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Natural gas — Guidelines to traceability in analysis

Gaz naturel — Lignes directrices pour la traçabilité en analyse

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Contents

Annexes

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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 14111 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas.*

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

Introduction

At a time when assurances of measurement accuracy in natural-gas analyses are increasingly being sought, every analytical chemist responsible for the design and operation of systems used in such analyses needs to be aware of, and adopt, suitable means by which he or she will be able to provide these assurances. This implies that the analyst must employ validated methods in which each result is securely linked, through a series of reference materials (reference gas mixtures), to accepted metrological standards. The formal structure which the analyst creates in doing this constitutes what is called a traceability chain. Only by this means will the analyst be able to secure and support a proper estimate of measurement accuracy (uncertainty).

This seemingly simple concept is elaborated in considerable detail in this International Standard. The practical considerations involved in the establishment of a satisfactory traceability chain give rise to challenging problems, particularly in natural-gas analysis, but relevant and useful advice is provided.

At present, traceability of measurement is universally defined through the existence of unbroken calibration chains ending at the level of international or national measurement standards realizing appropriate SI units. This concept originates from the field of physical metrology, where it has been implemented with apparent success. Transfer of the metrological scheme to chemical analysis and other domains in the field of testing is, however, a highly difficult task, for which standard methods are not yet available. Therefore it is not possible, at present, to standardize the implementation of measurement traceability in natural-gas analysis, or in other areas of chemical analysis.

For the reasons indicated above, this International Standard does not give any specific traceability protocols. Instead, its purpose is to

- clarify fundamental concepts involved in chemical traceability;
- identify basic problems in the application of metrology in chemistry;
- indicate feasible solutions on a reference material basis;
- assist in the design of practical implementations using reference gas mixtures;
- serve as a reference document for the application of the traceability concept in other International Standards for natural-gas analysis.

Natural gas — Guidelines to traceability in analysis

1 Scope

This International Standard provides general guidelines on the implementation and application of traceability concepts in the analysis of natural gas. Its purpose is to lay down the foundations for the development of specific traceability protocols in other International Standards for natural-gas analysis.

NOTE — Besides the field of natural-gas analysis, this International Standard could also be useful as a guidance document in other areas of gas analysis and in related fields such as air quality measurement, vehicle emission monitoring and reference-gas mixture preparation.

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 3534-1:1993, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms.*

ISO 5168:—[1], *Measurement of fluid flow — Evaluation of uncertainties.*

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

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a measurement method.*

ISO 5725-4:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 4: Basic methods for the determination of the trueness of a standard measurement method.*

ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values.*

ISO 6142:1981, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods* (including addendum 1).

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[1] To be published. (Revision of ISO 5168:1978)

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

ISO 6711:1981, *Gas analysis — Checking of calibration gas mixtures by a comparison method.*

ISO 6974-1:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis.*

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

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

ISO 9001:1994, *Quality systems — Model for quality assurance in design, development, production, installation and servicing.*

ISO 10012-1:1992, *Quality assurance requirements for measuring equipment — Part 1: Metrological confirmation system for measuring equipment.*

ISO 10723:1995, *Natural gas — Performance requirements for on-line analytical systems.*

ISO Guide 30:1992, *Terms and definitions used in connection with reference materials.*

ISO Guide 33:1989, *Uses of certified reference materials.*

ISO Guide 35:1989, *Certification of reference materials — General and statistical principles.*

BIPM/IEC/ISO/OIML/IFCC/IUPAC. International vocabulary of basic and general terms in metrology (VIM), second edition, 1993.

3 Definitions

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

3.1 traceability: A property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.

NOTES

1 The concept is often expressed by the adjective "traceable".

2 The unbroken chain of comparisons is called a "traceability chain". [VIM]

3.2 (measurement) standard, etalon: A material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve or reproduce a unit or one or more values of a quantity to serve as a reference.

EXAMPLES

a) 1 kg mass standard;
b) 100 Ω standard resistor;
c) standard ammeter;
d) caesium frequency standard;
e) standard hydrogen electrode;
f) reference solution of cortisol in human serum having a certified concentration. [VIM]

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

3.3 reference material: A material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method or for assigning values to materials.

NOTE — A reference material may be in the form of a pure or mixed gas, liquid or solid. Examples are water for the calibration of viscometers, sapphire as a heat-capacity calibrant in calorimetry, and solutions used for calibration in chemical analysis. [ISO Guide 30]

3.4 Terms related to accuracy and uncertainty

NOTE — Since traceability essentially serves the purpose of assessment and control of accuracy, viz the uncertainty of measurement, the following terms relating to accuracy and uncertainty are also key terms of this document. The definitions, taken from ISO 3534-1, have been adapted to usage in the field of measurement instead of testing, by substitution of corresponding terms ("measurement result" instead of "test result", and "true value" instead of "accepted reference value"). In some cases, the notes to the definitions have also been modified.

3.4.1 accuracy: The closeness of agreement between a measurement result and the true value of the measurand.

NOTE — The term accuracy, when applied to a set of measurement results, describes a combination of random components and a common systematic error or bias component. [Adapted from ISO 3534-1]

3.4.2 trueness: The closeness of agreement between the average value obtained from a large series of measurement results and the true value of the measurand.

NOTES

1 The measure of trueness is usually expressed in terms of bias.

2 Until recently, "accuracy" was used with the meaning of "trueness". This usage no longer conforms with international standardization. [Adapted from ISO 3534-1]

3.4.3 precision: The closeness of agreement between independent measurement results obtained under prescribed conditions.

NOTES

1 Precision depends only on the distribution of random errors and does not relate to the true value.

2 Precision is a qualitative term relating to the dispersion between the results of measurements of the same measurand, carried out under specified conditions of measurement. Quantitative measures of precision such as variance or standard deviation critically depend on the variation implied by the specified measurement conditions. Repeatability and reproducibility are two particular concepts of precision, relating to the endpoints on the scale of variability in measurement conditions. [Adapted from ISO 3534-1]

3.4.4 uncertainty: An estimate attached to a measurement result which characterizes the range of values within which the true value is asserted to lie.

NOTES

1 Uncertainty of measurements comprises, in general, many components. Some of these components may be estimated on the basis of the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. Estimates of other components can only be based on experience or other information.

2 Uncertainty should be distinguished from an estimate attached to a measurement result which characterizes the range of values within which the expectation is asserted to lie. This latter estimate is a measure of precision rather than of accuracy and should be used only when the true value is not defined. When the expectation is used instead of the true value, the expression "random component of uncertainty" must be used. [Adapted from ISO 3534-1]

For suggested further reading see annex C, reference [17].

3.4.5 Further comment on main terms

Since the terminology relating to accuracy/uncertainty of measurement has recently undergone substantial changes, a short comment on the meaning of the main terms will be given.

"Accuracy", "trueness" and "precision" are qualitative terms used to express the smallness of expected measurement errors. Hereby accuracy as the more general term refers to the total measurement error, trueness to the systematic component(s) of the measurement error and precision to the random component(s) of the measurement error.

"Uncertainty", "systematic uncertainty" and "random uncertainty (dispersion)" are qualitative terms used to express the extent of expected measurement errors, as the counterparts of accuracy, trueness and precision, respectively. Accuracy and uncertainty are reciprocal terms: high accuracy is equivalent to small uncertainty, and the same is true for both the other pairs of reciprocal terms — trueness/systematic uncertainty and precision/random uncertainty (dispersion).

For quantitative expressions of accuracy or uncertainty, the common measures, derived from the results of repeated measurements, are:

"bias" for systematic uncertainty

and

"standard deviation" for random uncertainty (dispersion).

NOTES

1 This clause gives those terms and definitions which are essential to understand before proceeding further in the text. Other terms and definitions used in the text, for which it is not necessary to have an exact understanding at this stage, are given in annex A.

2 This document mainly employs terms which have been defined previously by committees within ISO, OIML (International Organization of Legal Metrology), BIPM (Bureau International des Poids et Mesures) and IEC (International Electrotechnical Commission), as well as terms and definitions which are being proposed with revisions of other International Standards or Guides.

3 In producing this document, it has been acknowledged that there are serious problems in applying some terms, which originate from physical metrology, to the field of chemical metrology. Furthermore, no international vocabulary of basic and general terms for chemical metrology is yet available. Therefore additional notes and remarks are appended to the definitions given both here and in annex A wherever this has been felt necessary for clarification.

4 Fundamental principles of metrological traceability

4.1 Traceability and accuracy

In recent years, the term "traceability" has come into considerable vogue, but in doing so it has (in common with many other technical terms) tended to lose its proper scientific pedigree. Thus it has been turned into a general-purpose catchword, (mis)used in a variety of generous interpretations, extending down as far as nothing much more than a tenuous synonym for reliability. In this document, however, it is used exclusively in the original and authentic scientific sense of metrological traceability.

In this sense, traceability is essentially a means of providing an assurance that the accuracy of the results from one measurement system or technique can be related in a known way (transferred) to the results from another. For example, the result of an "everyday" (field) method should be demonstrably traceable to the result of a reference method, and the result of a reference method should be demonstrably traceable to the result of a definitive method. Traceability is usually mediated by some kind of (certified) reference object or material having known metrological qualities.

4.2 Structure of traceability chains

Self-evidently, the literal meaning of traceability is the ability to trace. In metrology (the science of measurement) this implies the existence of an unbroken, identifiable and demonstrable pathway between the measurement process in question and some quantity or set of quantities regarded as "fundamental" or "indisputable". Such a pathway is called a traceability chain; the most complete chains have clear links all the way back to SI units.

The purpose of all claims for traceability is to establish, or guarantee, the accuracy of measurement. Measurement consists almost always of the comparison of an unknown, the value of which is desired, with a standard, the value of which is taken as known. In physical measurements, the known is often an object calibrated (using a defined method) against a higher standard within a hierarchical structure. By moving upwards through the various levels in such a hierarchy, traceability to primary standards can be obtained.

The major conceptual elements which are usually present in a typical traceability hierarchy are indicated in figure 1; what is needed in order to address any real metrological question is the existence, at each level, of reference objects or materials that can be used in realizing the standard represented by that level.

Level 0 SI units
↑↓
(Fundamental method)
↑↓
Level 1 Primary standard reference object or material
↑↓
(Definitive method)
↑↓
Level 2 Secondary standard reference object or material
↑↓
(Reference method)
↑↓
Level 3 Working standard reference object or material
↑↓
(Field method)
↑↓
Level 4 Test sample

Figure 1 — Conceptual traceability hierarchy

The transfer of information between the various levels in the hierarchy is accomplished by methodology interconnections which create the traceability chain. Such a chain typically has many links between each level in the hierarchy. Each link is formed by either the whole or, more commonly, some sub-system or part of the defined method, and will probably involve auxiliary standard objects or materials (e.g. thermometers or mass pieces) which realize values or scales of subsidiary or subordinate physical properties.

In apt analogy with a mechanical chain, it is clear that a traceability chain is no stronger than its weakest link. The best chains have few links, each of which is very secure. When the pathway is fully defined and documented, an assignment of uncertainty can be made at any point in the chain and at each level in the hierarchy. If the pathway is broken (that is, if linking information is missing), uncertainties of measurement cannot be assigned at that point, and complete traceability cannot be obtained. Consequently, the measured value is then not traceable to SI units, perhaps not even to primary or secondary standards, but just as far as to where the break occurs. A statement about traceability without reference to the end-point of the chain is of no value.

4.3 Traceability in chemical analysis

In essence, then, traceability is an information retrieval process. In chemical analysis, the information needed to support the result comprises details of the analytical methods and reference materials used, together with all the associated uncertainties.

As discussed in greater detail in ISO Guide 35, traceability is much more difficult to realize in quantitative chemical analysis (chemical metrology) than in physical metrology, mainly due to the complexities of the overall analytical process. Nevertheless, the concept of traceability is similar, at least in principle.

Analyses must be made by comparison of the relevant attributes of the sample against the known attributes of reference materials. This may be done either directly, or indirectly by means of scales or instruments that have been calibrated using (one or more) accepted reference values.

The additional complexities arise because a proper correspondence between the sample and reference material may be difficult to achieve for a variety of reasons.

Firstly, several reference materials realizing various levels of composition for each target component may be required for a multi-component sample. Secondly, the matrix which contains the analyte could have a significantly disturbing effect on the analysis. Similarly, any other chemical compound present in the sample may have an interferent effect on the determination of the target compound. Finally, the sampling procedure itself is a significant error source, e.g. due to lack of homogeneity of the bulk material from which the sample is taken, and to contamination as well as degradation of the sample.

The exact requirements and procedures (protocols) necessary to ensure traceability must, therefore, depend upon the specific problem being addressed. In chemical metrology, the proper transfer of accuracy can only be achieved with very detailed protocols. Any such protocol should be considered as a fundamental part of the particular analytical method, and can therefore become an integral part of an international standard method.

5 Elaboration of the traceability concept

5.1 Distinction from related concepts

Despite what may appear above as a clear identification of what is meant by traceability, there remain differing interpretations of just what the concept can involve. These differences seem to arise because usage of the term is fed not from a single discipline, but from such diverse sources as legal regulation of operational practices, monitoring the performance standards of instruments or machines, and quality assurance in manufacturing processes, as well as from pure metrological science.

Thus, the current main interpretations of traceability, discernible to the present authors, are

a) Traceability = Ability to provide complete information about every step involved in or relevant to arriving at a measurement result, by documented records.

b) Traceability = Ability to provide evidence that measurement results are equivalent to results obtained by an authoritative laboratory.

c) Traceability = Ability to demonstrate that a measuring system regularly produces accurate results on selected measurands.

d) Traceability = Ability to prove the validity of individual measurement results by complete reduction to, for example, property values realized by measurement standards or reference materials, or to accepted values of physical constants.

These concepts are termed, respectively, "administrative", "authoritarian", "demonstrative" and "definitive". They are increasingly purposeful in the order given.

The administrative concept (a) is of little concern in science because, while extensive documentation may be necessary, it is not sufficient to achieve the intent of traceability, namely the assurance of adequate accuracy of measurement. With regard to this goal, the authoritarian concept (b) is also rather unsatisfactory, since it merely refers to apparently correct results instead of demanding procedural correctness (i.e. the presence of proper metrological links).

The definition of traceability given in 3.1, adopted from the International Vocabulary of Basic and General Terms in Metrology (VIM), permits interpretation in the senses intended by both concept (c) and concept (d). As the main difference, traceability according to the definitive concept (d) implies assurances of validity for individual measurement results, and therefore demands considerably more than the demonstrative concept (c) where the aim is verification of overall measurement system performance.

5.2 Requirements for secure traceability chains

The formal requirements for secure metrological traceability are clearly embedded in definition 3.1, interpreted and illuminated in accordance with the definitive concept (d) defined in 5.1. The main features can be enumerated in more detail as follows.

a) There shall exist an unbroken traceability chain between the test object or sample and the standard reference object or reference material to which traceability is to be claimed. The latter should normally be a national or international standard, which may be a realization of the appropriate SI unit.

b) The traceability chain normally has to include intermediate standard objects or materials in a hierarchical structure. These intermediate standards shall be of established metrological provenance.

c) The various levels in the hierarchical structure shall be linked by specified and validated test methods which, by comparisons between objects or materials, allow the transfer of information pertaining to accuracy from one level to the next lower level. The protocols by which comparisons are made shall be sufficiently well defined that a result is adequately reproducible.

d) For each test method, any auxiliary standard objects or materials used shall be traceable to relevant definitive standards through an auxiliary traceability chain.

e) It shall be possible to assign an estimate of uncertainty to each measurement in the traceability chain, and to transfer or combine all of these in such a way that the desired result carries a proven assurance of accuracy.

5.3 Applications to chemical analysis

In (quantitative) chemical analysis, direct traceability of individual results to (realizations of) fundamental units is normally prohibitive, in particular for field analyses, due to the reasons explained in 6.4. As an executable alternative, traceability of performance (see 7.2.3), in particular of calibration, but e.g. also of separation or specificity, can be established using either reference analytical methods of known performance or reference materials of known accuracy. Concerning the latter alternative, as the more typical one in chemical analysis, traceability of performance is essentially reduced to traceability of the reference materials used in calibration. These, in turn, must be traced back further along a chain consisting of higher-level reference materials and measurement systems or methods, until reaching a reference standard of definitive accuracy. Then, in consequence, accuracy can be assessed on every lower level down to the field measuring system.

As explained in more detail in 6.3, chemical composition can, in principle, be traced back to (primary realizations of) an SI unit of a physical quantity of composition, and the chemical species concerned. In fortunate cases such as major parts of gas analysis, traceability of reference material to fundamental units can be established, cf. 7.2 and 8.3.

However, in many other fields of chemical analysis, the step relating complex material composition to fundamental units, through a fundamental method, is too wide to be implemented with full command of accuracy. Then traceability chains necessarily terminate at the level of primary reference materials, of complex composition. As a consequence, alternative methods are needed for the assessment of accuracy of these primary reference materials.

6 Chemical composition and the SI system

6.1 Quantities for portions of substances

In chemical metrology, the relationships between quantities associated with samples of substances are elaborated. Since matter is usually defined as "anything that has a mass and occupies space", the two most commonly recognized physical quantities designating the amount of a sample of matter are mass m (unit: kg) and volume V (unit: m^3).

The number of entities N (no unit, dimensionless) in a sample of substance is another such quantity. These entities may be atoms, molecules, ions, etc., or any combinations of these.

A fourth such quantity is the amount of substance n (unit: mole). The mole is directly based on a specific number of entities, the number of atoms in 12 g of carbon-12. When the mole is applied, the elementary entities have to be specified. For the mole, it is not possible yet to realize an unambiguous standard. Therefore standards for molar quantities are made using the standard of mass and accepted reference values of atomic/molar masses as proportionality constants.

6.2 Quantities and units of chemical composition

The basic task of chemical analysis is to determine the composition of substances. As an extreme case, complete analysis of an entirely unknown substance amounts to the qualitative identification of all its constituents and the quantitative determination of their proportions. In general, the task will be to determine accurately the content of one or several specified constituents of a substance with approximately known composition. Here the meaning of the term "constituent" largely depends on the context. In the case of a pure substance, that is, of a chemical compound, composition usually refers to the constituent chemical elements, while in the case of a mixture it refers to the constituent pure substances.

From the side of physical metrology, it is often argued that chemical analyses are essentially measurements of a single physical quantity, the amount of substance n, and therefore, in principle, should be traceable to the mole as the SI unit of the amount of substance. This assertion is based upon a fundamental misconception. In mixture analysis, the measurand never happens to be the amount of substance as such but always in conjunction with a specified chemical species, the content of which is to be determined in a given mixture. Obviously the misconception mentioned above is due to erroneously considering chemical species as measuring objects. In mixture analysis, however, the measuring objects are the mixtures to be analysed, while the individual chemical species define the various measurands, that is, the quantities to be measured. The determination of the contents of two different species in a mixture, e.g. the determination of the water content and the determination of the sulfur dioxide content in air, are two fundamentally different measuring tasks — such as the determination of the mass and the determination of the volume of a material body.

The claim that chemical analysis essentially deals with the measurement of a single quantity of composition is mistaken. Instead, the scope of chemical analysis consists of measurement of as many different quantities of composition as there are different analytically relevant chemical species.

For the expression of mixture composition, a number of different quantities are used, which are quotients of two (not necessarily like) quantities, expressing the amount of a specified mixture component and the amount of the mixture. The common quantities of composition are mass concentration, volume concentration and amount-of-substance concentration (molar concentration), and mass fraction, volume fraction and amount-of-substance fraction (molar fraction). Among these, the mass fraction and the molar fraction have the benefit of being independent of the state (temperature and pressure) of the mixture. In gas analysis, however, the volume fraction is still in use.

From the previous argumentation it follows that mixture composition cannot be adequately expressed in the SI system, unless it is complemented by the chemical species of the mixture constituents. In fact, specification of the composition of a mixture requires

a) specification of every mixture constituent;

b) the numerical value of the proportion or concentration of every mixture constituent.

6.3 Traceability of mixture composition to fundamental units

As explained in the previous subclause, specification of the composition of a mixture with N components involves $(N + 1)$ fundamental metrological units or entities: N qualitative ones, defining the mixture components, and a single quantitative one, defining the scale on which component proportions or concentrations are measured.

As a consequence, metrological traceability of mixture composition involves more than just traceability to an SI unit. In addition, it involves traceability to reference materials as measurement standards, providing primary realizations of the chemical species present in the mixture. In mass spectrometry, traceability even refers exclusively to chemical species. This is due to the fact that in this method molar fractions are measured directly, as relative particle numbers, and counting does not refer to any scale or unit.

Additional complications arise if measurement-related interferences among mixture components have to be taken into account. In the absence of any such interactions, a multicomponent mixture, consisting e.g. of several target components and a single balance component can be rigorously related to a corresponding number of binary mixtures, each realizing the content of one of the target components. If interferences among mixture components cannot be safely excluded, such reduction to binary mixtures is not possible. As a consequence, traceability can then only be established among multicomponent mixtures of closely related composition. In such cases — which, unfortunately, are numerous among current analytical problems as e.g. in environmental monitoring — traceability chains necessarily terminate at complex reference materials of composition similar to that of the analyte. Tracing further back to (realizations of) fundamental units, that is, to chemical species and SI units of composition, is discouraged due to the enormous increase in uncertainty that would be the consequence.

6.4 Impracticality of direct traceability to SI units

Due to the complexity of chemical-composition analysis, it is utterly impractible to try to trace back, directly, every individual analytical result to measurement standards realizing the totality of SI units involved — such as mass, volume, temperature and pressure, as well as to standards for all the chemical species involved. This would imply ending up with an uncertainty budget built up from specified uncertainties attributed to every single step or item. However, in any such costly exercise there will inevitably be missing links in the "traceability network".

Moreover, due to cumulative effects, extended error propagation calculations aiming at identification of all error sources, quantification of their individual contributions and combination into a measure of the overall uncertainty typically result in notoriously high estimates of uncertainty. This is related to the fact that uncertainty estimation aims at conservative upper bounds of expected errors which invariably add and never cancel unless correlation between different error sources is taken into account — which is clearly out of reach for everyday practice.

As an alternative to this "genealogical" approach in uncertainty estimation, the accuracy of an analytical method can be investigated empirically by direct comparison of measurement results with corresponding reference values realized by reference materials or obtained by reference methods of measurement. For example, the performance of a method of composition analysis can be evaluated using suitable reference materials as standards of composition. For this purpose, the analytical procedures must be fixed as closely as possible, thereby minimizing the number of variance components that contribute to the dispersion of results. By repeated analysis of reference materials of known composition (known within definitive uncertainty limits), precision as well as trueness, and with that the accuracy, of the analytical method can be estimated. Of course, these estimates properly refer to isolated points on a multidimensional range of composition only, with extension by interpolation and extrapolation requiring utmost care, e.g. in assessing the additional uncertainty caused by these mathematical procedures. An approach like this is well suited to provide traceability of performance (in particular of calibration) to reference materials as standards of composition.

As another example, the uncertainty on the calorific value of natural gas, determined by composition analysis and calculation in accordance with ISO 6976, could be investigated by two different methods, as follows:

a) Genealogical approach: Extended error propagation calculation taking into account errors in composition caused by the analytical method, errors in the calorific values of natural-gas constituents and deviations from the mathematical model (linear combination of component calorific values). The uncertainty of the analytical method — typically gas chromatography — is traced back to various sources.

b) Empirical approach: Direct comparison of results obtained by the method under investigation and a suitable reference method (calorimetry) on a number of gas mixtures covering the composition range considered.

Summarizing, in chemical analysis, direct traceability for every single analytical measurement to (realizations of) all the relevant SI units, as propagated by metrological standards and guidelines, is often beyond reach, due to the complexity of the corresponding traceability networks. Reference materials then can provide "intermediate" standards, realizing appropriate composition levels, with traceability chains sufficiently short to enable realistic uncertainty assessment. In analytical chemistry, it has become more and more common practice to use reference materials and especially certified reference materials as intermediate standards.

6.5 Role of fundamental methods

The measurement methods used in present-day chemical analyses are typically indirect methods in which the target quantity, the concentration or proportion of a specified chemical species, is not measured directly. Instead, the measured quantity is an appropriate instrumental response variable. Such measuring systems, therefore, require calibration in the sense that the functional relationship between the response variable and the target variable is determined empirically, by measuring the response to known values of the target variable, as realized e.g. by corresponding reference materials as calibrants.

In contrast to indirect methods (also termed comparison methods or relative methods), fundamental methods are those in which the target quantity is measured directly. For example, many of the typical methods of "wet analytical chemistry" are fundamental methods, where the target species is separated from the sample, identified and quantified, e.g. by weighing. Such methods evidently do not require calibration in the sense described above. However, their performance must be validated, that is, their measurement uncertainty (or recovery rate) must be determined empirically.

Besides fundamental methods of analysis (also called direct methods or absolute methods), an equally important branch of fundamental methods are methods for the production of reference materials, e.g. the manufacture of mixed substances from pure compounds by gravimetry.

Evidently, fundamental methods are indispensable for establishing the final links of traceability chains at the level of fundamental units. As explained in 6.3, for composition analysis these fundamental units are the SI unit for the considered physical quantity of composition, and the chemical species of the considered mixture constituents. Only if this final link can be firmly established, within definitive uncertainty limits, can definitive uncertainty limits also be attributed to all of the lower-level measurement systems, measurement standards and reference materials.

In the field of gas analysis — with the exclusion of trace analysis and reactive components — gravimetric preparation of reference gas mixtures is generally considered as a high-accuracy fundamental method. This is true, provided that all the relevant uncertainty components are assessed carefully, as e.g. the impurities of the parent gases. Subclause 8.3.1 contains a detailed discussion of the uncertainty components in gravimetric gas mixture preparation.

7 Traceability in natural-gas analysis

7.1 Analysis of natural gas

Natural gas and natural-gas substitutes are multicomponent gas mixtures, with the major constituents including a range of hydrocarbons (mostly alkanes) and a number of permanent gases (e.g. helium, nitrogen, carbon oxides and hydrogen), plus a multitude of trace components such as water vapour and volatile sulfur compounds.

The scope of natural-gas analysis comprises the following:

a) analysis of composition, in the sense of quantitative determination of each component that is considered relevant to the calculation of some bulk property of interest, such as calorific value, relative density or Wobbe index;

b) analysis for important trace components, such as hydrogen sulfide, heavy hydrocarbons or mercaptans.

For the analysis of natural gas, the importance of appropriate reference materials to serve as calibration standards for analytical instruments is self-evident.

In the composition analysis of real natural gases taken from commercial sources and intended for custody transfer, traceability of the calibrated and validated analytical system is maintained by artificially prepared gas mixtures. The strength of this traceability chains is mainly determined by the ability to establish, by means of analysis, the impurity level of the parent gases from which the artificial mixtures are derived.

7.2 Traceability on a reference gas basis

7.2.1 General considerations

Due to the complexity of natural-gas composition and, equally, due to the complexity of the overall analytical procedure, direct and complete traceability of every single measurement result of natural-gas composition analysis to all of the fundamental units involved is clearly prohibitive, at the present state of the art. However, apart from particular cases, as e.g. in the preparation or validation of primary standard gas mixtures (c.f. 8.3.1), it is definitely not necessary for the purpose implied by the current traceability requirements in international quality assurance guidelines.

For the purpose of maintaining traceable control of the performance of measuring systems for natural-gas composition analysis, it is perfectly sufficient to execute, on a regular basis, a calibration or validation procedure of known performance, using calibration gases of appropriate composition and known accuracy. Hereby, the problem of tracing back analytical performance, in particular calibration but also e.g. separation or selectivity, is essentially reduced to the problem of tracing the composition and accuracy of the calibration gases to reference standards of definitive accuracy. The method proposed in these guidelines to solve this problem is to proceed along traceability chains involving higher-level reference gas mixtures and validated analytical comparison methods, terminating at the level of primary-standard gas mixtures (PSMs).

However, in view of the limited availability of PSMs, it should be stressed that it is not necessary in every case to trace back up to the highest level of accuracy, if for a lower-level reference gas mixture or reference measuring system the accuracy can be safely assessed by alternative methods instead of tracing back to primary realizations of fundamental units.

For the reason stated above, this document considers exclusively traceability on the basis of reference gas mixtures as measurement standards, realizing appropriate levels of natural-gas composition. At the base level of measuring systems, traceability is primarily taken as traceability of calibration, either "pointwise" for the validation of individual high-accuracy analytical data, or "rangewise" for the validation of performance of routine measurement systems.

In an algorithmic manner, the statement above can be expressed as follows:

> The performance of an analytical system is traceable if the procedure of performance evaluation is validated and if the calibration gases used are traceable.
>
> A calibration gas is traceable if its composition has been validated, within specified uncertainty limits, through comparison with traceable reference gas mixtures.

There are then several topics that need to be clarified conceptually and implemented practically, as follows:

traceability of individual analytical results to reference gas mixtures;
traceability of analytical performance to reference gas mixtures;
traceability of calibration gases to reference gas mixtures;
traceability of reference gas mixtures to primary-standard gas mixtures;
traceability of primary-standard gas mixtures to fundamental units.

In these descriptions, as well as in the following subclauses, the term "traceability of/to gas mixtures" is used as a short form of "traceability of/to gas mixture composition".

7.2.2 Traceability of individual analytical results

Principle: An individual measurement result on the composition of a particular gas mixture can be validated by analysing a reference gas mixture of almost identical composition. If that analysis reproduces the "reference composition", the measurement result in question is confirmed within the uncertainty limits given by the precision of the analytical method.

The basic decision that the reference composition is reproduced involves statistical evaluation, taking into account specified uncertainties of reference materials and the precision of the analytical method.

Implementation: By a specific validation procedure, to be included — whenever technically feasible — in every International Standard method of natural-gas analysis. Questions to be settled there must include.

conditions for sufficiency of a single reference gas mixture;
closeness of bracketing by two (or more) reference gas mixtures, for secure linearity of response;
uncertainty assessment for the validated composition;
quality specifications, including uncertainty and traceability, for the reference gas mixtures employed;
contents of traceability statements.

Validation of individual analytical results is not necessarily performed separately, but can be incorporated into the calibration procedure by using additional reference gas mixtures beyond the minimum number required for the determination of the calibration curve.

7.2.3 Traceability of analytical performance

Principle: Performance of the analytical system is tested over a specified composition range, by analysing a number of reference gas mixtures, covering the range in question. In these tests, accuracy, separation and interference are the key elements.

For maintaining traceability of performance and, in particular, of calibration, evaluation is repeated on a regular basis.

Implementation: Essentially covered by ISO 10723, which contains detailed recommendations on how to design a sufficiently tight grid of composition levels for the reference gas mixtures to be employed. In applying ISO 10723 to a particular method of analysis, it will be necessary to include:

fixing the maximum interval for re-evaluation of the performance, or for re-calibration;

uncertainty assessment for the validated performance measurements, in particular for the calibration curve/function;

quality specification, including uncertainty and traceability, for the reference gas mixtures employed;

contents of traceability statements.

7.2.4 Traceability of calibration gases

Principle: The composition of a calibration gas — usually a working-reference gas mixture, in the terminology of clause 8 — is validated by comparison of its analyser response with that of one or several sufficiently similar reference gas mixtures.

As a rule, the comparison is performed on the basis of calibration over a composition range preferably small enough to allow for linear interpolation/regression. If sufficient knowledge of the performance of the analytical method (i.e. the response curve) is available and non-linear interpolation/regression is applied, then validation can be extended to wider composition ranges. Such methods, however, require a greater number of reference gas mixtures for an appropriate grid of reference compositions.

Again, validation is not necessarily performed separately but can be incorporated into a calibration exercise, by using more than the minimum number of reference gas mixtures.

Implementation: Partially covered by ISO 6143. In this method, however, the number of reference gas mixtures involved is restricted to the bare minimum necessary for the determination of the calibration curve, while this document proposes to incorporate at least one more reference gas mixture for a test of consistency.

Subjects to be included are again:

fixing the maximum interval for re-validation;

uncertainty assessment for traceability statements;

quality specification, including uncertainty and traceability, for the reference gas mixtures employed;

contents of traceability statements.

7.2.5 Traceability of reference gas mixtures to primary-standard gas mixtures

Principle and implementation are essentially the same as in 7.2.4.

The concept of primary-standard gas mixtures is explained in detail in 8.3.1.

7.2.6 Traceability of primary-standard gas mixtures to fundamental units

As explained in 6.3, for natural-gas composition analysis, the fundamental units are the SI unit for the considered physical quantity of composition, e.g. the molar fraction, and the chemical species of the considered natural-gas constituents. Only if this final link can be firmly established, within definitive uncertainty limits, can definitive uncertainty limits also be attributed to all of the lower-level reference gas mixtures.

Since primary-standard gas mixtures are, as a rule, prepared by the gravimetric method, the topic addressed in this subclause is essentially the validation of composition for gas mixtures prepared by gravimetry, paying particular attention to long-term stability. Validation in this case refers to the assessment of the uncertainty budget of the gravimetric method, as detailed in 8.3.1. A specific problem in this field is caused by the lack of direct, fundamental methods for analytical validation. Because of that, protocols for uncertainty assessment using comparison methods need to be developed.

8 Hierarchy of reference gas mixtures

8.1 Introduction

For the purpose of this document, the standard terms in the fields of reference materials and measurement standards have been adapted to the area of (natural) gas analysis as shown in table 1.

Table 1 — Adaptation of standard terminology

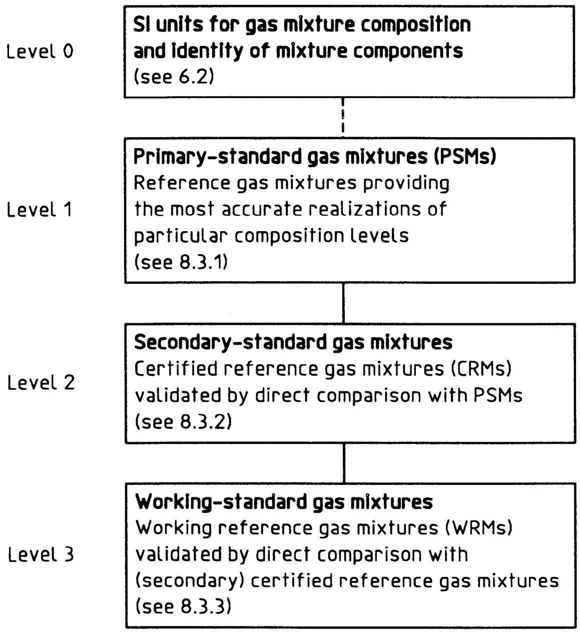
Standard terminology	Adapted terminology
Reference material (3.3)	Reference gas mixture
Certified reference material (A.9)	Certified reference gas mixture
Working reference material In-house reference material	Working reference gas mixture
Primary standard (A.10)	Primary-standard gas mixture
Secondary standard (A.11)	Secondary-standard gas mixture
Reference standard (A.14)	(No correspondent)
Working standard (A.15)	Working-standard gas mixture

With one exception, the definitions of the standard terms are given in clause 3 or annex A. The adapted terms together with their descriptions given in the following subclauses are not to be mistaken as formal, normative definitions.

Similar to the hierarchy of measurement standards in physical metrology, the hierarchy of reference gas mixtures in natural-gas analysis, as presented in this document, is based on analytical comparison of lower-level standards with standards of the next-higher level. However, in contrast with physical metrology, where this comparison can often be performed on a one-to-one basis, validation of a reference gas composition usually requires analytical comparison with several higher-level reference gas mixtures. The relationship between reference gas mixtures and SI units of chemical composition is also less simple than in physical metrology. These and other differences between physical and chemical metrology have already been explained in details in previous clauses.

8.2 Designation of levels in the hierarchy

Figure 2 presents the hierarchy of reference gas mixtures, as discussed in this clause, emphasizing analogy with the hierarchy of measurement standards in physical metrology.



NOTE — Certified reference gas mixtures provide the typical case of a secondary-standard gas mixture, but they are not restricted to this level.

Figure 2 — Hierarchy of reference gas mixtures

8.3 Designation of reference gas mixtures

8.3.1 Primary-standard gas mixtures

By definition, a primary-standard gas mixture realizes a particular composition at the highest quality level, quality referring primarily to accuracy and stability. Note that the specifications of primary quality can vary dramatically between different gas mixture types, as e.g. in the case of percentage levels of carbon monoxide in nitrogen as opposed to that of trace levels of sulfur dioxide in air.

Primary-standard gas mixtures are generally prepared gravimetrically by successively weighing into a pressure cylinder samples of the pure constituent gases, or samples of gas mixtures prepared previously. Prior to use, these parent gases must be analysed for relevant impurities. The uncertainty on the resulting mixture composition is assessed, using error propagation methods, by determining and combining the uncertainty contributions from all the various steps and influences involved, e.g.

a) the determination of the mass of the parent gas samples (local uncertainties: e.g. due to the weighing procedure; imported uncertainties: e.g. due to the mass pieces);

b) the determination of the amount of substance of the parent gas samples (e.g. uncertainties on molar masses, on the contents of detected impurities, due to the limited accuracy of their analysis, and on the levels of non-detects);

c) manipulation of the gas samples (concerns the manufacture of the mixtures as well as their storage, sampling and transfer to the point of subsequent use);

d) physico-chemical interferences (e.g. selective condensation or adsorption, and chemical interactions of mixture components among each other and with cylinder materials).

Some of these uncertainty components [typically from a) or b)] can be determined adequately. Other contributions to uncertainty, due to imperfections and interferences [c) or d)], can only be estimated roughly at the present state of the art for primary-standard gas mixtures in the field of natural-gas analysis. Therefore, alternative techniques must be employed. In current practice, there are essentially two different approaches in use to handle this problem.

1) For the purpose of safely covering the unknown uncertainty contributions, the standard deviation resulting from the feasible uncertainty budget (relating essentially to gravimetry and impurities) is multiplied by a confidence factor. Unfortunately, this subjective factor is often not stated or even omitted completely.
2) The uncertainty contributions due to the effects mentioned are investigated empirically, by analytical comparison of larger numbers of mixtures of similar composition but of different history, age and origin.

Ideally, such validation should be performed by a direct, fundamental method of analysis. In natural-gas analysis, however, direct methods of analysis are not available for the majority of analytical problems, or are inadequate with respect to accuracy or quantification limit. Therefore, typically, analytical validation is performed by means of a high-precision indirect (comparison) method, such as gas chromatography or infrared spectrometry, in accordance with a strategy of simultaneous testing of consistency among compositions, determined by a fundamental method of preparation , and analyser responses on several gas mixtures with closely related compositions.

NOTES

1 Due to the lack of direct, fundamental methods of (natural) gas composition analysis to complement the uncertainty assessment of primary-standard gas mixture preparation, traceability chains relating to reference gas mixtures typically end at the level of primary standards. At present, as a rule, these measurement standards cannot be rigorously traced back further to the basic SI units without also considering the uncertainties due to interferences and imperfections. Therefore, consistency checking among primary-standard gas mixtures is of paramount importance.

2 For the reasons indicated above, international collaboration in the field of primary-standard gas mixtures will be indispensable. For some specific types of primary-standard gas mixtures, such interlaboratory comparisons are currently performed by some national metrology laboratories, e.g. in an interlaboratory study recently initiated by the Comité International des Poids et Mesures (CIPM).

3 Due to the expense of the production and maintenance of primary-standard gas mixtures, these have been and will be developed only in very small number by very few laboratories in the world. Up to now, national metrology laboratories have taken a leading part in this field. It should be noted, however, that production and maintenance of primary-standard gas mixtures is not restricted to national metrology laboratories.

4 Internationally accepted guidelines or standards on quality requirements and qualification protocols for primary-standard gas mixtures are not available at present.

5 It is well recognized that, at the present state of the art, the number of primary-standard gas mixtures currently available is far too small to cover the wide range of compositions of natural gases.

8.3.2 Certified reference gas mixtures (CRMs)

Due to the reasons indicated at the end of 8.3.1, the use of primary-standard gas mixtures will be restricted to validation and certification of secondary-standard gas mixtures of similar composition.

A level-2 certified reference gas mixture is a reference gas mixture the composition of which is certified as having been validated by direct analytical comparison with primary-standard gas mixtures of closely related composition.

As a rule, calibration of the analytical method employed in such validation (e.g. gas chromatography) requires several primary standards in order to establish the analyser response in the neighbourhood of the composition to be validated. The approach according to this definition constitutes a typical case of "certification by a definitive method" as described in ISO Guide 35.

It should be noted, however, that there is yet another principle for certification of reference gas mixtures that is generally accepted in cases where certification by means of comparison with primary-standard gas mixtures is not achievable. This is the concept of "certification by interlaboratory testing" as described in ISO Guide 35. In contrast to the former approach, where certification implies establishing traceability to primary standards of measurement, certification in accordance with the interlaboratory concept amounts to adopting the consensus values resulting from round-robin analyses. As a characteristic of this method, the consensus values are not traceable to related measurement standards and can therefore be substantially biased. The statistical methods typically employed in analyses of interlaboratory test results (ANOVA methods) do not permit any estimation of the systematic error of the consensus value, due to the built-in hypothesis of random distribution of individual systematic errors. This hypothesis, however, is rarely fulfilled in real-life round-robin testing with small numbers of participants. In addition, the interlaboratory procedure often yields certified values of rather low precision, that is, the random uncertainty of the consensus value turns out rather high, as compared with the "definitive" approach.

With regard to the hierarchy of reference gas mixtures, certified reference gas mixtures certified by interlaboratory methods can be used as substitutes, but not equivalents, of primary-standard gas mixtures. However, they inevitably lack the qualification to be met by primary-standard gas mixtures (refer to the example in annex B).

Level-2 certified reference gas mixtures as described in the second paragraph of this subclause constitute the level of secondary measurement standards in natural-gas analysis. Their typical use is that of transfer standards, providing traceability of working reference gas mixtures to primary-standard gas mixtures. That is, level-2 certified-reference gas mixtures are used to validate — and also to certify — the composition of reference gas mixtures for daily routine work, e.g. in the calibration of measuring systems and control of measurement performance, when traceability to primary standards is required.

The general aspects of certification of reference materials and the uses of certified reference materials are covered by ISO Guides 33 and 35.

8.3.3 Working reference gas mixtures (WRMs)

A level-3 working gas mixture is a reference gas mixture the composition of which has been validated by direct analytical comparison with level-2 certified reference gas mixtures of closely related composition. In accordance with this definition, the composition of a level-3 working standards is traceable to that of primary-standard gas mixtures within specified uncertainty limits which, however, will be larger than those of related level-2 standards.

As already mentioned in the previous paragraph, reference gas mixtures of this type — possibly certified as well — are used in daily routine procedures such as calibration and monitoring of measuring systems, when traceability to primary measurement standards is required.

Requirements on working reference gas mixtures belong to the scope of standards for individual analytical methods as well as for general analytical methodology.

9 Role of traceability in uncertainty assessment

In order to maximize the precision of a measurement method, that is, to minimize random measurement errors, the acknowledge recipe is to strictly follow a written operational procedure where all the performance steps and the experimental conditions are fixed in detail. In addition, the standard deviation can, in principle, be reduced by a factor of $1/\sqrt{N}$ by averaging over series of N repeated measurements, provided they are independent, instead of averaging over single results. In international standardization of methods of natural-gas analysis, precision is determined as a rule by interlaboratory tests in accordance with ISO 5725.

In order to maximize the trueness of a measurement method, that is, to minimize systematic measurement errors, the measuring system must be calibrated (and the validity of calibration must be monitored) using accurate measurement standards.

For the assessment of the trueness of a measurement method, the accuracy of the measurement standards used in calibration and validation must be known. The acknowledged recipe to accomplish this is to use exclusively measurement standards that are traceable to primary standards and/or to accepted values of physical constants. That is, the values attributed to the measurement standards are derived from accepted reference values, in accordance with known relations, within specified uncertainty limits.

In natural-gas analysis, as a rule, the measurement standards used in calibration and validation are reference gas mixtures. For the assessment of the trueness of analytical methods, the method recommended in these guidelines is to use reference gas mixtures that are traceable to primary-standard gas mixtures, as described in 8.3. That is, the composition of these reference gas mixtures has been validated against primary-standard gas mixtures of closely related composition in an unbroken chain of comparison measurements.

For the assessment of the accuracy of the composition attributed to the reference gas mixtures used in calibration and validation, the accuracy of the primary standards and the uncertainty of the comparison measurements involved must be known.

An acknowledged recipe for the accuracy assessment of primary-standard gas mixtures is not available at present. It is, however, generally accepted that primary quality of reference gas mixtures for natural gas analysis can be realized by the gravimetric method of gas mixture preparation. For this method, uncertainty assessment in accordance with the error propagation method suffers from the fact that major uncertainty contributions cannot be quantified adequately. As an alternative, an empirical approach to uncertainty assessment, based on correlation studies on larger numbers of gas mixtures, could be rewarding. Accuracy assessment of the gravimetric method of gas mixture preparation needs to be considered in the forthcoming revision of ISO 6142.

The topic of how to combine measurements of precision and of trueness into a measurement of overall uncertainty has been under controversial discussion, raised in the course of ISO activities responding to the recommendations of the Comité International des Poids et Mesures (CIPM). This discussion is not yet finished, and it is not clear whether there will be a single method standardized in the end. International standardization will possibly offer several methods of uncertainty combination, designed for different purposes.

The only International Standard currently available that deals with the controversial subject of uncertainty combination is ISO 5168. Responding to the recommendations of CIPM [18] to treat systematic and random uncertainties essentially alike, the topic has been on the scope of several working groups in ISO and the Western European Calibration Cooperation (WECC). A number of documents have been elaborated, such as *Guide to the expression of uncertainty in measurement* [17] and *Guidelines for the determination of uncertainty of measurement in calibrations* [19], produced by working groups in ISO/TAG 4 and WECC, respectively. Hopefully, the state of the art in this field will be clarified in the near future. Until that, the choice among the methods described in these and other references is free, which implies that the method chosen must be fully explained and documented.

In order to discriminate between the various terms related to the interpretation of measurement results, an example is given in annex B, based upon a hypothetical interlaboratory exercise. Unfortunately, real-life measurements are too often in line with this example.

10 Implementation of traceability in International Standards for natural-gas analysis

10.1 General considerations

The purpose in requiring traceability to acknowledged standards of measurement is to maximize and to quantify the trueness of measurement methods and results. The appropriate place to specify traceability aspects in an International Standard for a method of natural-gas analysis, therefore, is in the clause dealing with accuracy (or uncertainty) of measurement.

In standardizing methods of natural-gas analysis, it has been general practice to evaluate the precision only. In future International Standards, evaluation of trueness needs to be incorporated as well. This can be done conveniently by interlaboratory analyses on reference gas mixtures of known accuracy, from which measures of precision and of trueness can then be derived simultaneously. The recommended method to fulfil the condition of "known accuracy" is to use reference gas mixtures that are traceable to primary standards.

Methods for assessing the trueness of measurement methods and results have been (and partly still are) standardized in the revision (and extension) of ISO 5725.

For an analytical method, traceability to primary standards is established and maintained if measurement accuracy is assessed and monitored in accordance with a validated procedure, using, as calibration gases, reference gas mixtures that are traceable to primary-standard gas mixtures.

International Standards supposed to describe methods that produce traceable analytical results must therefore specify in sufficient detail how to establish and maintain definite control of accuracy of measurement, that is, of both precision and trueness, by means of appropriate reference gas mixtures (or other calibration standards). Such descriptions must include or address, among others, the topics explained in the subsequent sections.

10.2 Relevant traceability chains

Typically, the measurement result obtained on a given sample depends on a number of additional parameters which characterize the state of the measuring system and the state of the sample, such as input/output of calibration measurements, environmental conditions, etc. All these influence quantities must be identified, and their contribution to the overall uncertainty of measurement must be estimated. For this purpose, one has to know how tightly the state parameters are under control and how sensitively the measurement results respond to variations of state parameters.

For the critical parameters identified through this kind of analysis, traceability should be established by using appropriate measurement standards. In any case, traceability of calibration must be established by means of reference gas mixtures or other calibration standards which in turn are traceable to primary standards of measurement. If laboratory conditions are critical in the sense described above, calibrated measuring equipment is mandatory. If e.g. measurement results critically depend on the length of the measuring time interval, time measurement should be made traceable to national standards of time measurement, e.g. by using clocks triggered by the national time radio pulses.

International Standards on methods of natural-gas analysis must specify how to establish and maintain traceability of calibration. In addition, they should identify the other critical state parameters which significantly affect the measuring results, and indicate how to obtain traceability of their values.

10.3 Protocol for accuracy assessment

The methods used in the estimation of uncertainty, that is, in quantitative assessment both of precision (relating to random components of uncertainty) and of trueness (relating to systematic components of uncertainty), and in combining both to give a measurement of total uncertainty, must be fully documented and proven to be correct and adequate for the given purpose.

This requirement is difficult to realize at present, due to the lack of appropriate International Standards in the field of measurement uncertainty (cf clause 9). The methods used in International Standards on gas analysis, such as ISO 6142, ISO 6143 and ISO 6711, are clearly outdated and need substantial revision. The only possibility then is to adapt published methods used in other fields. Documentation must be sufficiently detailed to permit valid proof of correctness and adequacy.

It should be kept in mind that there are essentially different approaches to accuracy assessment, as explained in detail in 6.4:

statistical estimation, based on detailed analysis of error sources and uncertainty propagation;

empirical investigation, using reference materials or reference methods of measurement.

10.4 Measuring range

The measuring range considered for an analytical method depends of course on the composition range of the gas mixtures considered as samples and on the capability of the measuring equipment. Beyond these "natural" restrictions, it will often be necessary to restrict the measuring range to those parts of the working range where the error of measurement can be ascertained to lie within specified limits (uncertainty limits). Typically, the uncertainty due to calibration, as obtained by regression calculations, critically depends on the number and closeness of calibration points. Therefore the number of calibration gas mixtures, their composition and the uncertainty of their composition are essential parameters that must be carefully optimized with respect to the goals of maximizing the measuring range, minimizing uncertainty due to calibration and minimizing efforts as well as expense.

10.5 Calibration and validation gases

See 10.4 and 10.9.

10.6 Qualification intervals

According to ISO 10012-1, qualification is the status given to an "item" — that is, to a measuring system — when it has been demonstrated that it is capable of meeting specified requirements.

Measuring systems shall be qualified at appropriate intervals (usually periodic), established on the basis of their stability, purpose and usage. In natural-gas analysis, qualification of measuring systems is implemented by performance evaluation in accordance with ISO 10723. International Standards on individual methods of natural-gas analysis must specify how to apply, modify or supplement the general methods described there.

As a rule, the main item in qualification will be calibration and recalibration. International Standards on methods of natural-gas analysis should indicate how to devise appropriate (re)calibration intervals for different uses of the analytical method considered.

10.7 Documentation and report of accuracy surveillance

In addition to specifying methods of accuracy surveillance (and other qualification procedures), International Standards on methods of natural-gas analysis should indicate in which detail to document the method used and how to report the results.

10.8 Traceability of reference gas mixtures and other measurement standards

International Standards on methods of natural-gas analysis must demand that the property values realized by reference gas mixtures and other measurement standards to be used in calibration or in determination of other critical parameters (cf 10.2) are traceable to primary-standard gas mixtures or other primary standards of measurement. In addition, they should indicate how to establish traceability and how traceability should be documented.

10.9 Validation of individual measurement results

As explained in previous sections, a major topic in the standardization of methods of natural-gas analysis is validation of performance, in particular of calibration, using traceable reference gas mixtures and other measurement standards. In addition, supplementary methods for validation of individual results, to be used e.g. in certification of reference gas mixtures, should be included. However, in contrast with performance evaluation, there is at present no International Standard available that covers the state of the art of validation analyses in the natural-gas field. Some general guidelines on certification principles are given in ISO guide 35, which, however, are not readily applicable to natural-gas analysis, due to specific features of this field of measurement.

10.10 Limitations with respect to traceability

Due to the limited availability of primary-standard gas mixtures, it will often be impossible to establish traceability over the full measuring range of the analytical method considered. International Standards should therefore indicate how to establish and maintain restricted traceability, referring to specified parts of the measuring range.

In some cases, traceability can be transferred to other parts of the measuring range, applying mathematical modelling which brings into the uncertainty budget the contribution of the uncertainty of the model.

If, for a particular analytical method, there is no means of establishing traceability of measurement, this should be clearly stated and the reasons given.

11 Examples

11.1 The ISO/TC 193/SC 1 methodology for on-line gas chromatography

For the direct determination of major natural-gas constituents using on-line gas-chromatographical measuring systems, ISO/TC 193/SC 1 has adopted a specific methodology that is, at present, described in the documents on tailored analysis (ISO 6974-1 and ISO 6974-2) and performance evaluation (ISO 10723). As a first example, this methodology is reviewed with regard to traceability aspects. For a full description, the relevant documents should be consulted.

Basically, the approach developed by the respective working groups of ISO/TC 193/SC 1 is a combination of global calibration and local validation/correction. In the following section, the term "X-concentration" is (mis)used as a short form of "molar fraction of X", where X symbolizes a natural-gas constituent.

For each constituent X determined directly, the measuring range (X-concentration range) is specified. A number of reference gas mixtures (range calibration gases) are chosen such that their X-concentrations adequately cover the specified measuring range. For this range, the response function, relating X-concentration and analytical response, is determined, by polynomial regression of appropriate degree, from calibration data obtained on the range calibration gases. This response function is supposed to remain unchanged, except from possible minor deviations that can be corrected locally, during the use of the analytical system over extended periods of time. For a specified application, that is, for a narrow range of sample compositions, the validity of the response function is assessed locally, and errors due to local deviations from the response function are corrected, using additional calibration data obtained from analysis of an appropriate local validation gas. This is a reference gas mixture chosen to have a composition close to that anticipated for the sample, where, ideally, the X-concentration would be located in the middle of the specified analytical range. If the original response function is found to be invalid, that is, if local deviations beyond a prescribed critical level occur, the response function needs to be re-established.

In this approach, the random uncertainty (precision) of the method is assessed globally, that is, over the complete measuring range, by regression analysis of the range calibration data. For this purpose, the composition of the range calibration gases must be known within reasonable uncertainty limits. But definitive data on the uncertainty of composition are not required since no such data enter into the assessment of precision. Therefore traceability is not of particular importance for the composition of the range calibration gases.

The systematic uncertainty (trueness) of the method is determined locally, that is, for a narrow analytical range, by analysis of local validation data. In this assessment, the uncertainty on the composition of the local-validation gas must be considered explicitly. Therefore traceability of composition is indispensable for a valid assessment of systematic uncertainty. Indeed, case studies have shown that the uncertainty on the composition of the local-validation gas typically constitutes one of the largest contributions to the overall uncertainty of the method.

It can be concluded that, for the analysis of natural-gas composition in accordance with the methodology explained above, the assessment of uncertainty primarily requires a local validation gas whose composition is close to that of the sample. For each component, the concentration must be known within definitive uncertainty limits. This last requirement can be fulfilled by using reference gas mixtures whose composition is traceable to appropriate certified reference gas mixtures or, ideally, to primary-standard gas mixtures (cf 8.3). At the present state of the art, the best choice would be reference gas mixtures which are prepared gravimetrically, and whose composition is validated by analytical comparison with appropriate certified reference gas mixtures or primary-standard gas mixtures.

11.2 Example of a measurement design for natural-gas metering

The following methodology has been designed for, and implemented in, a natural-gas metering system. In this system, the calorific value of pipeline natural gas is measured, at various metering stations, using process gas chromatographs. These "field chromatographs" are calibrated, for a narrow analytical range, against a reference chromatograph, operated at a central laboratory. In this calibration two different types of reference gas mixture (A_2 and B) are involved as transfer standards. The reference chromatograph, in turn, is calibrated globally and validated locally, using essentially the same method as described in 11.1.

The local validation gas used here (A_1) is traceable to primary-standard gas mixtures maintained at a national metrology laboratory while the range calibration gases (C) are binary mixtures prepared gravimetrically by the central laboratory itself.

This method uses three types of reference gas mixture:

A_1 synthetic six-component mixture (components: N_2, CO_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}); composition representative for B; certified against primary-standard gas mixtures;

A_2 same composition as A_1; validated against an A_1 mixture;

B pipeline natural-gas samples; approximately constant composition;

C synthetic binary mixtures (N_2/CH_4, CO_2/CH_4, C_2H_6/CH_4, C_3H_8/CH_4, n-C_4H_{10}/CH_4); six compositions each.

The A-mixtures are prepared, by a commercial producer, in accordance with a gravimetric batch-preparation procedure, yielding a set of N cylinders with identical compositions. Two cylinders chosen at random from this set are certified at a national metrology laboratory, by analytical comparison with appropriate primary-standard gas mixtures. These two cylinders are intercompared at regular time intervals in order to test the long-term stability of the mixture composition. For the other $N - 2$ cylinders, the composition is validated, and its uncertainty determined, by analytical comparison with the certified ones. These cylinders are used for the calibration of the field chromatographs. There are two cylinders kept at each metering station. One cylinder is kept sealed for the purpose of settling possible cases of doubt on the calibration gas in use.

The C-mixtures are prepared at the central laboratory itself, by the gravimetric method. They are used for the calibration of the reference chromatograph at that laboratory. This calibration is performed, separately for each component, over the whole concentration range spanned by the calibrant concentrations, using linear or polynomial regression. After this multipoint calibration, the certified A_1-mixture is used, as a local validation gas, for local validation and correction of the response function. After this correction, other cylinders of the same batch are analysed in order to validate their composition and assess their uncertainty. The composition of these A_2-mixtures is then also traceable to primary-standard gas mixtures, via the certified ones. They are used as calibration gases for the field chromatographs operated at the metering stations. Due to the narrow measuring range required for these analytical systems, one-point calibration is sufficient.

Finally, the B-mixtures are samples of pipeline natural gas, filled into cylinders and analysed jointly with the non-certified A_2-mixtures. These cylinders are used as additional calibration gases (check gases) for the field chromatographs operated at the metering stations.

Using the approach sketched in figure 3, an unbroken traceability chain can be built up relating the field measurement of pipeline natural-gas composition, and, from that, its gross calorific value, to primary-standard gas mixtures. Implementation of this scheme therefore appears to be promising. To serve the purpose of traceability, this implementation should be backed up by a detailed assessment of uncertainty propagation along the links of the traceability chain. As indicated in figure 3, this is a traceability network rather than a traceability chain. That is, there are additional links which contribute significantly to the accuracy as well as to the reliability of measurement. However, at the present state of uncertainty assessment, the contribution of such additional links is difficult to evaluate adequately.

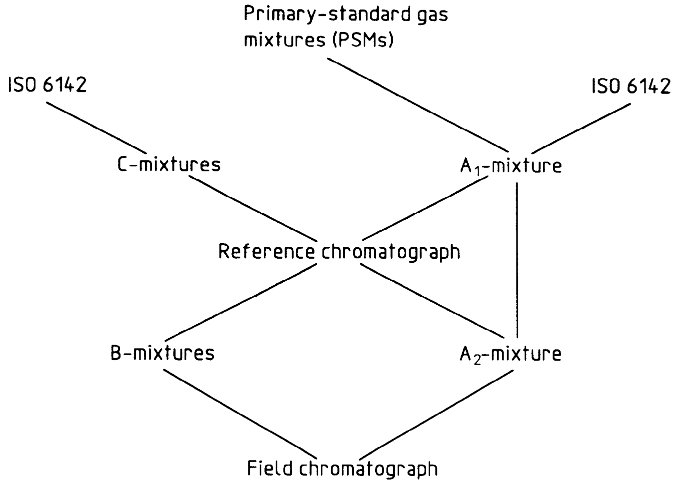


Figure 3 — Traceability network for a field measurement design

12 Summary

As explained in detail in the previous clauses, traceability is no primary target of quality assurance in measurement. The requirement of traceability of measurement rather serves another purpose: to introduce the obligation to provide evidence for the accuracy attributed to measurement results, primarily for trueness besides precision. This observation is fully supported by the pertinent quality assurance standards such as the ISO 9000 series. The main requirement on measuring equipment, which in fact defines the scope of traceability in measurement, is that measurement uncertainty shall be known and be consistent with the required measurement capability (cf ISO 9001:1994, subclause 4.11).

For the purpose of emphasizing the scope of traceability, the definition given in clause 3 could be rephrased as follows:

traceability: The ability to provide evidence of the overall accuracy attributed to measurement results, through documented calibrations, using measurement standards of known accuracy, and comparison measurements of known performance.

NOTES

1 The purpose of traceability is *known* accuracy, but not necessarily high accuracy.

2 Traceability refers to the *overall* accuracy of measurement. If major uncertainty components cannot be assessed adequately, traceability cannot be claimed for the complete measurement.

Annex A
(informative)

Supplementary terms and definitions

A.1 Terms related to accuracy and uncertainty

NOTE — Some of definitions A.1.1 to A.1.5, designed for the testing field, have been adapted from ISO 3534-1 for the present usage through substituting the original term "test result" by "measurement result". In the 1993 edition of the International vocabulary of basic and general terms in metrology (VIM) (see clause 2), "reproducibility conditions" are defined in a more general sense than used currently.

A.1.1 bias: The difference between the expectation of the measurement results and an accepted reference value. [Adapted from ISO 3534-1]

A.1.2 repeatability: Precision under repeatability conditions. [ISO 3534-1]

Additional remark: Repeatability is expressed quantitatively, based on the standard deviation of the results.

A.1.3 repeatability conditions: Conditions where independent measurement results are obtained with the same method on identical measuring objects in the same laboratory by the same operator using the same equipment within short intervals of time. [Adapted from ISO 3534-1]

A.1.4 reproducibility: Precision under reproducibility conditions. [ISO 3534-1]

Additional remark: Reproducibility is expressed quantitatively based on the standard deviation of the results.

A.1.5 reproducibility conditions: Conditions where measurement results are obtained with the same method on identical measurement objects in different laboratories with different operators using different equipment. [Adapted from ISO 3534-1]

A.2 Terms related to measurement and calibration

A.2.1 measuring system: A complete set of measuring instruments and other equipment assembled to carry out specified measurements.

NOTE — The system may include material measures and chemical reagents. [VIM]

EXAMPLES

a) apparatus for measuring the conductivity of semiconductor materials;

b) apparatus for the calibration of clinical thermometers.

A.2.2 material measure: A device intended to reproduce or supply, in a permanent manner during its use, one or more known values of a given quantity.

NOTE — The quantity concerned may be called the supplied quantity.

EXAMPLES

- a) a weight;
- b) a measure of volume (of one or several values, with or without a scale);
- c) a standard electrical resistor;
- d) a gauge block;
- e) a standard signal generator;
- f) a reference material. [VIM]

A.2.3 calibration: A set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards.

NOTES

1 The result of a calibration permits either the assignment of values of measurands to the indications or the determination of the corrections with respect to indications.

2 A calibration may also determine other metrological properties such as the effect of influence quantities.

3 The result of a calibration may be recorded in a document, sometimes called a calibration certificate or a calibration report. [VIM]

Additional remark: A laboratory which performs calibrations can be accredited for this activity. In order to assess the traceability of the calibrations, published protocols covering the relevant uncertainty analysis and other quality assurance elements are required.

A.2.4 certified reference material: A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence. [ISO Guide 30]

A.3 Terms related to measurement standards

A.3.1 primary standard: A standard that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity.

NOTE — The concept of a primary standard is equally valid for base quantities and derived quantities. [VIM]

Additional remark: A primary standard is never used directly for measurements other than for comparison with duplicate or reference standards. In general, the national metrology laboratory is responsible for the conservation of a primary standard in a country.

A.3.2 secondary standard: A standard whose value is assigned by comparison with a primary standard of the same quantity. [VIM]

A.3.3 international (measurement) standard: A standard recognized by an international agreement to serve internationally as the basis for assigning values to other standards of the quantity concerned. [VIM]

A.3.4 national (measurement) standard: A standard recognized by a national decision to serve, in a country, as the basis for assigning values to other standards of the quantity concerned. [VIM]

Additional remark: A national metrology laboratory assures that the national standards are primary standards.

A.3.5 reference standard: A standard, generally having the highest metrological quality available at a given location or in a given organization, from which measurements made there are derived. [VIM]

A.3.6 working standard: A standard that is used routinely to calibrate or check material measures, measuring instruments or reference materials.

NOTE — A working standard is usually calibrated against a reference standard. [VIM]

A.3.7 transfer standard: A standard used as an intermediary to compare standard. [VIM]

Annex B
(informative)

Example of typical interlaboratory test results

One cylinder containing a multicomponent gas mixture has been prepared and has been analysed by four laboratories, for one component, in accordance with a proposed ISO standard. The manufacturer indicated a nominal concentration.

Figure B.1 summarizes the results obtained by the four laboratories. The circles give the results of ten or more independent measurements made at each laboratory.

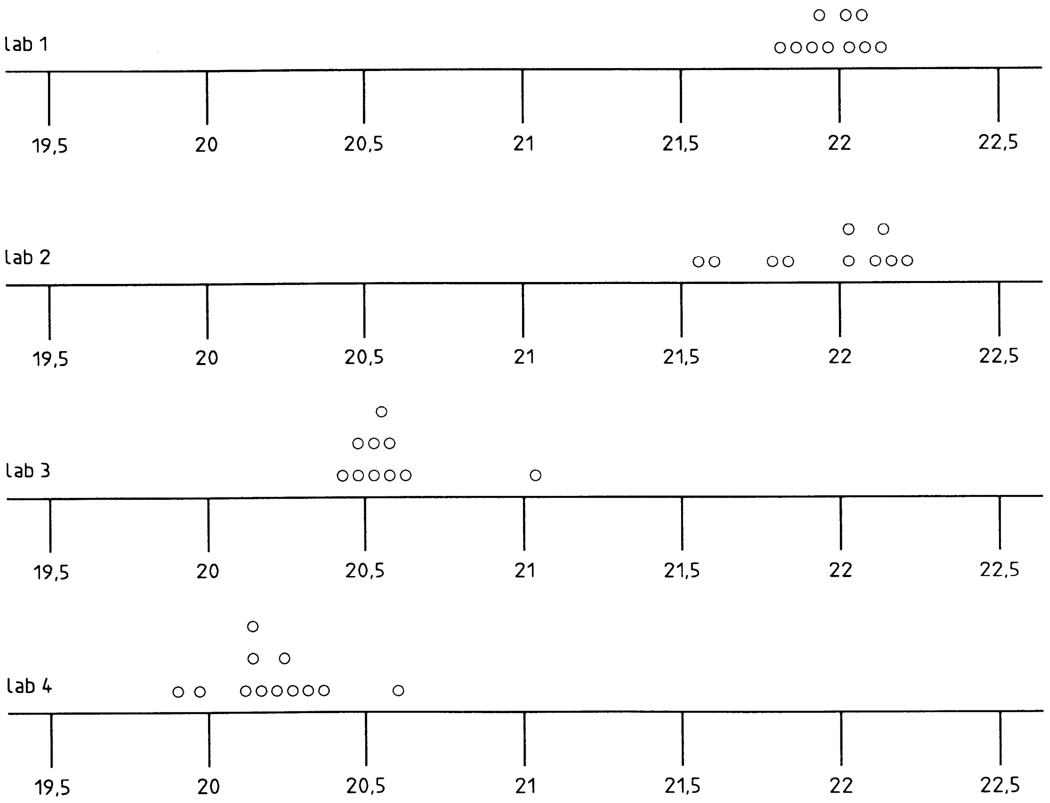


Figure B.1 — Summary of results

Lab 1 shows a high precision, lab 3 shows an even better precision if one measurement is rejected as an outlier.

In general, it should be stressed that it is very useful to investigate why an outlier has occurred; it may lead to a better understanding of the measurement procedure, and in that sense an outlier has to be considered as a valuable measurement.

Labs 2 and 4 are less precise, but improvement seems possible based upon the results of the other labs.

Labs 1 and 2 are happy to learn that the nominal concentration of the mixture, given after the exercise, is 21,9, and that the averages of their random samples (both 22,0) are not significantly different from the nominal concentration.

However, the true value has been established independently, within narrow uncertainty limits, to be 20,45, and the averages of labs 3 and 4 do not deviate significantly from that value. This leads to the following conclusions:

lab 1:	high precision, large bias (trueness is poor), low accuracy;
lab 2:	poor precision, large bias (trueness is poor), low accuracy;
lab 3:	high precision, practically no bias (trueness is excellent), high accuracy;
lab 4:	poor precision, practically no bias (trueness is excellent), good accuracy.

Given the case that yet another laboratory, lab 5, would come up with results similar to those of labs 1 and 2 and this exercise was performed to certify a reference gas mixture in accordance with the consensus concept, this could in fact, without the knowledge of the true value, lead to the following erroneous decisions:

rejection of the results of labs 3 and 4;

assignment of a certified concentration and uncertainty on the basis of the results of labs 1, 2 and 5.

In some cases, mostly due to the limited number of participating laboratories, the measurement results of all the laboratories, without rejection of outliers, are used to calculate the certified composition of the reference gas. Although this could increase the trueness of the certified value, the uncertainty will be of such a magnitude that one will doubt to apply this reference gas mixture for calibration purposes.

This is one of the reasons why the establishment of primary-standard gas mixtures with traceability to higher standards in the metrological hierarchy and more accurate validation methods (preferably definitive methods) have to be pursued.

Annex C
(informative)

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