Traceability: Reference Materials

3

Abstract

The primary purpose of this chapter is to explain the integral concept of traceability and illustrate its use in Analytical Chemistry. The most immediate impact of traceability on Analytical Chemistry is that on analytical chemical standards, which are key tools for a metrological discipline relying on measurements. The direct relationship of traceability to standards is used to describe in a systematic manner the different types of standards used in Analytical Chemistry and their practical implementation. This is followed by a discussion of the different meanings of traceability in relation to various analytical chemical concepts. The meanings are harmonically related to facilitate their seamless integration. The chapter ends by relating the different analytical meanings of traceability to capital analytical properties, which are dealt with at length in Chap. 2, in order to strengthen consistency among the essential principles of Analytical Chemistry explained in Part I.

Teaching Objectives

- To introduce students to the integral concept of traceability.
- To highlight the crucial role of standards in Analytical Chemistry.
- To describe the different types of standards relevant to Analytical Chemistry.
- To integrate the different meanings of traceability and relate them to specific facets of Analytical Chemistry.
- To relate traceability of a result to capital analytical properties.

Electronic supplementary material The online version of this chapter (doi:10.1007/978-3-319-62872-1_3) contains supplementary material, which is available to authorized users.

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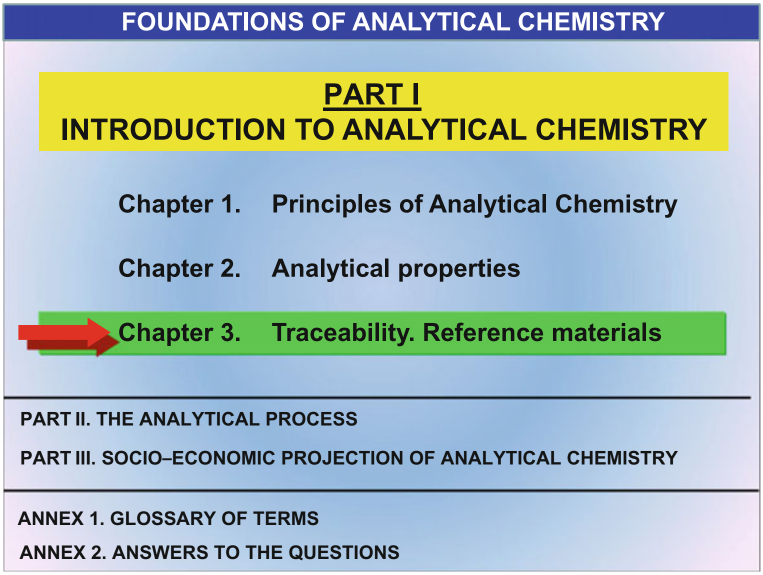
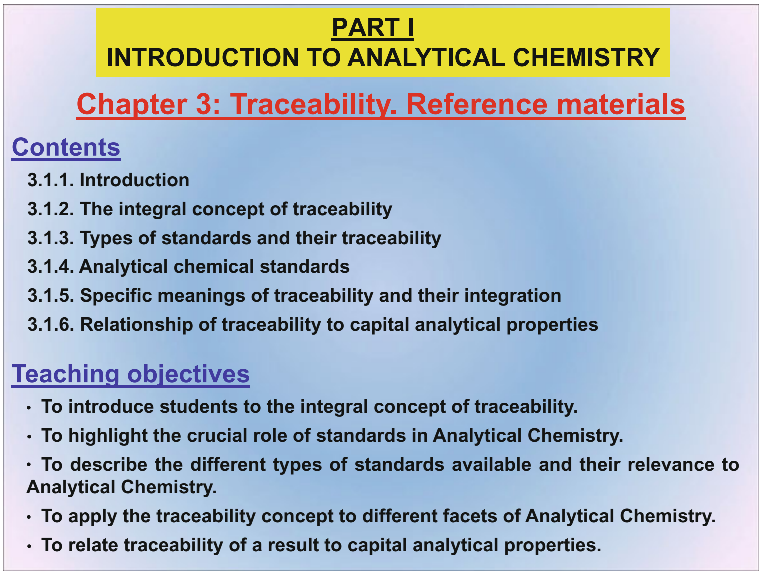
3.1 Explanation of the Slides

Slide 3.1



This slide places Chap. 3 in Part I (Introduction to Analytical Chemistry) and shows the other two parts. Chapter 3 is the third, last chapter presenting a basic approach to Analytical Chemistry.

Slide 3.2

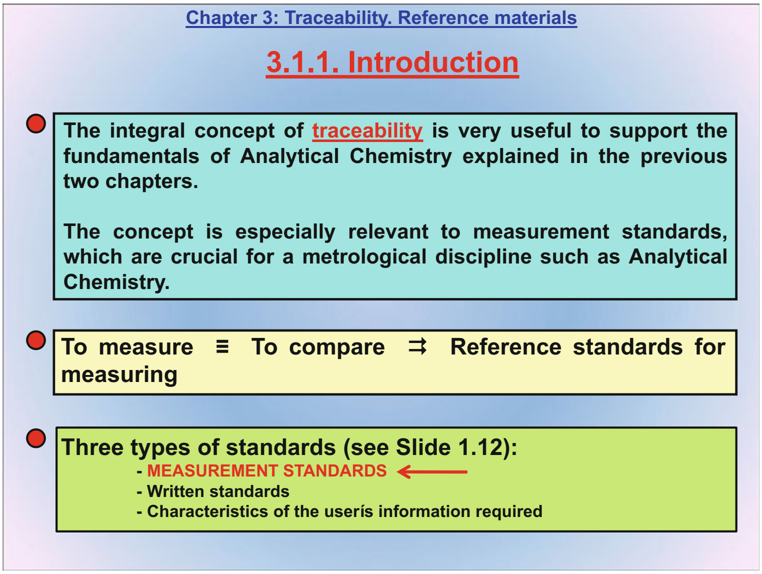


3.2.1. These are the six sections of this chapter.

3.2.2. The slide also shows the teaching objectives as regards traceability, its use in Analytical Chemistry and the key standards for this scientific discipline.

3.1.1 Introduction (1 Slide)

Slide 3.3

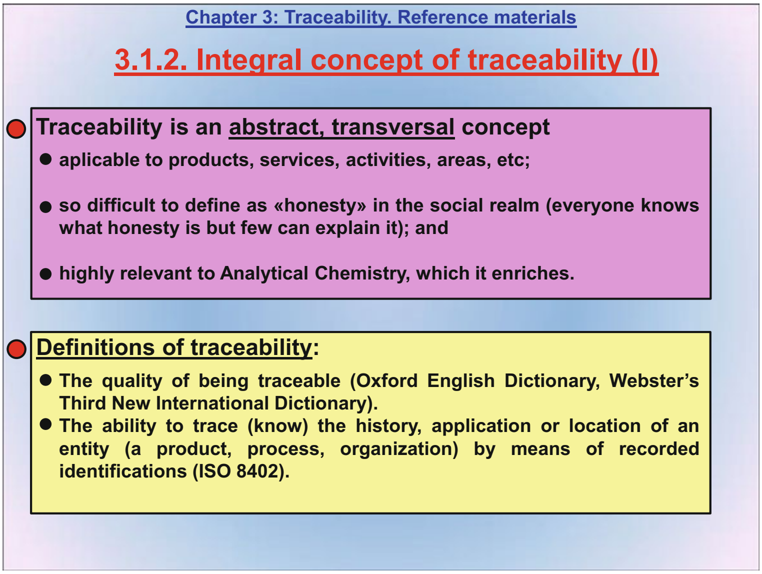


3.3.1. This is a general introduction to the chapter contents, which encompass traceability and analytical chemical standards. The aim is to summarize the relationship of Traceability to Analytical Chemistry (particularly to the tangible standards used for measurement).

3.3.2. Measurement standards play a crucial role in Analytical Chemistry, an essentially metrological discipline. Measurement standards constitute one of the three basic types of standards described in Sect. 1.3 (see Slide 1.12).

3.1.2 The Integral Concept of Traceability (4 Slides)

Slide 3.4

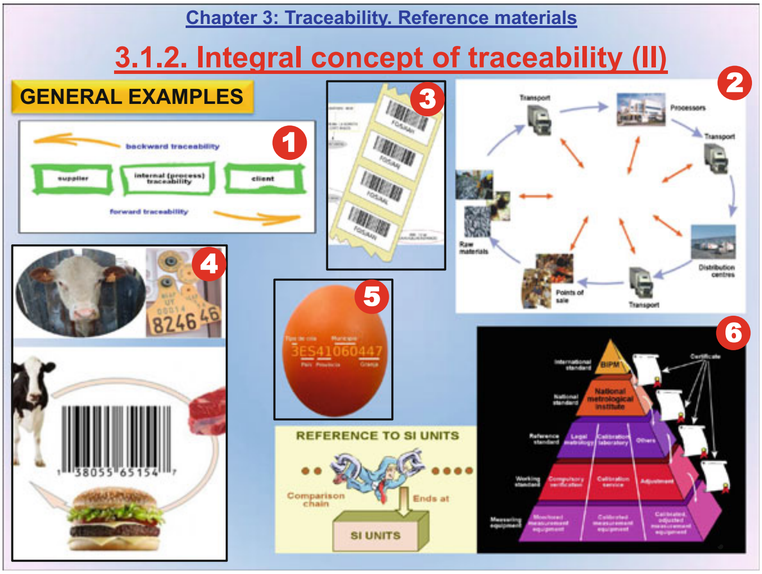


3.4.1. This slide introduces Sect. 3.2, which is concerned with the integral concept of traceability.

3.4.2. This is a generic description of "traceability", a transversally applicable abstract concept that is certainly difficult to define in a precise manner.

3.4.3. The definitions of "traceability" in dictionaries and written standards are far for friendly. Properly understanding what traceability is requires a more detailed description of its two main connotations ("reference" and "history"), which are used jointly in this chapter to build the integral concept of traceability.

Slide 3.5



These are selected graphical examples illustrating the integral concept of traceability.

1. Traceability in a production chain: the chain links the raw materials obtained from a supplier to the finished product received by the client. Traceability in this context can be classified in two different ways, namely:

   – *External and internal traceability*. The former applies to *inputs* and *outputs*, and the latter to processes of the production system.

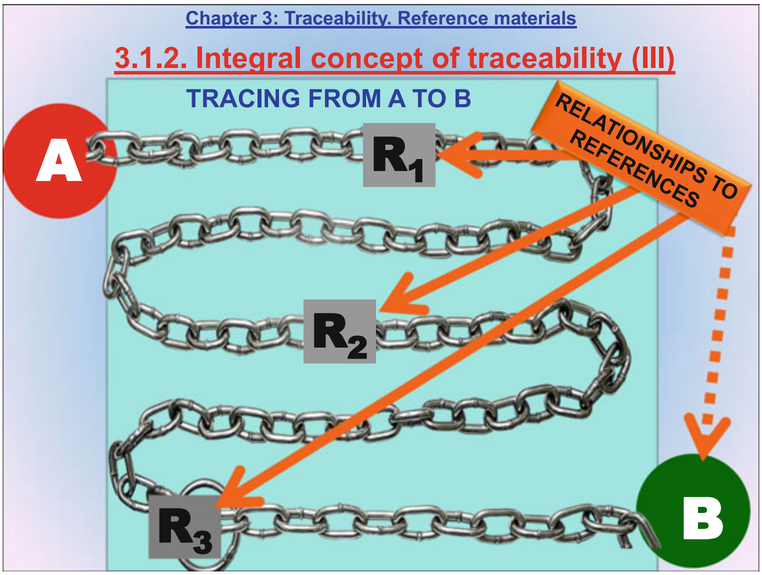
   – *Backward and forward traceability* around a circle connecting the raw materials to the product (forward) for quality-related purposes or the product to the raw materials (backward) for purposes such as dealing with clients' claims.

2. This is a more precise description of traceability of a product including transportation, distribution centres and points of sale, among others. The circular nature of traceability is clearer here. The arrows represent links in the traceability chain.
3. Bar coding is essential for proper monitoring—an unavoidable requirement with a view to ensuring traceability. Such is the case, for example, with blood or urine collection in the first step of clinical analyses at hospitals and outpatient clinics. The urine cup and blood collection tubes for each patient are identified with a unique bar code in order to start the sample custody chain. The samples

are sent to different laboratories and the analytical results compiled by appropriate software for delivery. In this way, traceability between patients and their results is assured.

4. Traceability in the agri-food industry is not only essential but also a legal requirement as per a European Union directive and the recommendations of the Food and Agriculture Organization of the United Nations (FAO). For example, a hamburger must be unequivocally traceable to the cow from which the meat came. Traceability here is established by using ear tags and bar codes.
5. A consumer-ready box of eggs on a supermarket shelf is labelled with a code identifying the type, country, place, farm and plant where the eggs were laid. In some countries, the eggs themselves have a printed bar code on the shell, but this identification system is less user-friendly.
6. The last example illustrates the typical traceability chain for measurements of physical parameters such as temperature, time or current intensity. Each step in the pyramid is connected to the next through a traceability link that should be certified. In this example, a measurement made with a given piece of equipment, and its calibration, are connected to an SI unit held as a top-quality international standard at the top of the pyramid. The links in the traceability chain, which should never be broken, include the standards prepared and used by the laboratory, which should be successively compared with commercially available reference standards. The commercial standards in turn are connected to national standards kept by a national organization. Unfortunately, no such well-defined hierarchy can be constructed for chemical measurements. In fact, the highly diverse nature of potential samples (industrial, clinical, environmental) would require having a number of national centres for chemical metrology in each country.

Slide 3.6

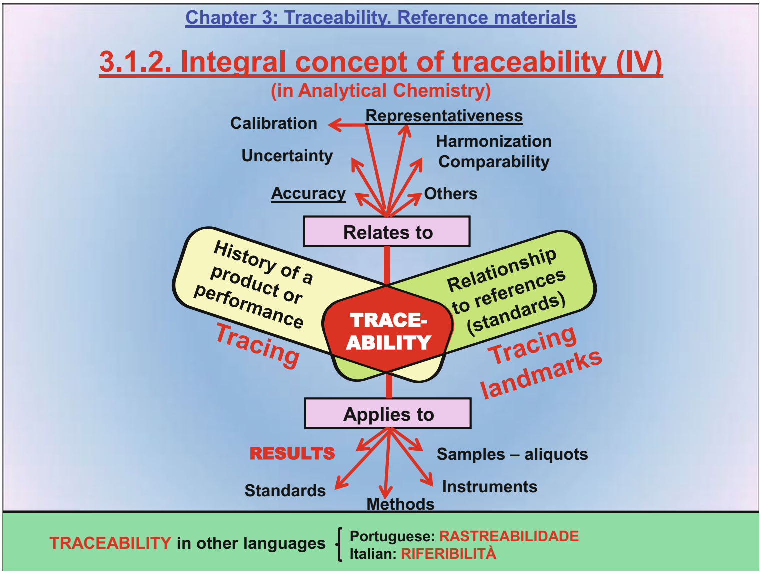


3.6.1. This is an imaginary traceability chain connecting A to B through an unbroken series of comparisons with three intermediate references (R_1, R_2 and R_3). Provided the chain is not broken, A and B can be said to be traceable to each other.

3.6.2. Tracing one end of the chain to the other requires using the "history" of the comparison made or relationship established at each individual link. Obviously, this is situation is unrealistic because traceability chains contain many fewer links in practice.

3.6.3. Connecting links to well-established references requires a sound knowledge of their nature and meaning. Frequently, end B is a reference itself (e.g., when an analytical result A is traced to a certified reference material B as described below).

Slide 3.7



3.7.1. From Slides 3.4 and 3.6 it clearly follows that defining traceability in an integral manner entails using its tracing and relational connotations jointly.

The tracing facet has to do with the documented history of (a) a production process from the raw materials or (b) the performance of an object or system. Such is the case, for example, with a laboratory instrument, for which there should be a detailed record of all actions including installation, servicing, calibration and measurements.

The other facet is the relationship to references, which are tracing landmarks (see Sect. 3.6.3) and, most often, standards of some type.

3.7.2. The unambiguous presence of the previous two facets in traceability is clearly apparent in its translations into some languages of Latin origin. Thus, the

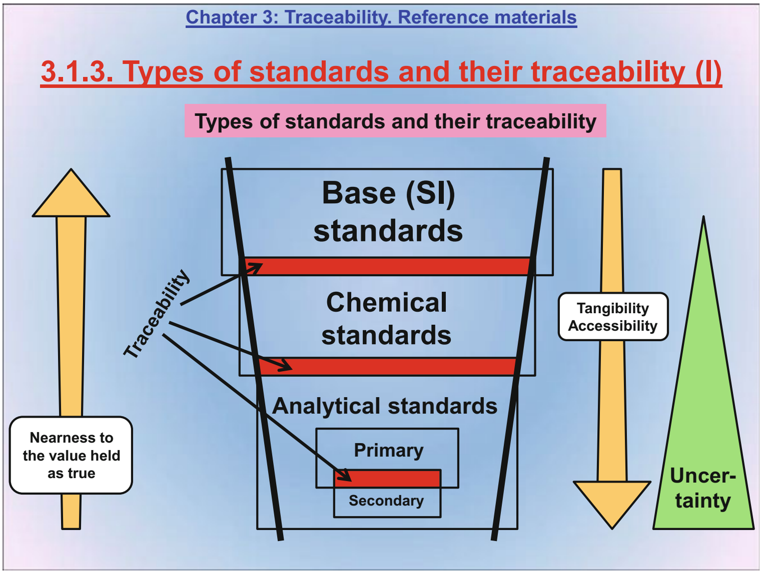
Portuguese word for “traceability” is *rastreabilidade* (tracing facet), whereas the Italian word is *riferibilità* (referential facet).

3.7.3. Traceability in Analytical Chemistry is related to such important concepts as accuracy, uncertainty, calibration, representativeness, and laboratory comparability and harmonization.

3.7.4. The integral concept of traceability is applicable to analytical chemical entities such as analytical results, standards, analytical methods, instruments and samples. The specific connotations of traceability are all discussed below.

3.1.3 Types of Standards and Their Traceability (4 Slides)

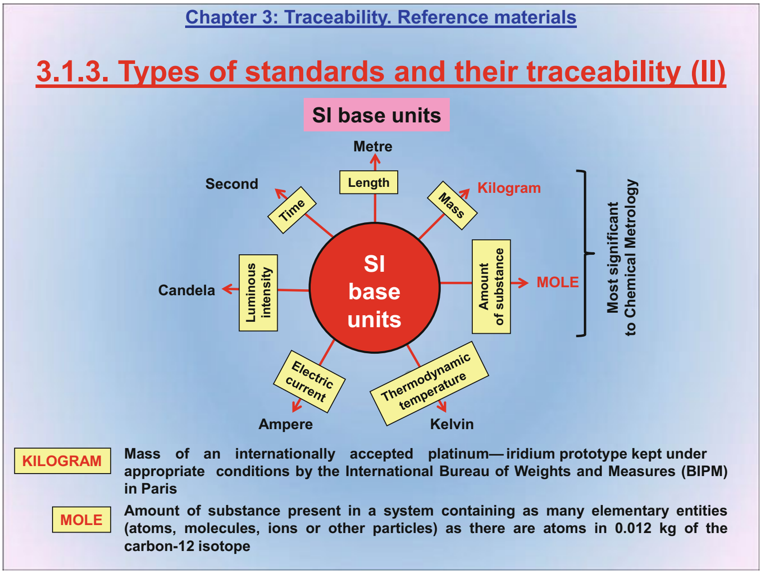
Slide 3.8



3.8.1. The pyramid of traceability in physical measurements (Example 6 in Slide 3.5) is not directly applicable to chemical measurements but can be replaced with a simpler traceability chain connecting analytical chemical standards (the tangible standards used in practice) to base standards (SI units) through so-called “chemical standards”, which are intended to serve as traceability links. The two types of chemical standards (primary and secondary) can also be connected by a traceability chain.

3.8.2. In this simple ranking of traceability among standards in relation to chemical measurements, nearness to the true value for each type of standard increases from bottom (secondary chemical standards) to top (base standards). Consequently, specific uncertainty decreases in the same direction, and so do tangibility and accessibility.

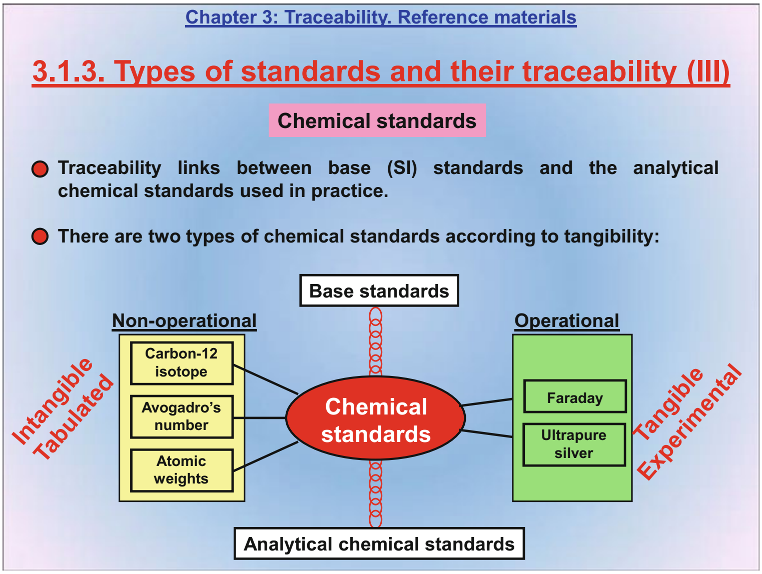
Slide 3.9



This slide shows the seven base units of the International System, namely: the metre for length, second for time, candela for luminous intensity, ampere for electric current, kelvin for thermodynamic temperature, mole for amount of substance and kilogram for mass.

The kilogram and the mole are the two most relevant to Metrology in Chemistry. The slide shows their classical definitions. Note that defining the mole requires mentioning the mass unit (the kilogram).

Slide 3.10

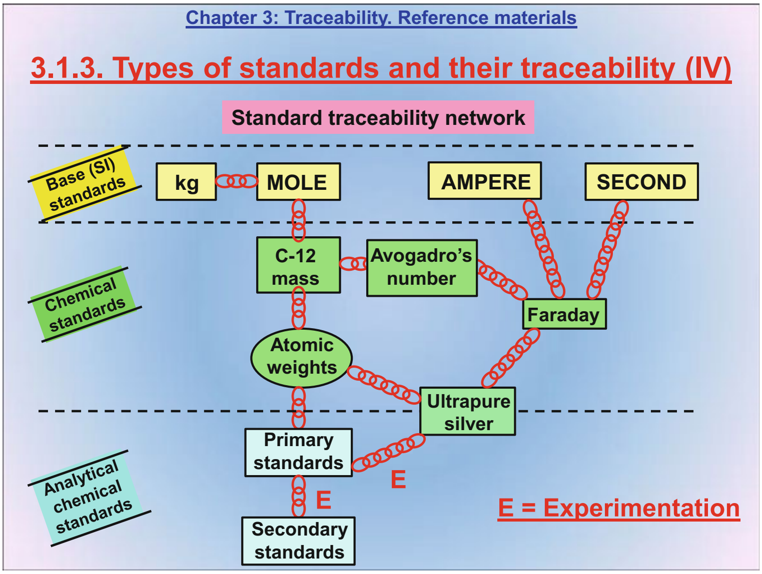


3.10.1. As stated in Slide 3.8, chemical standards are intended to serve as traceability links between base standards (SI units) and the analytical chemical standards used in the laboratory. Consequently, chemical standards play a crucial role in Analytical Chemistry because they determine the quality of laboratory standards.

3.10.2. There are two types of chemical standards according to tangibility:

– *Intangible standards*, also referred to as "non-operational standards", which are tabulated and include the mass of carbon-12, Avogadro's number and atomic weights.
– *Tangible standards*, also known as "operational standards", which require some experimentation prior to use. The most salient standards of this type are the faraday, which requires electrochemical equipment for verification, and ultrapure (>99.999% silver), also known as "five nine silver", which is extremely expensive.

Slide 3.11



This is an orderly depiction of the three types of standards relevant to Analytical Chemistry in a (traceability network) typical of chemical measurements. The mutual connections between standards are represented by red chains.

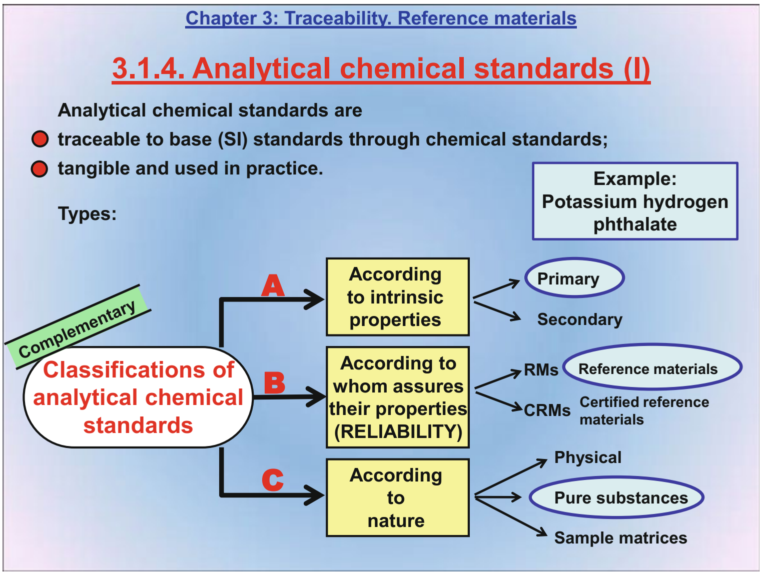
– As can be seen as regards SI standards, the mole cannot be defined without the kilogram.
– Base standards (SI units) are connected to chemical standards through three traceability chains, namely:

- one unequivocally linking the mole to the mass of carbon-12;
- another between the ampere and the faraday (1 C = 1 A × 1 s); and
- a third between the second and the faraday.

– Most traceability links occur in the realm of chemical standards. Thus, the mass of carbon-12 is related to the atomic weights used in chemical calculations and to Avogradro's number, which is in turn related to the faraday.
– Ultrapure silver is at the boundary between chemical standards and analytical chemical standards. In fact, it is so pure that it can be considered a chemical standard itself—one that is related to the chemical standards atomic weights and the faraday. Likewise, it can be exceptionally used in practice to standardize primary chemical standards by experimentation (E).
– Primary chemical standards can be traced to atomic weights and ultrapure silver. On the other hand, secondary standards can only be traced to primary standards (through experimentation). Primary and secondary standards are defined in the following section.

3.1.4 Analytical Chemical Standards and Their Integration (10 Slides)

Slide 3.12

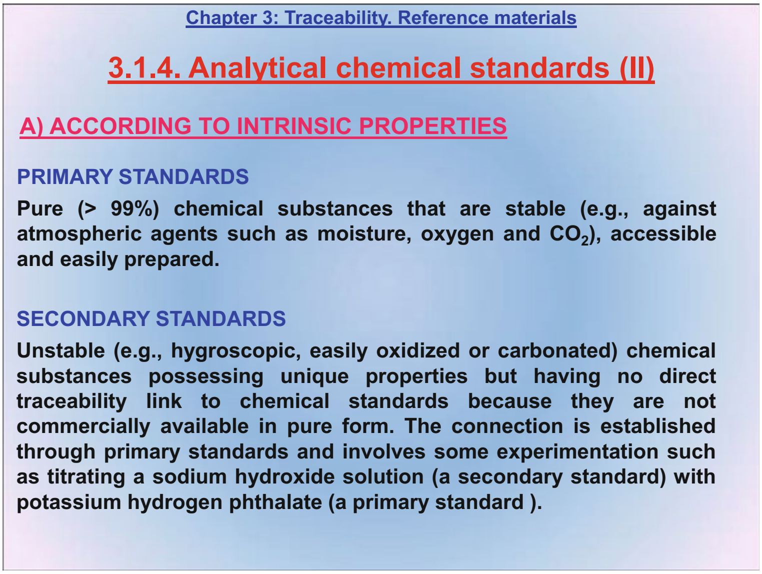


3.12.1. This slide defines and classifies analytical chemical standards. By definition (see Slide 3.8), they are at the bottom of the significance hierarchy of standards relevant to Metrology in Chemistry because their associated values are the farthest from the value held as true and also the most uncertain; by contrast, they are the most tangible and accessible, and hence the most commonly used in practice. Analytical chemical standards can be traced to SI units through chemical standards (see Slide 3.11).

Analytical chemical standards are confusingly or even contradictorily defined in the scientific literature. An integral approach to their characteristics enables their classification according to three different criteria, namely: (A) intrinsic properties, (B) reliability and (C) nature. Each classification is discussed in one of the next three slides.

3.12.2. For example, potassium hydrogen phthalate is a primary standard commonly used to standardize solutions of sodium hydroxide (classification A). Also, however, it can be considered a reference material (classification B) and a pure substance (classification C).

Slide 3.13



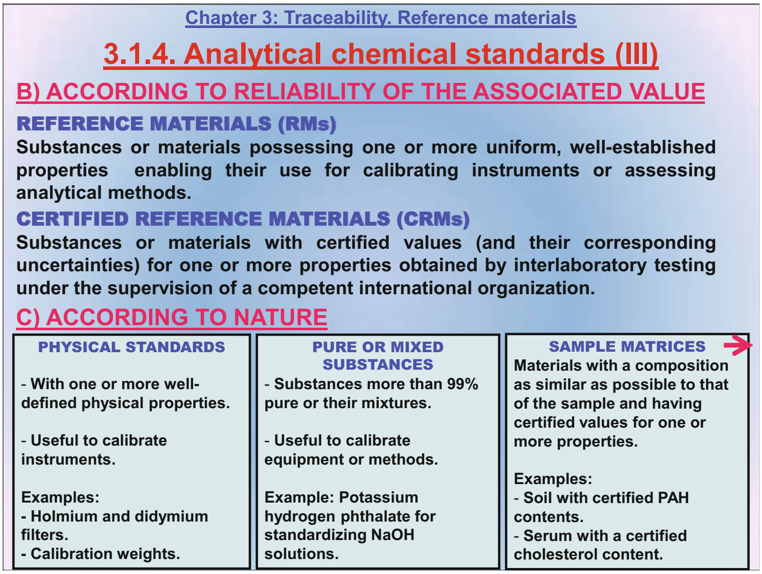
The analytical chemical standards used in the laboratory can be of two types according to their intrinsic properties, namely:

– *Primary standards*. These are chemical substances fulfilling two essential requirements:

  1. a high purity (above 99 or 99.5%) that makes them traceable to atomic weights and ultrapure silver (Slide 3.11); and
  2. stability against atmospheric agents (water, oxygen, carbon dioxide).

– *Secondary* standards. These are neither pure nor stable but can be useful for some purposes. However, they can only be made traceable by connection to a primary standard through experimentation (E in Slide 3.8).

Slide 3.14



There are two types of analytical chemical standards according to reliability or traceability to base standards (see classification B in Slide 3.13), namely: reference materials (RMs) and certified reference materials (CRMs). The former (RMs) are usually commercially available with a label stating their characteristics. The latter (CRMs) are produced by renowned international organisms that supply them with certificates stating with their associated values and their uncertainty. CRMs are usually of the sample matrix type.

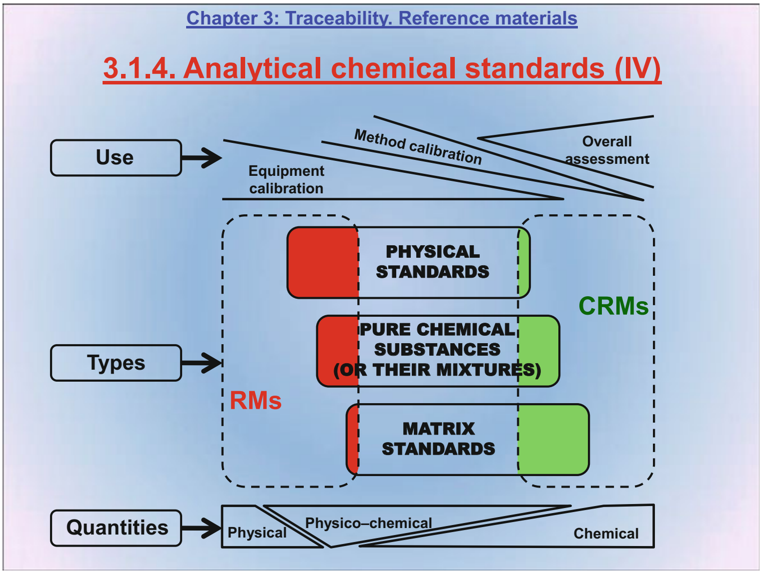
Analytical chemical standards can be of three types according to nature (classification C), namely:

– *Physical standards.* These are used as received for equipment verification (calibration). Thus, a UV–visible spectrophotometer can be checked with holmium and didymium filters for correct operation of its wavelength monochromator. Similarly, a balance is typically calibrated with so-called “transfer weights”, which are traceable to the kilogram standard (an SI unit).
– *Pure substances or their mixtures.* These are analytical chemical standards (see Slide 3.13)—and hence, pure, stable substances—that can be used for both equipment and method calibration (e.g., with a calibration curve as in Slide 2.36).

Some are mixtures of pure substances (e.g., vials containing several C_3–C_6 hydrocarbons for calibrating gas chromatographs).

– *Sample (matrix) standards*. These are either certified reference materials (CRMs), which are described in Slide 3.17, or laboratory-made materials (working standards). Matrix standards are high-quality—and expensive—materials mimicking the composition of a sample and having the value of an associated quantity certified by a competent organization. Such is the case, for example, with a soil standard having certified contents and uncertainties in polycyclic aromatic hydrocarbons (PAHs), a milk standard with a certified aflatoxin content or a liophilized serum standard with a certified cholesterol content.

Slide 3.15

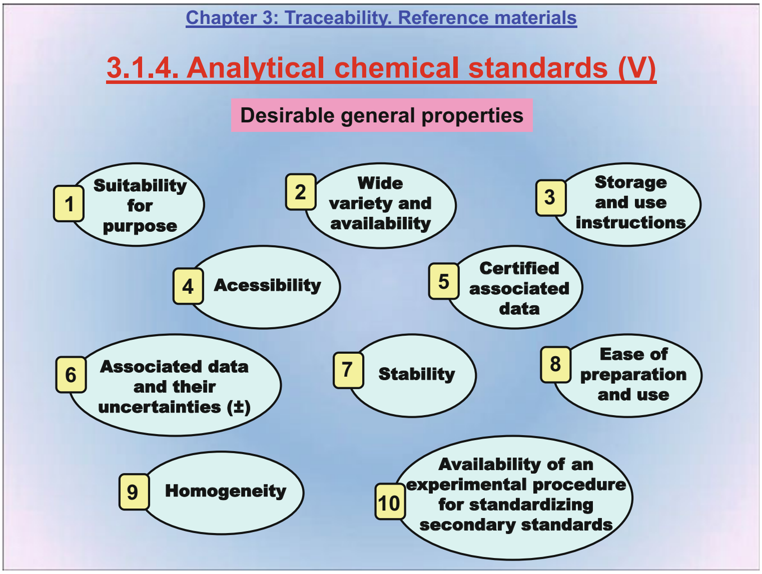


3.15.1. This scheme harmonizes the classifications of Slides 3.12 and 3.14 by classifying the three types of analytical chemical standards according to nature (classification C) in terms of reliability (classification B). Thus, physical standards are largely reference materials, whereas pure substances and their mixtures can be reference materials (RMs) or certified reference materials (CRMs), and matrix standards are mostly CRMs.

3.15.2. The use of each type of standard is described in detail below. In any case, RMs are used mainly for equipment and method calibration, whereas CRMs are typically used for the overall assessment of analytical methods.

3.15.3. The quantities involved can be physical (particularly with RMs), chemical (more commonly with CRMs) or, very often, physico–chemical.

Slide 3.16



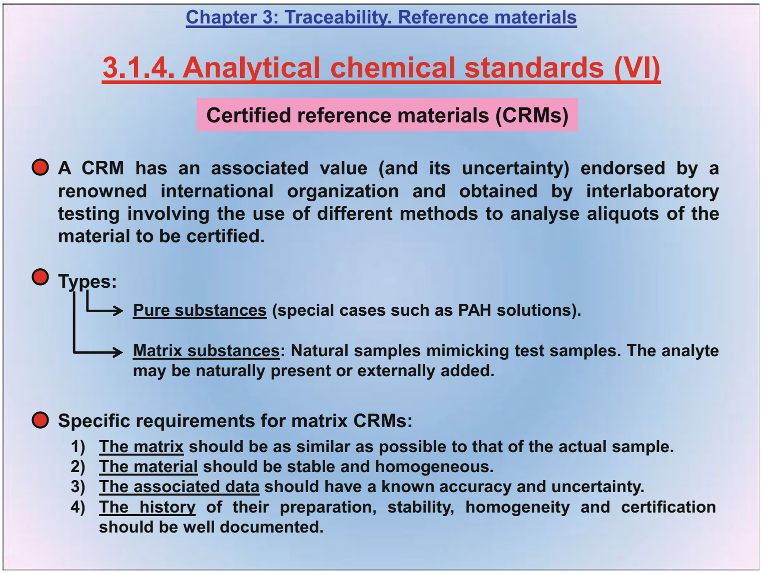
These are the ten desirable or indispensable properties for an analytical chemical standard.

The *indispensable* properties are as follows:

- Usefulness for the task concerned (that is, suitability for purpose) (1).
- Stability (7), homogeneity (8) and a well-defined uncertainty (6) for primary standards, in addition to certified values (5) for CRMs.
- Experimental traceability to primary standards (10) for secondary standards.
- Detailed storage and use instructions (3).
- Wide variety and availability (2).

The *desirable* properties include accessibility (4) and ease of preparation and use (8).

Slide 3.17

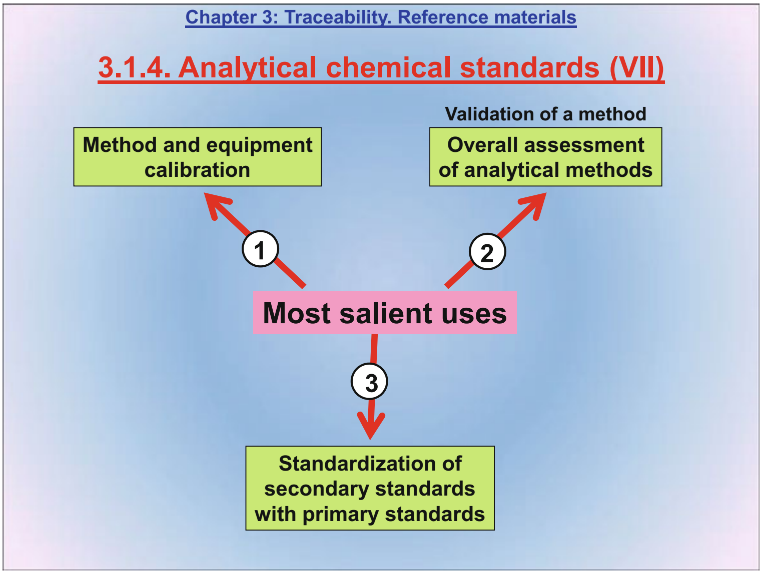


This is a brief description of *certified reference materials* (CRMs), which are standards having associated values and their uncertainties endorsed (certified) by a renowned non-profit international organization responsible for assuring that these atypical standards meet their requirements. They correspond to the so named "referential quality" (see Slide 1.17). The associated values and their uncertainties can only be established via interlaboratory exercises involving the use of different analytical processes. CRMs are usually expensive because they take long to prepare and can only be obtained in small amounts.

- Most CRMs are of the sample matrix type and mimic actual samples to be analysed by a laboratory. The analyte may be already present in the sample or externally added later. Some organisms also certify the purity of solutions containing substances such as dioxins or PAH.
- The slide shows the four requirements for a matrix-type CRM, which have to do with the sample matrix, homogeneity and stability in the material, the associated data and the history of the material from preparation to delivery.

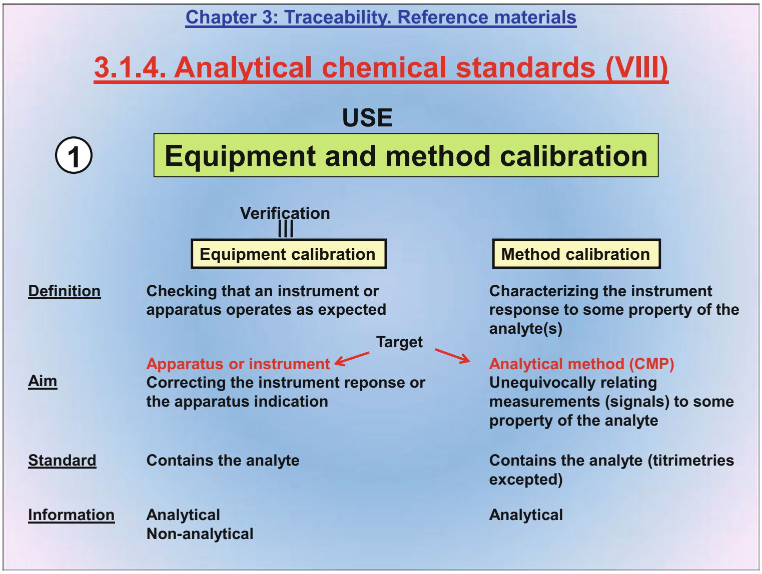
Interestingly, a CRM has several analytical connotations of traceability. Thus, the value for the associated quantity (e.g., the content, in ng/kg, in toxic dioxins of ash from an industrial incinerator) should be unequivocally connected to a chemical standard (referential facet): also, its characteristics and production should be accurately known (tracing facet).

Slide 3.18



These are the three main uses of analytical chemical standards in the laboratory. The first two are discussed in Slides 3.19–3.23. The third (Slide 3.23) is the use of primary standards such as potassium hydrogen phthalate to standardize secondary standards such as sodium hydroxide, which are those used in practice (delivered from a burette) to determine acids in samples by titration.

Slide 3.19



Analytical chemical standards are useful for both equipment and method calibration, which should be clearly distinguished by analytical chemists.

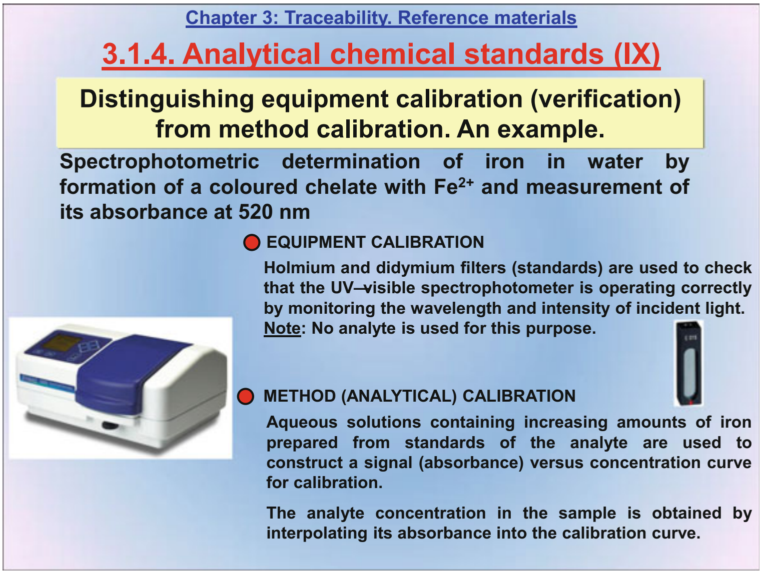
Thus, as implied by the designation, the target of *equipment calibration* or *verification* is an instrument or apparatus (the two are distinguished in Slide 1.25). The aim is to assure proper functioning of the instrument or apparatus concerned. For example, if the measurement delivered by an instrument in response to a standard (usually a physical reference material) departs from the value for the associated quantity, then the instrument should be adjusted to have the response coincide with that expected from the standard. An instrument delivers analytical information whereas an apparatus produces non-analytical information. There follows an example of each type of equipment.

- pH buffering solutions with a certified value including two decimal figures for calibrating pH-meters. If the experimental response does not coincide with the certified value, then the potentiometer of the instrument should be adjusted until it does.
- Calibrated thermocouples for monitoring the temperature inside stoves. If the temperature in the digital display of the apparatus departs from the reading of the thermocouple, then the stove should be adjusted to have the two temperatures coincide.

The target of method calibration is a *chemical method of analysis*. The aim is to characterize in an unequivocal manner the relationship between the instrument response and the presence and/or concentration of an analyte in the sample. This entails constructing a signal–concentration curve for calibration (see Slide 2.36 in relation to the analytical property "sensitivity"). This calibration procedure is not applicable to apparatuses because the information to be processed is purely analytical. The standard usually contains the analyte (unless, for example, a secondary standard such as a sodium hydroxide solution is to be standardized with a primary standard such as potassium hydrogen phthalate).

These two types of calibration are exemplified in the next slide.

Slide 3.20

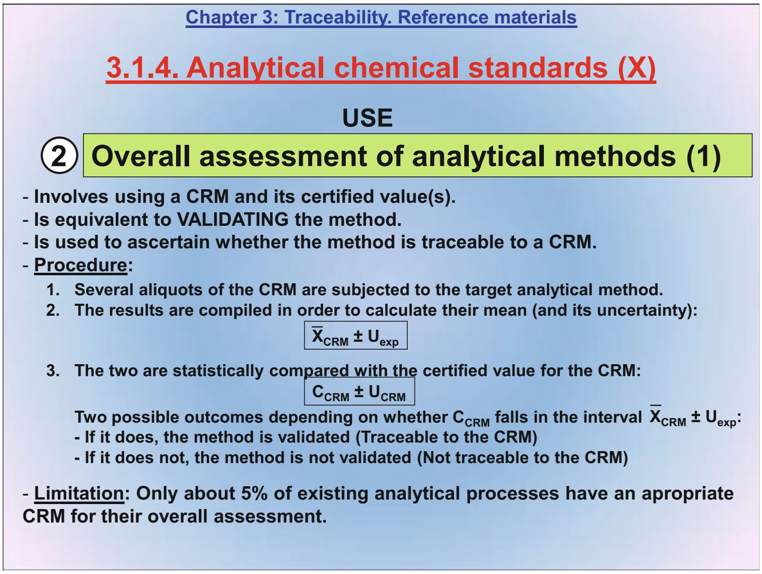


The following example distinguishes equipment calibration from method calibration with the spectrophotometric determination of iron in water by formation of a coloured chelate.

The target of *equipment calibration* here is the spectrophotometer and the calibration tools are physical standards rather than the analyte. A UV–visible absorption spectrum is obtained with a holmium filter (shown in the slide) in place for comparison with the spectrum associated to the standard. If the maxima in the two spectra fail to coincide, then the monochromator of the instrument is adjusted accordingly.

The purpose of *method calibration* in this example is finding the relationship between the absorbance and the concentration of iron by using a calibration curve constructed from standard solutions of the analyte. The iron concentration in the sample is determined by interpolating its absorbance into the curve.

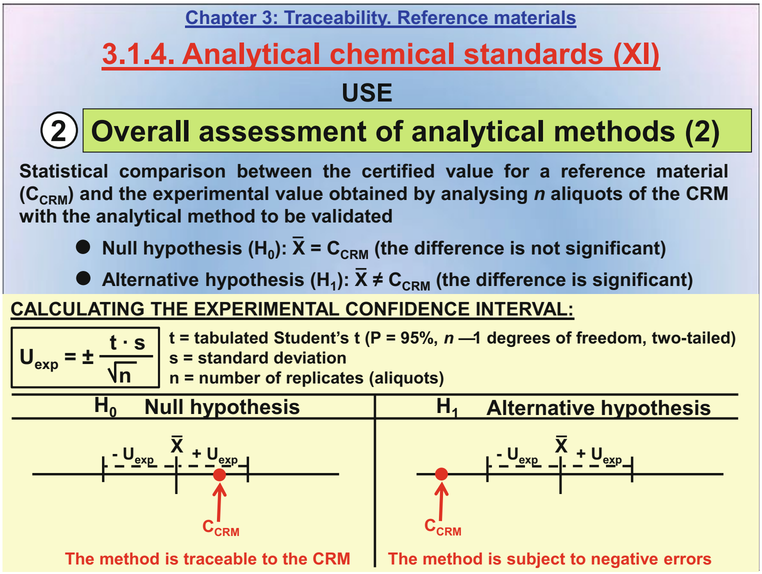
Slide 3.21



Another purpose of analytical chemical standards is the overall assessment of analytical processes by using standards (usually matrix-type certified materials) as references. As can be seen, the procedure involves comparing the result obtained from *n* aliquots of the CRM with its certified value, either qualitatively or statistically (see next slide). If the two values coincide, then the method in question is traceable to the CRM and has thus been "validated".

It should be noted that only a very low proportion of existing analytical processes can be assessed in this way. In most cases, an alternative solution must be found (see Slide 3.31).

Slide 3.22



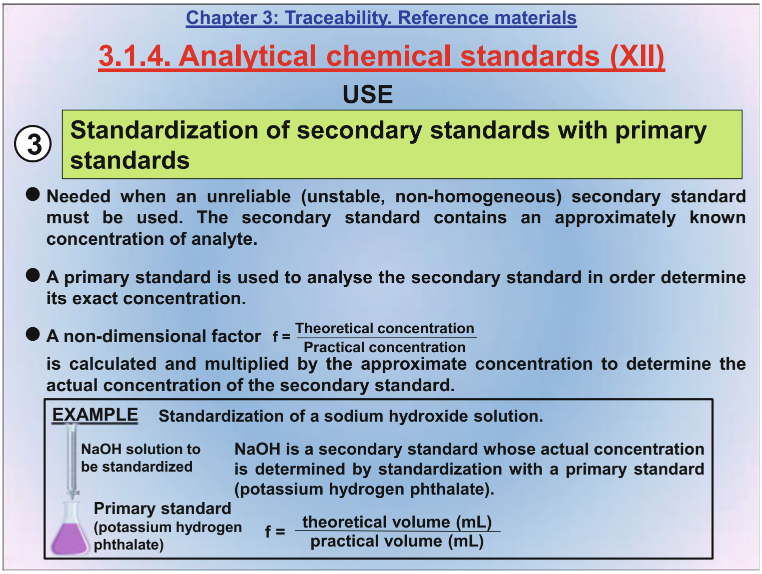
This slide compares in statistical terms the certified value of a reference material to the experimental value obtained by analysing *n* aliquots of the CRM with an analytical method for validation. The null hypothesis is that the two values will be identical and the alternative hypothesis that they will not.

A more rigorous comparison can be made by considering the specific uncertainty of the experimental value, using tabulated Student's *t*-values. The specific uncertainty is used to determine the uncertainty interval around the result at a given probability level (e.g., 95%).

The null hypothesis (H_0) and the alternative hypothesis (H_1) can be represented graphically for easier interpretation.

- If the value associated to the CRM (C_{CRM}) falls within the uncertainty interval, then the method (H_0) will be traceable to the CRM and hence validated.
- If the associated value falls outside the uncertainty interval (H_1), then the method will be subject to positive or, as shown in the slide, negative errors, so it cannot be validated.

Slide 3.23



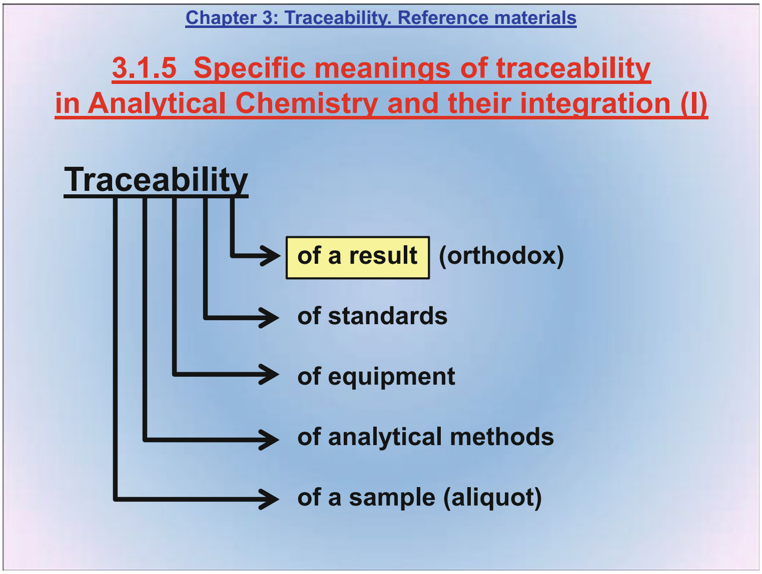
To standardize means to establish a (generally experimental) link from a standard to another of a higher rank (nearness to the true value) in the hierarchy. This is the third potential use of analytical chemical standards.

Standardizing is indispensable with a view to unequivocally connecting a secondary standard highly suitable for a given purpose (e.g., an NaOH, $KMnO_4$ or $Na_2S_2O_3$ solution) to a primary standard (potassium hydrogen phthalate, sodium oxalate and potassium iodate, respectively).

This procedure is also known as “factoring” because it involves calculating an experimental non-dimensional factor (below 1) by which the approximate concentration of the secondary standard is to be multiplied in order to determine the actual concentration. The slide shows an example of factoring: the standardization of an NaOH solution with potassium hydrogen phthalate.

3.1.5 Specific Meanings of Traceability in Analytical Chemistry and Their Integration (10 Slides)

Slide 3.24

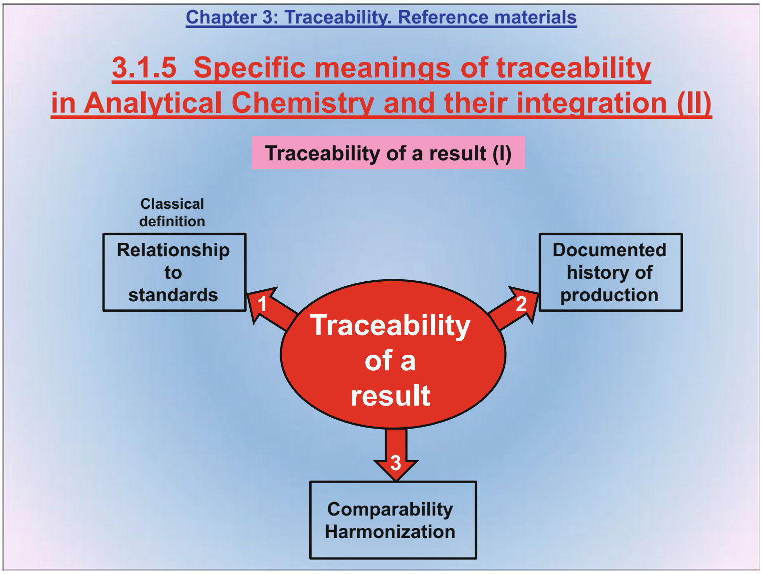


This slide illustrates different meanings of traceability in Analytical Chemistry.

Traceability of a result is the only possible, "orthodox" meaning in the realm of Metrology in general. The other uses of the word "traceability" in the slide are unorthodox because they are adapted to the specificities of Metrology in Chemistry. All are associated to the integral concept of traceability, which includes the tracing and referential facets—by exception, *traceability of a sample (aliquot)* only possesses the tracing facet and is thus the most unorthodox term.

These concepts are described in detail in Slides 3.25–3.33

Slide 3.25

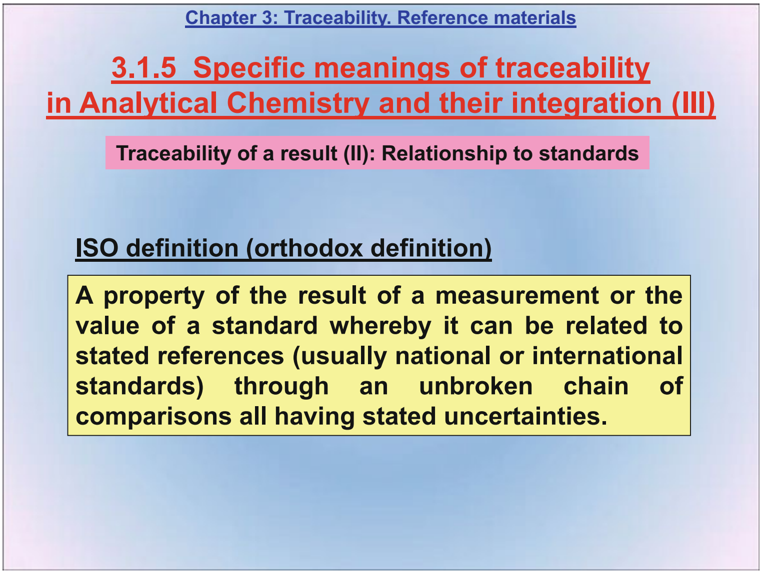


These are the three basic meanings of the integral concept of *traceability of a result*.

(1) A relationship to standards (referential facet), which is the classical, most orthodox definition.
(2) A documented history of the production of the result (the tracing facet), which directly influences its quality.
(3) Comparability and harmonization of laboratories (a practical consequence).

The integral concept of traceability can only be properly understood by considering all three meanings, which are discussed in detail in the following slides.

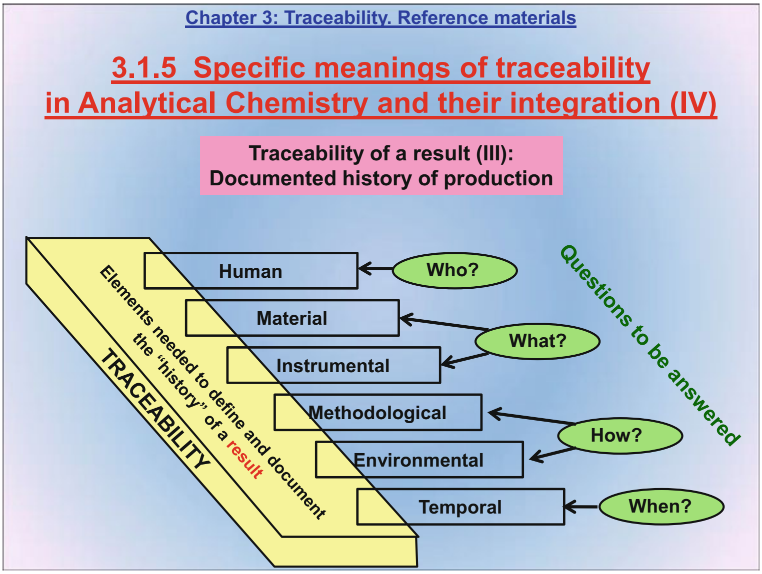
Slide 3.26



The most orthodox definition of *traceability of a result* is that based on its relationship to standards. In some cases, the relationship is established through intermediate landmarks (lower-rank standards). The description of this relationship constitutes the tracing facet. This is apparent from the ISO definition, shown in the slide, which holds quite well for physical measurements—in fact, it was issued specifically for them (see Example 6 in Slide 3.5).

As can be seen, the definition contains concepts extraneous to Metrology in Chemistry. What is a national (or international) standard? How distant is an analytical chemical laboratory from a base (SI) standard? Only with physical standards such as transfer weights for calibrating balances can the pyramid in Example 6 of Slide 3.5 be constructed.

Slide 3.27



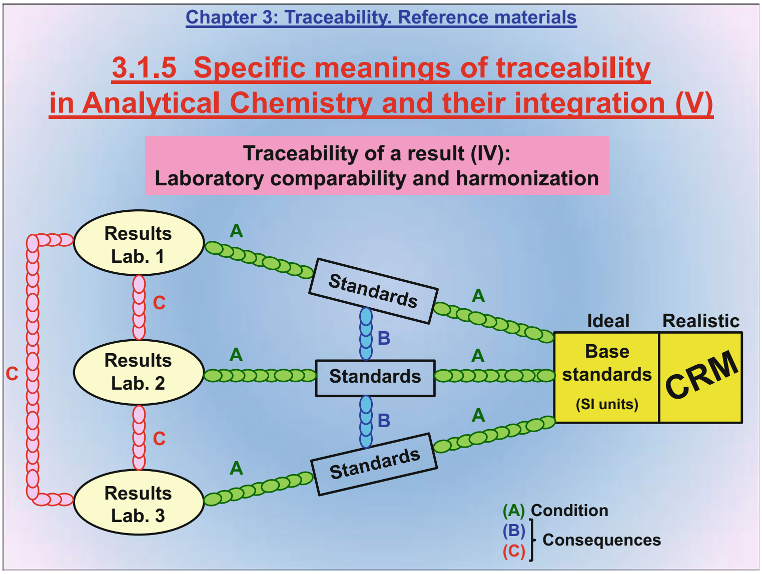
The second facet of traceability of a result is the documented history of its production. It is thus a tracing facet. The questions to be answered in this respect are as follows:

- Who performed the analytical process?
- What materials and equipment were used?
- When and how was the process performed?

Example: A laboratory determining a dioxin content of 0.1 ng/kg in a properly identified sample (e.g., code rd33245f-2012) of landfill ash analysed on February 4, 2012 should keep an accurate record of the persons taking part in the process of obtaining the result (who?); the materials (reagents, standards) and equipment used (what?); and the analytical method and environmental conditions in the laboratory (how?). Computers and, especially, bar codes, are indispensable for monitoring purposes in this context (that is, for the tracing facet of traceability).

Properly answering the previous questions is unavoidable with a view to fulfilling the requirements of laboratory accreditation in ISO 17025:2014 (see Chap. 8). Oddly, this standard imposes traceability in the results but does not refer specifically to the concept.

Slide 3.28



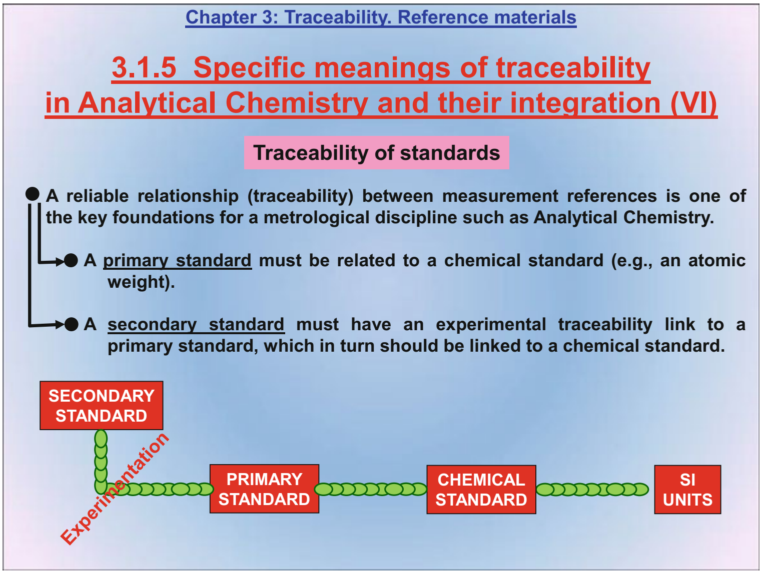
3.28.1. The practical consequence of *traceability of a result* is the ability to compare, harmonize and trace laboratories to one another.

For example, if three laboratories in Beijing, Barcelona and San Francisco (Labs 1–3 in the slide) are independently traceable through the unbroken green chains (A) in the determination of the same analyte in the same sample to an SI unit—only in theory—or the same CRM through different intermediate standards (e.g., standards obtained from national suppliers), then

3.28.2. The intermediate standards will be comparable and traceable to one another (blue chains, B); and

3.28.3. The results of the three laboratories for the same analysis or determination will be comparable and traceable to one another. Therefore, the three laboratories will be in harmony, which will make them highly competitive on the international market (the tree can be *mutually confident*). Thus, acceptance by a German dealer in alcoholic drinks of the results of an analysis for total tannins in wine conducted by the in-house laboratory of a producer in La Rioja (Spain) may lead to the dealer deciding to import the wine.

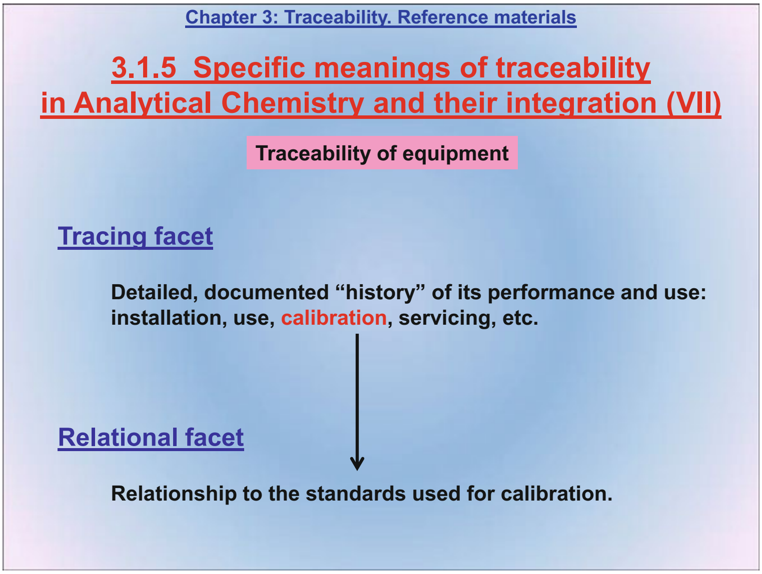
Slide 3.29



Traceability among standards is dealt with at length above (see, for example, Slide 3.8). This slide is simply a reminder of its significance to a metrological discipline such as Analytical Chemistry, where *traceability of a result* is also crucial.

The slide focuses on traceability in primary and secondary analytical chemical standards.

Slide 3.30

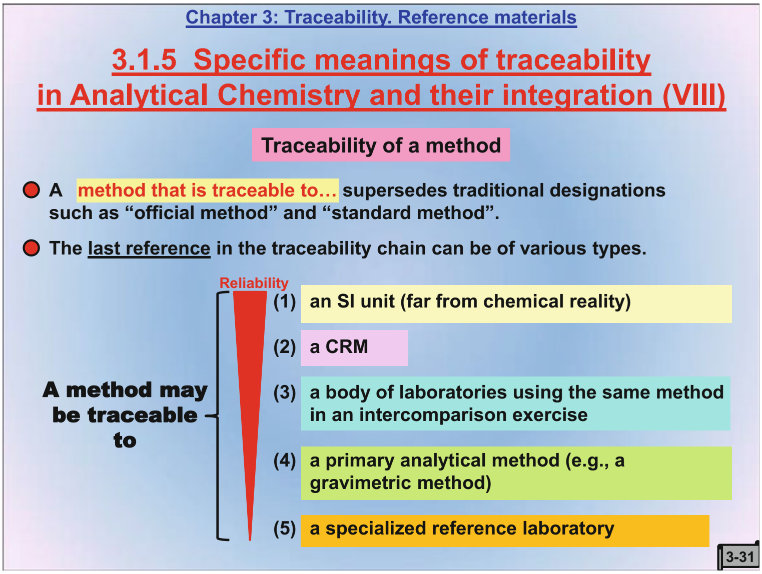


The *traceability of an instrument* delivering analytical chemical information provides an excellent example of the combination of the two basic facets of traceability.

– The *tracing facet* is inherent in the requirement set by ISO 17025:2004 for laboratory accreditation and involves recording the whole "history" of an instrument since it was installed.
– The *referential facet* focuses on the standards used to calibrate or verify the instrument (Slide 3.19).

The two facets are connected by calibration, which should be properly documented as well.

Slide 3.31



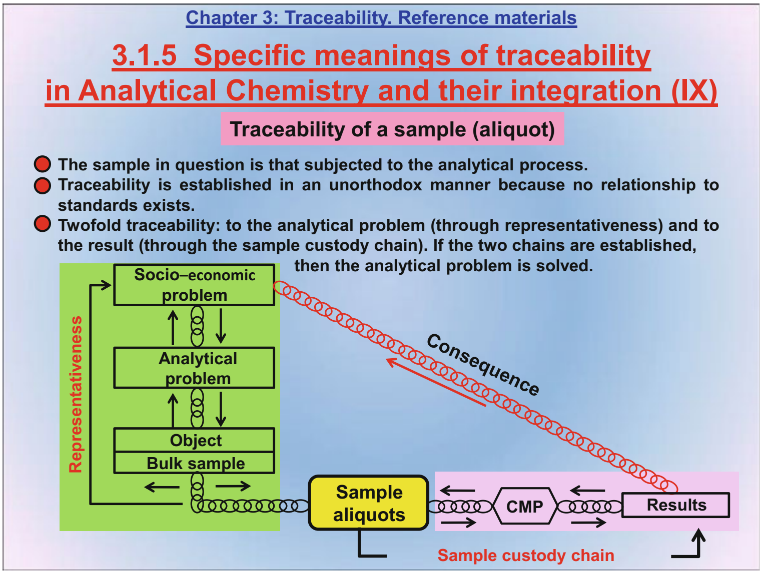
The terms "standard method" and "official method" formerly used to assure quality in analytical methods have been gradually replaced with "*a method traceable to…*" and led to the quality of a traceable method being judged by the particular reference at the end of the traceability chain.

(1) Ideally, the final reference should be an SI unit, but this virtually impossible in the chemical realm.
(2) The most realistic degree of quality is traceability to a certified reference material. However, the scarcity of CRMs makes it difficult to accomplish.
(3) A more affordable target is traceability to a body of laboratories using the same method to analyse aliquots of the same sample in an intercomparison exercise supervised by a widely acknowledged national or international competent organization.

(4) Next in the reliability ranking is traceability to a primary, absolute method using no analytical chemical standards (see Slide 5.12). Such is the case with gravimetric methods, for example. The problem arises when the same laboratory has to perform the target method and the primary method in the absence of external references.
(5) Traceability to a specialized international reference laboratory (a distinction issued by a competent international organization such as the European Union) is also limited in scope because most laboratories deal only with highly specific types of samples (e.g., bovine meat to be analysed for antibiotics or anabolic steroids).

As shown in the slide, reliability in the traceability chain decreases from 1 to 5.

Slide 3.32



3.32.1. The *traceability of the sample (aliquot)* subjected to an analytical process is very interesting for a number of reasons, namely:

(1) It is rather unorthodox in that it only encompasses the tracing facet of the integral concept of traceability.
(2) It represents traceability to two rather than one final reference: the information required and the results of two traceability chains, one corresponding to the capital property representativeness (Slide 7.10) and the other being the so-called "sample custody chain".
(3) It is cyclic: provided the partial traceability chains are not broken, the main goal of Analytical Chemistry (Slide 1.8) is reached. Such a goal is ensuring that the

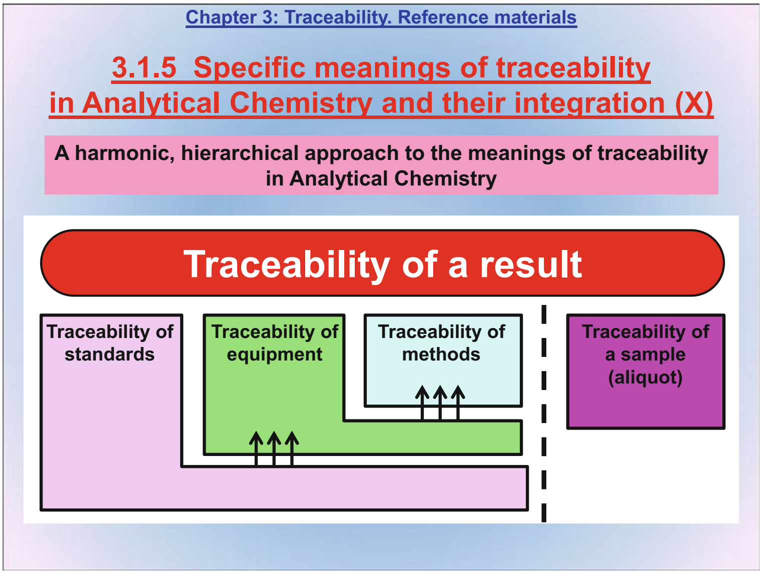
results fulfil the information demand because they are traceable to the specific socio–economic problem addressed (Slide 7.10).

3.32.2. Therefore, the sample aliquot that is subjected to the analytical process should be traceable to the information demand (the socio–economic problem) through unequivocal relationships to the bulk sample, the object and the analytical problem (see Chap. 7).

3.32.3. The second traceability chain starts at the aliquot, which should be unequivocally related to its results through the sample custody chain. The custody chain, which relies on the use of bar codes and computers, is essential for automated laboratories processing large numbers of samples each day. Thus, a clinical laboratory may lead to a healthy person being diagnosed with diabetic coma—or vice versa—if it does not ensure traceability of each sample (aliquot) to the patient from whom it was obtained.

3.32.4. The consequence of the two traceability chains that start at the sample aliquot not being broken is that the results are consistent with the information required and hence that the information demand is fulfilled. This is a permanent challenge for Analytical Chemistry (see Chap. 7, devoted to analytical problem-solving).

Slide 3.33



This hierarchical arrangement of the analytical meanings of traceability facilitates their integration.

At the top of the hierarchy is *traceability of a result*, which is the most orthodox concept and relies on the traceability of the standards, equipment and methods used to obtain it.

Traceability between tangible standards (analytical chemical standards) provides support for

– traceability of a result;
– traceability of equipment in its referential facet; and
– traceability of methods in its referential facet.

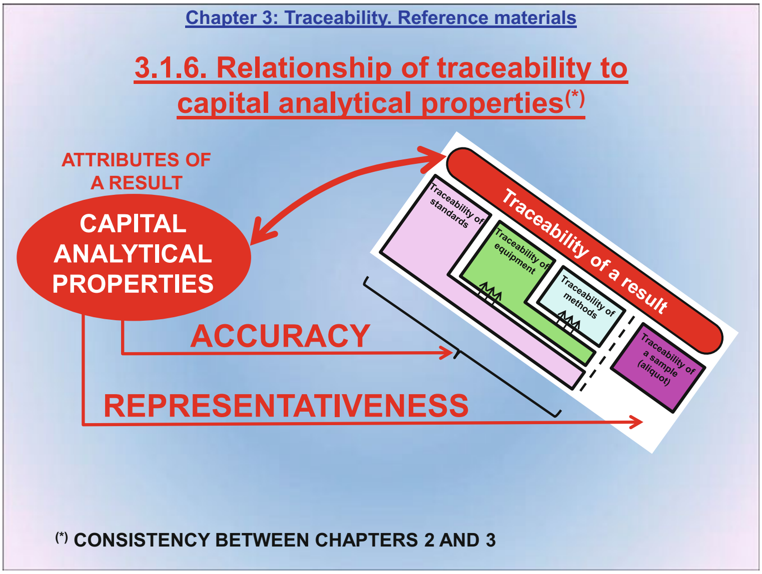
Traceability of equipment and methods relies on traceability of standards, which in turn rests on traceability of a result and traceability of a method.

Traceability of methods rests on traceability of standards and traceability of equipment, and provides support for traceability of a result.

This approach would be incomplete without an unequivocal relationship between the sample (aliquot) and the result in the context of *traceability of the sample aliquot*, which is an undeniable foundation of its traceability. It is separated from the previous types of traceability because it is a completely unorthodox concept—it lacks the typical referential facet of other meanings of traceability in Analytical Chemistry.

3.1.6 Traceability and Capital Analytical Properties (1 Slide)

Slide 3.34



This section harmonizes the contents of this chapter (Traceability. Reference materials) with those of the previous one (Analytical Properties).

3.34.1. Based on the general scheme of analytical properties in Slide 2.4, the capital properties (accuracy and representativeness) are attributes of the results.

3.34.2. Based on the integral view of the concepts behind *traceability of a result* (Slide 3.33), capital analytical properties are consistent with this form of traceability. Thus,

– *accuracy* is the first part of the support for traceability of a result, which relies on that of standards, equipment and methods; and
– *representativeness* corresponds to consistency of the sample aliquot with the information required and the results themselves.

Both properties are crucial (see Slide 2.13) with a view to assessing the quality of the results and building the integral concept of traceability.

3.2 Annotated Suggested Readings

BOOKS

Principles of Analytical Chemistry

M. Valcárcel

Springer-Verlag, Berlin, 2000.

This was the first book to start the teaching of Analytical Chemistry with its foundations before dealing with methods and techniques in order to provide students with an accurate notion of what Analytical Chemistry is and means.

This chapter overlaps to a great extent with Chap. 3 of Valcárcel's book, from which it borrows the title. This is a simplified version of that chapter, which, however, has been expanded in some respects to better illustrate abstracts concepts such as traceability, validation of analytical methods, and the relationship of traceability to analytical properties. Valcárcel's book can be used for direct consultation of the contents of this chapter.

Metrology in Chemistry and Biology: A practical approach

M. Valcárcel and 17 other authors.

O.O.P.E.C., UE (Luxemburg), 1999.

Scientists from 9 European countries led by Spain produced the first official publication on Metrology in Chemistry and Biology, which discusses coincidences with and differences from traditional Metrology (that is, Metrology in Physics). The most salient conclusion is the need to adapt general metrological principles to the specificities of chemical, biochemical and biological measurements. Some annexes to standards issued in the XXI century have echoed the recommendations. Many parts of this chapter are inspired by this document.

3.3 Questions on the Topic (Answered in Annex 2)

3.1. What are the main purposes of a sample matrix standard with a certified analyte content (a CRM)? Tick the correct answers.

[ ] Calibrating an instrument

[ ] Globally assessing an analytical process

[ ] Calibrating a method

[ ] Standardizing secondary analytical chemical standards

3.2. What is a matrix standard? What is its main use?

3.3. What are the essential requirements for establishing the traceability of an instrument?

3.4. Tick the type correct type of standard in each case.

	Standard			
	Basic	Chemical	Analytical chemical	
			Primary	Secondary
Carbon-12				
A 0.1 mol L^{-1} solution of $KMnO_4$				
Potassium hydrogen phthalate				
Ultrapure silver				
The faraday				

3.5. Describe the traceability network among standards relevant to Analytical Chemistry with emphasis on the connections between basic, chemical and analytical chemical standards.

3.6. How would you define “traceability of an analytical method (CMP)”?

3.7. The total free acid content of a wine sample is determined by acid–based titration with a sodium hydroxide solution previously standardized with potassium hydrogen phthalate. What standards are used in the process?

Chemical:
Primary analytical chemical:
Secondary analytical chemical:

3.8. Define “equipment calibration” and relate it to or distinguish it from “method calibration”.

3.9. What are the purposes of equipment calibration (verification)? Tick the correct answer(s).

[ ] Constructing a calibration curve
[ ] Adjusting faulty equipment
[ ] Globally assessing an analytical method
[ ] Distinguishing error types in Analytical Chemistry

3.10. Connect each of the following standards to its type in the column on the right.

Standard	Type
A 0.1 mol HCl L^{-1} solution	Basic
The atomic weight of Ca	Chemical
Sodium carbonate	Analytical chemical (Primary)
The faraday	Analytical chemical (Secondary)
The second	

3.11. Rank the reliability of the following types of standards with a score from 1 (least reliable) to 4 (most reliable).

Standard	Reliability
Secondary analytical chemical standard	
Chemical standard	
CRM	
Primary analytical chemical standard	

3.12. What role do analytical chemical standards play in the traceability of a result?
3.13. What type of standard (basic, chemical or analytical chemical) has the greatest associated uncertainty? Why?
3.14. A sample of powdered milk with a protein content certified in a document issued by a renowned independent organization is

[ ] A primary standard
[ ] A certified reference material
[ ] A secondary standard
[ ] A reference material

3.15. Name the types of chemical standards, state their differences and give some examples.
3.16. Give an example of each complementary criterion used to classify analytical chemical standards.
3.17. Comment on the tracing facet of traceability of a result. What should it be consistent with?
3.18. Describe a procedure for assessing (validating) a new analytical method in terms of its relationship to matrix-type certified reference materials.
3.19. What is the main limitation of CRMs for establishing the traceability of methods?
3.20. What types of standards prevail among (a) reference materials (RMs) and (b) certified reference materials (CRMs)?

3.21. Which base standard is the most relevant to Chemical Metrology? Why?
3.22. Why are secondary standards used even though they have unsuitable properties (e.g., instability, impurity)?
3.23. What are the requirements for a matrix-type CRM?
3.24. What are the three most salient general uses of analytical chemical standards?
3.25. What are the three principal meanings of traceability of an analytical result?
3.26. How is an analytical method assessed to assure reliability?
3.27. What analytical properties are related to traceability? Explain your answer.
3.28. On what should mutual recognition of the results of two or more laboratories rest?
3.29. What feature and twofold meaning does traceability of the sample aliquot subjected to an analytical process have?

3.4 An Abridged Version of the Chapter

The contents of this chapter can be shortened for teaching Analytical Chemistry to students not majoring in Chemistry, albeit to a lesser extent than those of others because of its transversal conception. The following 5 slides (15% of all) can be omitted for this purpose:

- Section 3.1.2: Slides 3.5 and 3.6
- Section 3.1.3: Slide 3.11
- Section 3.1.4: Slide 3.15
- Section 3.1.5: Slide 3.31