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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

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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).

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]

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,