) Statistical tests and methods	31
C (informative) Bibliography	43
Tables	
A.1 Test gas compositions	19
A.2 Area counts from one calibration interval	19
B.1 Grubbs' test for a single outlier	33
B.2 Grubbs' test for multiple outliers, all high or all low	34
B.3 Grubbs' test for two outliers, one high, one low	35
B.4 Cochran's maximum variance test	36
Figures	
1 Uniform repeatability	7
2 Variable repeatability	7
3 Response curve/straight lines	10
A.1 Typical chromatogram	18
A.2 First, second and third-order fits	24

National foreword

This British Standard is the official English language version of EN ISO 10723:2002.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural gas and gas analysis, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled “International Standards Correspondence Index”, or by using the “Search” facility of the *BSI Electronic Catalogue* or of British Standards Online.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, the EN ISO title page, the EN ISO foreword page, pages 1 to 43 and a back cover.

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Introduction

This International Standard describes a method for evaluating the performance of analytical systems intended for the analysis of natural gas. Natural gas is assumed to consist predominantly of methane, with other saturated hydrocarbons and non-combustible gases.

Performance evaluation makes no assumptions about equipment for and/or methodology of analysis but gives test methods which can be applied to the chosen analytical system, including the method, equipment and sample handling.

This International Standard contains an informative annex (annex A) which shows the application for an on-line gas chromatographic system which, as described, is assumed to have a response/concentration relationship for all components which is represented by a straight line through the origin. It contains two additional informative annexes (annexes B and C).

English version

Natural gas - Performance evaluation for on-line analytical systems (ISO 10723:1995)

Gaz naturel - Evaluation des performances des systèmes d'analyse en ligne (ISO 10723:1995)

Erdgas - Bewertung der Leistungsfähigkeit von On-line-Analysensystemen (ISO 10723:1995)

This European Standard was approved by CEN on 19 August 2002.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

The text of ISO 10723:1995 has been prepared by Technical Committee ISO/TC 193, 'Natural gas' of the International Organization for Standardization (ISO) and has been taken over as EN ISO 10723:2002 by the Technical Board of CEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2003, and conflicting national standards shall be withdrawn at the latest by March 2003.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Natural gas — Performance evaluation for on-line analytical systems

1 Scope

This International Standard specifies a method of determining whether an analytical system for natural gas is satisfactory, on the assumptions that

- a) the analytical requirement has been clearly and unambiguously defined, for the range and uncertainty of component concentration measurements, and the uncertainty of properties which may be calculated from these measurements;
- b) the analytical and calibration procedures have been fully described;
- c) the method is intended to be applied to gases having compositions which vary over ranges normally found in transmission and distribution networks.

If the performance evaluation shows the system to be unsatisfactory, all the stages, such as

- the analytical requirement;
- the analytical procedure;
- the choice of equipment;
- the choice of calibration gas;
- the calculation procedure;

must be re-examined in the light of the test data to assess where improvements can be obtained.

This International Standard is applicable to analytical systems which give the component concentrations and resulting uncertainties. With the present state of knowledge, the method chosen is likely to be gas chromatography.

Performance evaluation of an analytical system should be performed during installation, then at regular intervals, according to the application, and/or whenever any critical component of the analytical system is changed or replaced.

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

ISO 6974:1984, *Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C8 — Gas chromatographic method*.

ISO 6976:1995, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition*.

ISO 7504:1984, *Gas analysis — Vocabulary*.

3 Principle

The analytical system is set up according to the instructions so as to carry out the specified compositional analysis. The effectiveness of the system is demonstrated by analysing test gases with compositions covering a range rather wider than that for which the system has been specified.

Test gases prepared according to an appropriate standard are injected into the analyser to test:

- a) the ability of the system to measure the components specified in the analytical method (system efficiency);
- b) the repeatability of measurement of individual components over their specified ranges;
- c) the relationship between response and concentration of individual components over their specified ranges;
- d) the absence of interference between components at different concentration ratios.

The tests required for b) and c) above are conducted over intervals of time comparable with the normal period of use between regular calibrations. Because a number of parameters which can influence the analytical performance may vary on a day-to-day basis (barometric pressure variations are a case in point), it is recommended that the tests be repeated on at least three separate intervals, so that occasional inconsistencies may be recognized. However, it is acknowledged that there are circumstances (such as testing analysers installed in remote locations) where only a single set of tests can be obtained.

The results of the tests are analysed to assess analyser performance with respect to bias, repeatability and interference. The repeatability test b) shows the random error associated with the measurement of a component and whether this varies with concentration. The response function c) shows the likelihood of bias error arising from different component concentrations in the calibration standard and sample; bias can also result from component interference d).

Accuracy of measurement is not included in this list, since analytical accuracy is fundamentally and principally controlled by the accuracy with which the calibration gas composition is known. The procedures described in this International Standard allow a judgement as to the ability of the analytical method to provide accurate results if used with an accurate and appropriate calibration gas.

4 Suitability of analytical systems

The analytical system to be evaluated shall satisfy the following criteria.

- a) The analytical requirement has been carefully defined, for the range and uncertainty of component concentration measurement, or of physical or chemical property calculation, or of both.
- b) The analytical and calibration procedures, whether manual or automated, laboratory or process, have been fully described, preferably following appropriate interlaboratory testing. Changes in details of the method are not permissible during the series of tests. If, at the end of the tests, it is clear that the method fails to provide the desired performance, it shall be modified suitably and the entire test procedure reapplied.

- c) The method is not intended to be applied to gases having composition or physical or chemical properties that vary over a wider range than would be acceptable for mixing into a normal transmission or distribution system. Thus, in practical terms, it is unlikely that the concentration will vary for an individual component by more than a factor of 20, and the variation for most components is likely to be less than a factor of 10.
- d) The analytical system shall be capable of measuring, either individually or in groups, all components which are significant for the analytical requirement. Thus, for the measurement of calorific value, nitrogen, carbon dioxide, individual hydrocarbons from C_1 to C_5 and a composite C_{6+} are commonly required.

NOTE 1 When a number of hydrocarbons are identified and quantified as a group or groups, either the total is reported as though the group extends from the lowest carbon number of that group (e.g. C_{6+} , which indicates all hydrocarbons of carbon number 6 and above), or separate groups may be reported as the total of each carbon number (e.g. total C_6 , total C_7 , etc.), or further broken down to component types (e.g. C_6 alkanes, as distinct from benzene and C_6 cycloalkanes or naphthenes).

5 Test gases

5.1 Definition

Test gases are mixtures which are used to evaluate the response of the analyser to individual natural gas components, so that the measured response can be compared with the assumed one. They may be multi-component or binary mixtures. In all cases, the matrix gas shall be methane, so that the behaviour of the test gases is as similar as possible to that of natural gases. Binary mixtures can be prepared with smaller uncertainties than multi-component ones, but more mixtures must be made, one set for each non-methane component to be tested. Multi-component mixtures allow more repeats to be performed for each component/concentration combination.

Obviously, similar mixtures can be used to define the response functions of an analyser when it is initially installed, in which case they shall be referred to as range calibration gases.

NOTE 2 The analytical method may require that the response functions be defined upon installation, or, in the absence of such a requirement, the user may choose to establish them. Alternatively, the user may rely on the supplier's or manufacturer's assumptions about response function, which is usually that the response to all components is represented by a straight line through the origin. This latter approach is not likely to take full advantage of the potential accuracy of the method.

There is, of course, no point in defining a more complex response function if the data handling system available with the analyser will not fit response data to such a function.

Having used range calibration gases at a particular time (for example, on Day 1) to define the response, y_i , of a component i in terms of its concentration, x_i , as:

$$y_i = g_i(x_i)$$

subsequent analyses allow the concentrations of unknown samples to be calculated as

$$x_i = g_i^{-1}(y_i)$$

Rather than redefine the instrument response to each component for each new period of use, the assumption is usually made that each response function, g_i , remains broadly unchanged, but that it needs the minor adjustment of a scaling, or calibration factor, which is derived from the regular use of a single calibration gas. This single calibration gas would invariably be a multi-component mixture, chosen to have similar component concentrations to those anticipated in the unknowns. The scaling or calibration factor, a , is defined as

$$a_{ij} = \frac{\text{Response to component } i \text{ in single calibration gas on Day 1}}{\text{Response to component } i \text{ in single calibration gas on Day } j}$$

and the concentrations of the unknowns are calculated as

$$x_i = g_i^{-1}(a_{ij} \cdot y_i)$$

The frequency with which the single calibration gas needs to be used is a matter of experience, and instead of Day 1, we could refer to Hour 1 or Week 1 or Month 1. This frequency shall be defined as part of the analytical method.

The frequency with which the response function, g , if measured by the user, needs to be re-established will be found by applying these test procedures.

From the above, it can be seen that test gases and range calibration gases could be very similar, if not the same, mixtures. When referred to as test gases in this International Standard, they are used to define the up-to-date response function, f , which is then compared with the previously established or the assumed function g .

5.2 Test gas compositions

Test gases shall be chosen to be suitable for the intended application. However, it is not practicable to make up test gases which contain all the components in natural gas, given the complexity of the higher hydrocarbons which are commonly found, and the difficulty of preparing high quality mixtures containing condensible components. Neither can grouped components, such as C_6+ or total C_7 be used. It is therefore common to use test gases which contain only the major components; nitrogen, carbon dioxide, methane, ethane, propane and butane are commonly used, but any component expected to be present in a concentration greater than 1 % should be included.

Helium, C_5 and heavier hydrocarbons are usually present at such low concentrations that non-linearity of response is unlikely to be a problem. Their repeatability of measurement can be tested using real natural gases, ideally with a range of concentrations appropriate to the application.

The response/concentration relationship shall be tested over the range specified for each component present in the test gases, and ideally over a slightly greater range. It is unlikely that a response function more complex than a third-order polynomial will be useful and this is satisfactorily defined with seven points. In those instances where the range specified for a component is relatively large, it is possible that the repeatability may vary across the range. For this reason, repeatability testing is carried out with the same mixtures that are used to evaluate the response/concentration relationship.

It is rare that an analyser, however well configured, will measure the sum of components in a natural gas to be exactly 100 %. Consequently, it is common for analysers which have been set up for natural gas analysis to normalize the composition data to 100 %, or to some slightly lesser value if there is a small, constant and recognized contribution from an unmeasured component such as helium. This is based on the obvious premise that a natural gas contains 100 % of components, and not some other value. The method should quote limits within which such normalization would be acceptable; a measured total of between 99 % and 101 % may be deemed to be usual, with analyses producing wider-ranging totals being rejected. Analytical methods which calculate the methane by difference do not normalize in this way, but instead force the total to 100 %, with the calculated methane value absorbing the errors in all the other component measurements.

Repeatability is influenced by the normalization procedure; normalized data are usually significantly more precise than unnormalized data. At the same time, normalization allocates the errors involved in the fact that the total does not reach 100 % or thereabouts between the components *pro rata*. If the error is produced mainly by one component (for example, methane), the normalization process slightly increases the errors for all other components. This shall be recognized in the procedure. Simplistically, there are two types of error which contribute to totals other than 100 %, and hence to the need to normalize. The first type affects all components to the same extent, and in the case of a gas analyser is typically caused by, among other influences, variations in sample pressure within the sample introduction device. The second type affects components to a different extent, and could be for example due to random noise, or to variations between the measured and assumed response functions for individual components.

The first type can be compensated for by normalization, but not the second. Furthermore, normalization takes account of the total calculated composition, according to the equation

$$\text{Unnormalized total} = \sum_{i=1}^{i=n} x_i = \sum_{i=1}^{i=n} g_i^{-1} (a_{ij} \cdot y_i)$$

Consequently, while it might be interesting to use normalized calculated data, or to normalize raw instrument-response data according to the calculated unnormalised total, this requires assumptions about the response function, g_i , and the short-term calibration factor, a_{ij} , which are unlikely to be justified at this stage. The test gases should be used in circumstances which minimize errors of the first type, such as shutting off the sample flow before introduction of the sample. Only unnormalized data should be used for these tests.

Each component shall be tested at seven values of concentration. These shall be, so far as possible, equally spaced across the specified range, and also covering one point below and one point above the range. If the lowest and highest concentrations specified are x_L % and x_U %, the mixtures should contain:

Mixture	Concentration (%)
1	$x_L - 0,25 (x_U - x_L)$
2	x_L
3	$x_L + 0,25 (x_U - x_L)$
4	$x_L + 0,5 (x_U - x_L)$
5	$x_L + 0,75 (x_U - x_L)$
6	x_U
7	$x_U + 0,25 (x_U - x_L)$

Achieving these exact values may not always be possible, in which case the nearest practicable concentration should be the aim. Thus if $x_L = 1$ and $x_U = 10$, the concentration value for mixture 1 would be negative, and so a value of $(0,5x_L)$ % may be chosen. If $x_L = 0$, mixture 1 may be chosen to be near the limit of detection, and mixture 2 to be between this value and mixture 3. Similar problems may occur for methane. The uncertainty with which these target concentrations are met should be not greater than $\pm 0,1 (x_U - x_L)$ %. The uncertainty relating to knowledge of the exact concentrations achieved should, of course, be significantly smaller than this.

Where multi-component mixtures are to be used, it is unlikely that each one can be formulated to have a composition similar to that of an anticipated sample gas, and particular mixtures may contain more propane than ethane, for example. However methane will always be the major component.

These mixtures shall be prepared or certified by a method whose overall uncertainty is not greater than that specified for the analytical system under test, and preferably rather less.

6 Test procedures

6.1 System efficiency test

The analytical system shall be capable of measuring each component for which the method has been specified, over the expected range of concentrations. It shall not give false indications for any other components not specified in the analytical requirement, but which may reasonably be expected to be occasional contaminants in a sample. Furthermore, the system should not give any response for specified components in their absence.

The ability of the method to cope with the specified components shall be assessed by analysis of standard gases which have been prepared to contain these components at appropriate levels, or of natural gases the compositions of which have been defined by comparison with such standards. Exact quantitative accuracy is not needed here, so the methods of preparation may be selected for speed or convenience.

If the method is configured in such a way that one or more groups of components are measured as a single "pseudo-component" or series of "pseudo-components", the correct allocation of components to these groups shall be checked. A typical example would be a recombined (e.g. backflushed) C_6+ group, consisting of all C_6 and

heavier hydrocarbons. The timing of the backflushing operation shall not allow any C_6 or heavier components to fail to be included, nor C_5 or lighter components to be grouped where they should not be.

The approach to the presence of contaminants in a sample will vary according to whether or not remedial action is required. Air is a common contaminant if samples are taken for laboratory analysis, and can be recognized by the presence of oxygen. Usually, an analytical method will permit the composition to be recalculated on an air-free basis, provided that the concentration of air is below a defined value. In this case, the oxygen shall be measured with high accuracy, since the adjustment for a given observed amount of oxygen involves the removal of a calculated amount of nitrogen which is about four times larger. On the other hand, in particular circumstances other components may be expected to be present at concentrations comparable to those of the C_4 or C_5 hydrocarbons, but their measurement is not required for the purpose for which the analysis is performed. In this case, it shall be established whether or not the contaminant interferes with measurement of any of the expected components, and if so, how large an effect is seen.

Any response for a component in its absence can be tested by a blank experiment, which simulates all the activities of the analytical system. Thus, in the case of a chromatographic method, injection of carrier gas instead of sample gas would be appropriate.

Any detectable response at this stage should, if possible, be eliminated by suitable adjustment of the method. Otherwise, it will impose a fixed bias error on the response/concentration relationship.

6.2 Repeatability

Repeatability is often measured as that of instrument response; the standard deviation of peak area counts in the case of a chromatographic method. This measurement cannot be used in isolation for two reasons. The mean and standard deviation of a normally distributed (Gaussian) set of data are measures such that 67 % of all the data points lie within ± 1 standard deviation of the mean; thus, while the standard deviation is a convenient measure to use while assessing error contributions, it shall be converted at the end of the calculations to a value which more nearly describes what we understand by repeatability (see clause B.4). Also, a typical analytical result is derived using a relationship of the type

$$x_s = \frac{y_s}{y_{std}} \times x_{std}$$

where

x_s is the concentration in unknown (sample);

y_s is the response to unknown (sample);

x_{std} is the concentration in the standard;

y_{std} is the response to the standard.

Consequently, the repeatability of the result is influenced by the repeatability of both the unknown and of the standard. Uncertainty associated with the calibration gas standard also contributes, but is outside the scope of this International Standard. The evaluation procedure assesses the ability of the analytical system to provide high quality data, if used with a calibration standard which has a well-known composition and is appropriate for the application. The quality of such calibration standards is properly dealt with in other International Standards.

The repeatability of measurement of a component may be uniform over the expected concentration range, or it may vary as a function of concentration. Figure 1 illustrates the former situation, where the Gaussian curves superimposed on the response/concentration plot represent the repeatability distribution, which can be seen to be uniform across the range.

Figure 2 shows a plot where the repeatability increases with concentration. The likelihood of any particular measurement point deviating from the plotted line is indicated by the width of the Gaussian curve in that region.

The difference between these forms of behaviour is important, so that the repeatability for different components at different concentrations may be expressed appropriately.

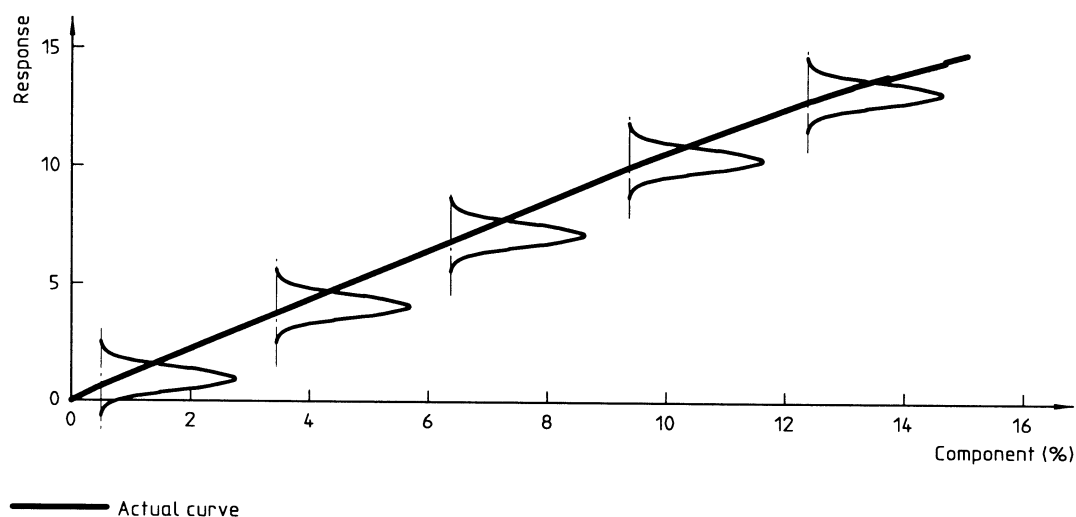


Figure 1 — Uniform repeatability

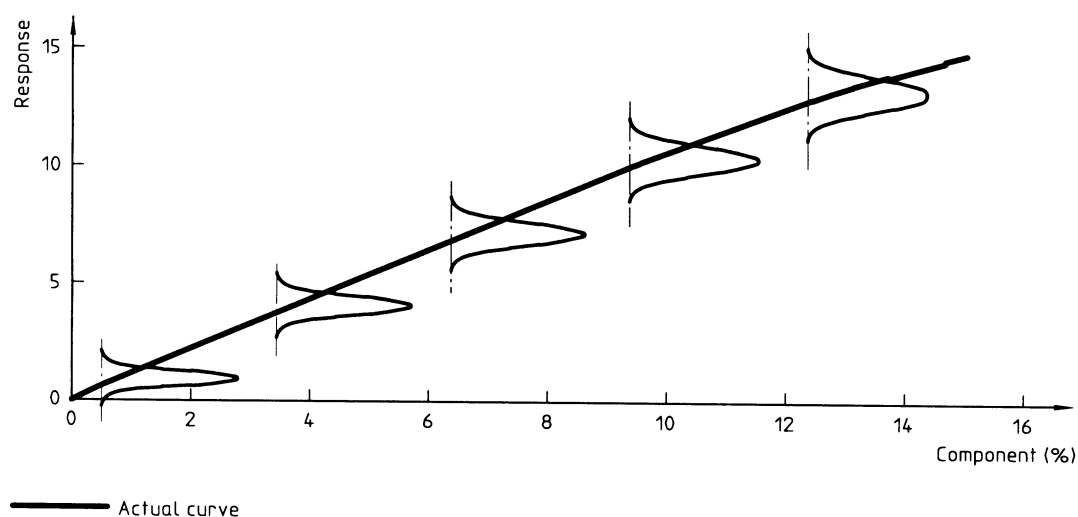


Figure 2 — Variable repeatability

6.2.1 Calibration interval

For the purpose of this test, the calibration interval is defined as that period of time during which the analytical system would normally be used between recalibrations. Experience will show over how long a period an instrument may be judged to be stable, and hence what the recalibration frequency should be. A laboratory instrument may be used throughout the working day after having been calibrated first thing in the morning, or may require separate calibrations for the morning and afternoon. A process analyser may operate for 24 h a day with automatic recalibration at midnight. It is important that one set of tests is conducted within one calibration interval and that they are spaced uniformly throughout it. The longer the calibration period, the longer the time for one set of tests.

6.2.2 Procedure

Calculate the number of analyses that can be performed within the calibration interval and then analyse the seven concentration levels, using a random sequence, as many times as possible. Five repeats at each level will usually give statistically useful data. (It is hardly practicable to exceed 10 repeats at each level: this implies $10 \times 7 = 70$ analyses during the calibration interval.)

Where possible, repeat this set of tests so as to have at least three sets of results, each achieved during a different calibration interval.

For each of e components ($i = [1, \dots, e]$), at each of seven concentration levels ($j = [1, \dots, 7]$), perform f repeat analyses ($k = [1, \dots, f]$) during each of g calibration intervals ($l = [1, \dots, g]$). Record each analyser response, y_{ijkl} , together with the component concentration, x_{ij} , which generated it.

Group the results by component and level from within one calibration interval, y_{ij11} , y_{ij21} , etc. Inspect each group for outliers or stragglers using Grubbs' test or some other suitable outlier test (see annex B). After rejection of any outliers, calculate the means, y_{ij1} , standard deviations, s_{ij1} , and adjusted numbers of analyses, n_{ij1} .

Where tests have been performed during different calibration intervals, compare the precision of sets of results between the calibration intervals s_{ij1} , s_{ij2} , ..., s_{ijg} , by Cochran's test (see annex B). If any group of results is shown to be significantly less precise than the others, the reason for this shall be investigated. In the absence of a clear reason, and one which would be expected to be evident in normal use, the tests shall be repeated.

Assuming that each component at each level shows uniform precision between the calibration intervals, a combined mean and standard deviation can be derived. The mean, y_{ij} , is calculated as

$$y_{ij} = \frac{\sum_{l=1}^{l=g} y_{ijl} \cdot n_{ijl}}{\sum_{l=1}^{l=g} n_{ijl}}$$

The combined standard deviation, s_{ij} , is calculated as

$$s_{ij} = \left[\frac{\sum_{l=1}^{l=g} (n_{ijl} - 1) \cdot (s_{ijl})^2}{\sum_{l=1}^{l=g} n_{ijl} - 1} \right]^{1/2}$$

If, in the examination of error structure (see 6.3.1), the standard deviation, s_{ij} , appears to be independent of the concentration, x_{ij} , a combined standard deviation, s_i , covering the full concentration range for component i , can be calculated from the standard deviations at each level, s_{ij} , and the total number of measurements at each level across all the calibration intervals, n_{ij} :

$$s_i = \left[\frac{\sum_{j=1}^{j=7} (n_{ij} - 1) \cdot (s_{ij})^2}{\sum_{j=1}^{j=7} n_{ij} - 1} \right]^{\frac{1}{2}}$$