

Abstract

This chapter uses definitions, descriptions and, especially, examples to highlight the importance of analytical properties with a view to ensuring quality in the analytical process and in quantitative results. Analytical properties allow one to compare methods in order to select the most appropriate choice for the analytical problem to be solved. In this chapter, analytical properties are classified according to a metrological hierarchy encompassing three levels, namely: capital properties, basic properties and productivity-related properties. The three types of properties and their associated parameters are described, and their computation explained with examples, in order to facilitate their understanding and mathematical calculation. The individual analytical properties are important, but their mutual relationships are even more so are. For this reason, Sect. 2.1.7 is exclusively devoted to such relationships, to the way each property depends on the others and to which are to be favoured depending on the particular analytical problem. The analytical properties pertaining to Qualitative Analysis (Chap. 6) are special and required adaptation to those dealt with in this chapter. The contents of this chapter are closely related to those of Chap. 7. In fact, analytical properties provide the ground on which effective problem-solving, and fulfilment of the client's information requirements. One other aim of this chapter is introducing students to numerical and statistical computations in Analytical Chemistry in context rather than in isolation as is usually the case.

Teaching Objectives


- To define analytical properties in a holistic manner.
- To assign analytical properties to specific facets of Analytical Chemistry.

Electronic Supplementary Material The online version of this chapter (doi:[10.1007/978-3-319-62872-1_2](https://doi.org/10.1007/978-3-319-62872-1_2)) contains supplementary material, which is available to authorized users.

- To establish mutual relationships among analytical properties.
- To relate analytical properties to analytical quality.
- To introduce students to numerical and statistical computations in Analytical Chemistry.

2.1 Explanation of the Slides

Slide 2.1

FOUNDATIONS OF ANALYTICAL CHEMISTRY	
PART I INTRODUCTION TO ANALYTICAL CHEMISTRY	
Chapter 1.	Principles of Analytical Chemistry
 Chapter 2.	Analytical properties
Chapter 3.	Traceability. Reference materials
PART II. THE ANALYTICAL PROCESS	
PART III. SOCIO –ECONOMIC PROJECTION OF ANALYTICAL CHEMISTRY	
ANNEX 1. GLOSSARY OF TERMS	
ANNEX 2. ANSWERS TO THE QUESTIONS	

This slide places in Part I (Introduction to Analytical Chemistry) and shows the other two parts.

This chapter describes analytical properties, their calculation and the ways quantitative results can be expressed.

Slide 2.2

PART I
INTRODUCTION TO ANALYTICAL CHEMISTRY

Chapter 2: Analytical properties

Contents

- 2.1.1. Introduction
- 2.1.2. The chemical metrological hierarchy
- 2.1.3. Errors in Analytical Chemistry
- 2.1.4. Capital analytical properties
- 2.1.5. Basic analytical properties
- 2.1.6. Productivity-related properties
- 2.1.7. Relationships among analytical properties

Accuracy	Representativeness		
Precision	Robustness	Sensitivity	Selectivity
Expediency	Cost-effectiveness	Safety/Comfort	

Teaching objectives

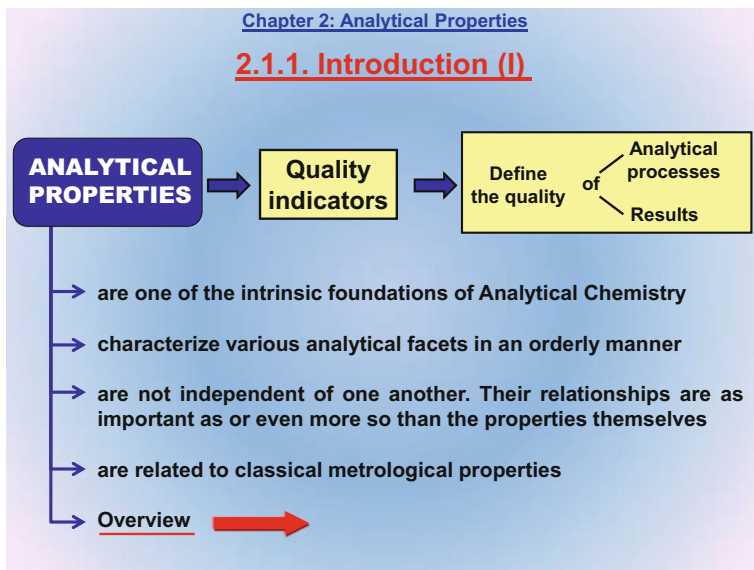
- To define analytical properties in a holistic manner
- To assign analytical properties to specific facets
- To relate analytical properties to one another
- To relate analytical properties to analytical quality
- To introduce students to basic numerical and statistical computations in Analytical Chemistry

2.2.1. The contents of this chapter are organized in 8 sections dealing with analytical properties through hierarchies and examples. A preliminary section deals with errors in analytical measurements and the types of uncertainty in analytical results.

2.2.2. These are the teaching objectives to be fulfilled, namely: knowing analytical properties, relating them to one another and to analytical quality, and assigning and favouring some over others depending on the analytical problem to be solved.

2.1.1 Introduction (2 Slides)

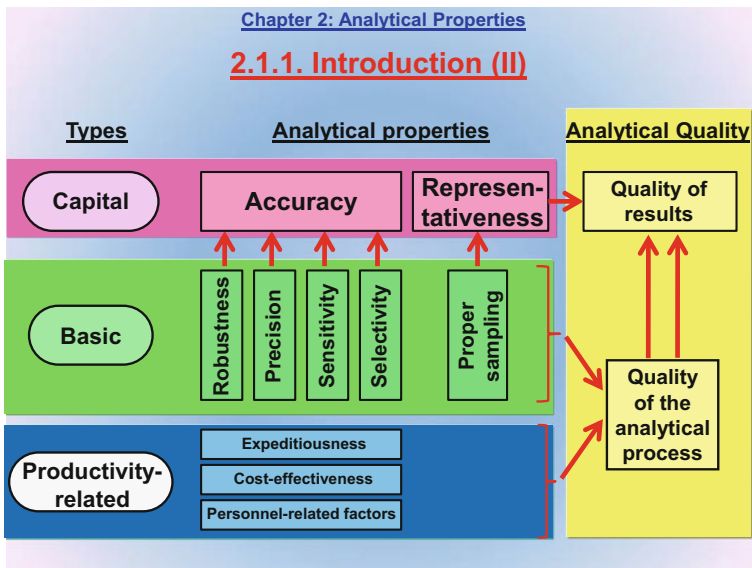
Slide 2.3



2.3.1. Analytical properties are the materialization of analytical quality. They are quality indicators for the analytical process and the results that facilitate their assessment and validation for solving specific analytical problems.

2.3.2. This slide shows the different facets and characteristics of analytical properties. Interestingly, the properties are not mutually independent; rather, they influence one another, whether directly or indirectly. A sound knowledge of the relationships among the properties is essential for analytical chemists to efficiently favour some over others depending on the analytical problem addressed (see Slides 2.56–2.61).

Slide 2.4



2.4.1. This is an overview of the three types of analytical properties (namely, capital, basic and productivity-related) in a top-to-bottom hierarchy.

Capital properties (accuracy and representativeness) only apply to results¹ and basic properties (robustness, precision, sensitivity, selectivity and proper sampling) only to the analytical process. The arrows in the scheme illustrate the dependence of capital properties on basic properties. Thus, robustness, precision, sensitivity and selectivity provide support for accuracy, and proper sampling is the basis for representativeness.

Like basic properties, productivity-related properties (expeditiousness, cost-effectiveness and personnel-related factors) also apply to the analytical process.

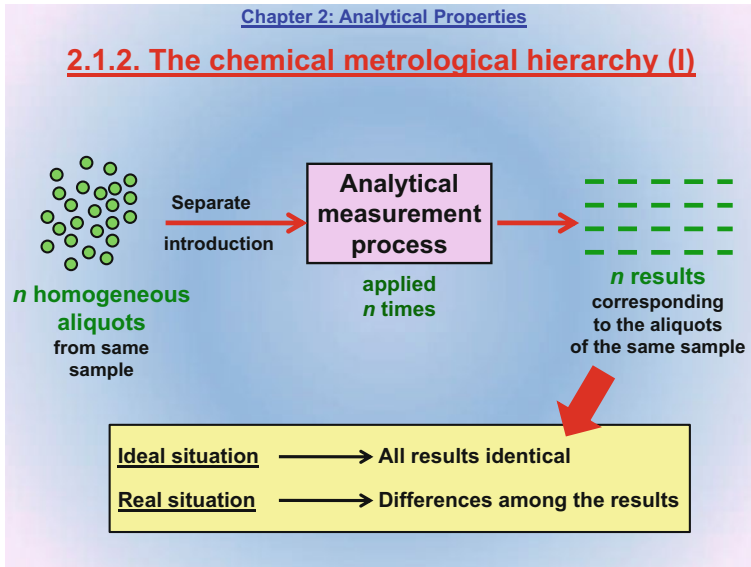
Each type of analytical property is dealt with individually in the following slides.

2.4.2. Capital analytical properties define the quality of results, whereas basic and productivity-related properties define the quality of the analytical process. As a whole, analytical properties are indicators of analytical quality.

¹It is therefore incorrect to say an analytical process is accurate except unless it provides accurate results.

2.1.2 The Chemical Metrological Hierarchy (3 Slides)

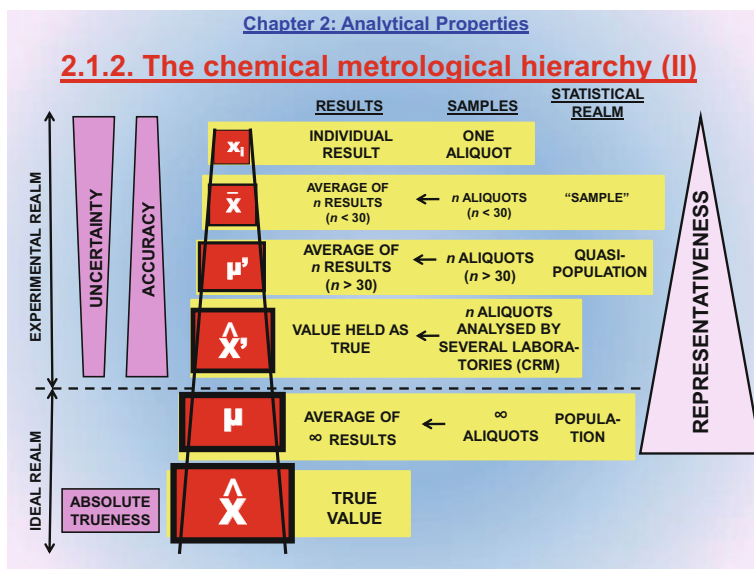
Slide 2.5



This is a simplified depiction of an analytical process starting with n aliquots of the same sample and leading to n results through a general chemical measurement process (CMP). The results can be

- Identical. This is the ideal situation, but highly unlikely in practice, where the results correspond to intrinsic information in the object and absolute trueness (see Slide 1.17).
- Different. This is usually the case in the laboratory because results tend to differ by effect of errors. This typical situation corresponds to analytical information (see Slide 1.17).

Slide 2.6



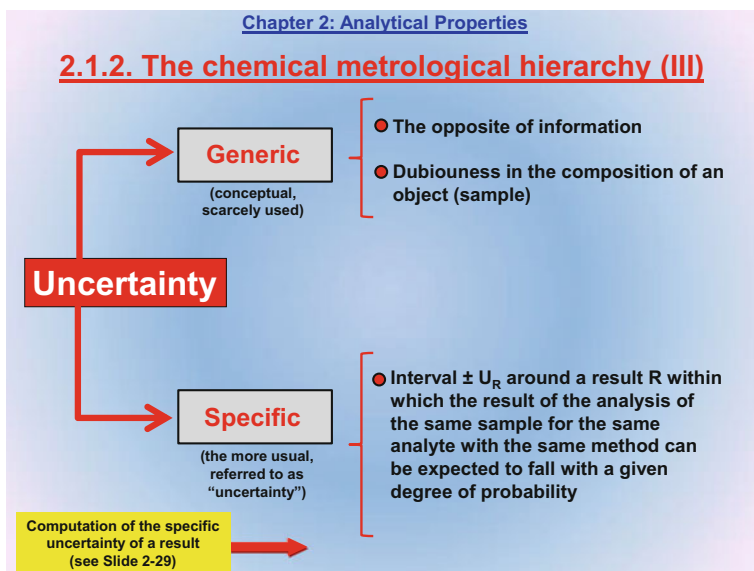
2.6.1. This is the metrological hierarchy of the results of a chemical measurement process, the sample (number of aliquots) from which they are obtained and the statistical designations assigned to some. The number of sample aliquots to be used in order to obtain the desired result increases from the top to the bottom. The results can be classified as follows:

- Individual results, averages and values held as true fall *in the experimental realm*. They can be determined in the laboratory and constitute analytical information accessible to the analytical chemist (see Slide 1.17).
- The average of infinite results and the true value fall *in the ideal realm*. They are inaccessible to the analytical chemist because it constitutes intrinsic information (see Slide 1.17).

2.6.2. Representativeness in the results increases with increasing number of aliquots analysed (that is, from the top to the bottom in the hierarchy). The average of an infinite number of results would correspond to the analysis of a whole population (that is, of all aliquots that can be extracted from a sample). Accuracy in the results also increases from top to bottom in the hierarchy (that is, as the results approach the reference value held as true). Uncertainty, decreases as the results approach the value held as true and also with increasing number of aliquots.

It should be noted that representativeness, accuracy and uncertainty do not apply to the true value because this represents absolute trueness.

Slide 2.7



Uncertainty in a result is the lack of certainty about its trueness. Analytical results can be subject to the two types of uncertainty shown here. While *generic uncertainty* represents complete dubiousness (that is, nothing is known about the sample), *specific uncertainty* (U_R) restricts dubiousness to a given interval (that is, the lack of knowledge is confined to a specific range of values) around a fixed value.

The procedure used to calculate specific uncertainty is described in Slide 2.29.

2.1.3 Errors in Analytical Chemistry (5 Slides)

Slide 2.8

Chapter 2: Analytical Properties

2.1.3. Errors in Analytical Chemistry (I)

- Two possible situations according to the landmarks of the metrological hierarchy:

- 1** Ideal situation (inaccessible)

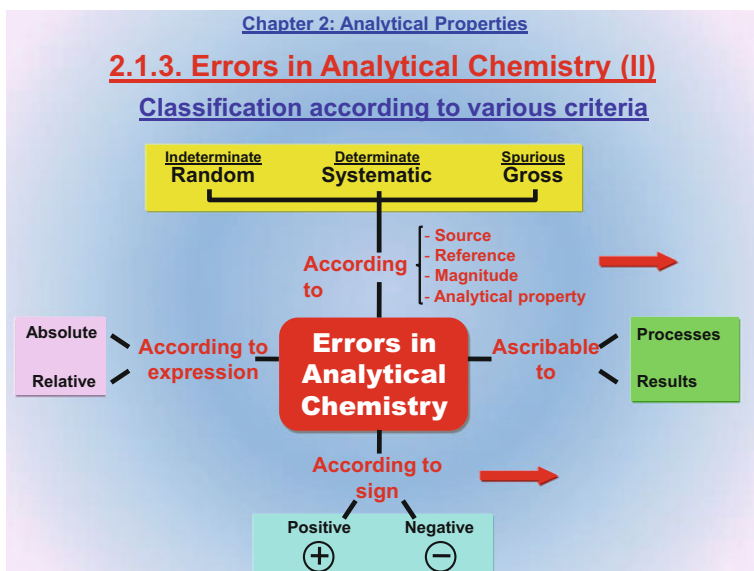
$$x_i = \bar{X} = \mu' = \hat{X}' = \mu = \hat{X}$$
- 2** Real situation: Differences among landmarks (errors)

<u>Data</u>	<u>Differences</u>	<u>References</u>
$\left. \begin{matrix} x_i, \bar{X} \\ \mu', \mu \end{matrix} \right\}$	\longleftrightarrow	$\hat{X}' (\hat{X})$
x_i	\longleftrightarrow	\bar{X}, μ', μ
\bar{X}	\longleftrightarrow	μ', μ

This slide shows two possible situations regarding results: the ideal situation and a real situation.

- In the ideal situation, all results are identical, so any result coincides with all others including the true value. This situation is inaccessible to the analytical chemist because chemical measurement processes (CMPs) are inevitably subject to errors (that is, differences between each individual result x_i and the true value, \hat{X}').
- In a real situation, which is typical of laboratories, the results are not identical and data differ from their reference values. Such differences, which can arise from various factors (Slide 2.9), are called “errors”.

Slide 2.9



2.9.1. This slide classifies errors according to various criteria. Errors can be assigned to factors of the analytical process (e.g., the operator, instrument sensitivity, calibration) and to quantitative results.

2.9.2. Errors can be random, systematic or gross depending on the type of reference used, magnitude (large or small) and analytical property concerned (see Slide 2.10).

2.9.3. Also, errors can be positive or negative depending on the sign of the difference between the result and the reference value.

2.9.4. Finally, errors can be relative (that is, without a quantity, such as percentages, fractions of unity) or absolute (with a quantity).

Slide 2.10

Chapter 2: Analytical Properties

2.1.3. Errors in Analytical Chemistry (III)

Types of errors	Distinguishing criteria				
	Source	Reference for definition	Sign	Relative magnitude (usually)	Analytical property affected
Random (indeterminate)	A → Chance	Average of a set \bar{X}, μ'	Variable \oplus \ominus	Small	Precision (specific uncertainty)
Systematic (determinate)	B → Well-defined alterations	$\bar{X}' (\bar{X})$	Unique \oplus Positive or \ominus Negative	Small	Accuracy (traceability)
Gross	C →			Large	

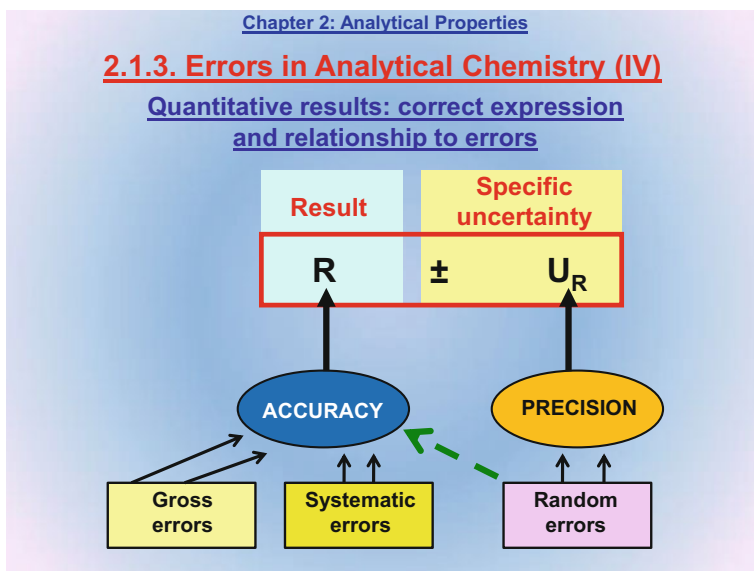
This slide depicts the three types of errors that can be made in making measurements and can affect the accuracy of a result. Their sources, the references used to express them and the analytical properties to which they are related, in addition to various other features, are stated.

A. *Random errors* are due to chance and hence indeterminate (that is, they cannot be known beforehand). Random errors are related to specific uncertainty, which influences the precision of the analytical process and establishes a confidence interval around the mean of the results (see Slides 2.7 and 2.29); hence, it has a variable sign (\pm).

B. *Systematic errors* are due to a well-defined alteration such as a failure in the analytical process (e.g., a poorly calibrated pipette) and are thus determinate (that is, they can be known). Systematic errors influence the accuracy of a result and are defined in terms of a reference value held as true (e.g., the value for a certified reference material) (see Slides 3.17 and 3.18). This type of error can be positive or negative.

C. *Gross errors* share some traits with systematic errors but are typically much larger (e.g., the error arising from spillage in transferring a liquid between vessels and ignoring it in computing the result).

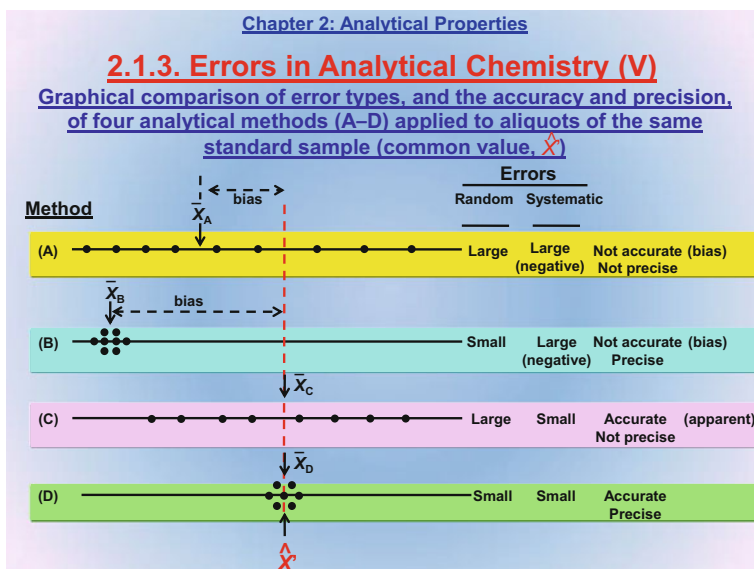
Slide 2.11



2.11.1. Any result R obtained from a series of measurements in an analytical process should be accompanied by its specific uncertainty, U_R , and expressed as shown in this slide. Accuracy is a property of a result that arises in comparing it with a reference value (e.g., a certified value). Precision is a property of the analytical process and is expressed in terms of the specific uncertainty accompanying the result.

2.11.2. As can be seen, errors influence the properties accuracy and precision, and hence results and their specific uncertainty. Systematic and gross errors have a direct impact on accuracy and cause results to depart in either direction from the reference value (see Slide 2.10). Random errors influence precision mainly and materialize in specific uncertainty. Because they are the source of differences among results for the same analytical process, they can also have an indirect impact on the accuracy of a result representing the average of a data series.

Slide 2.12

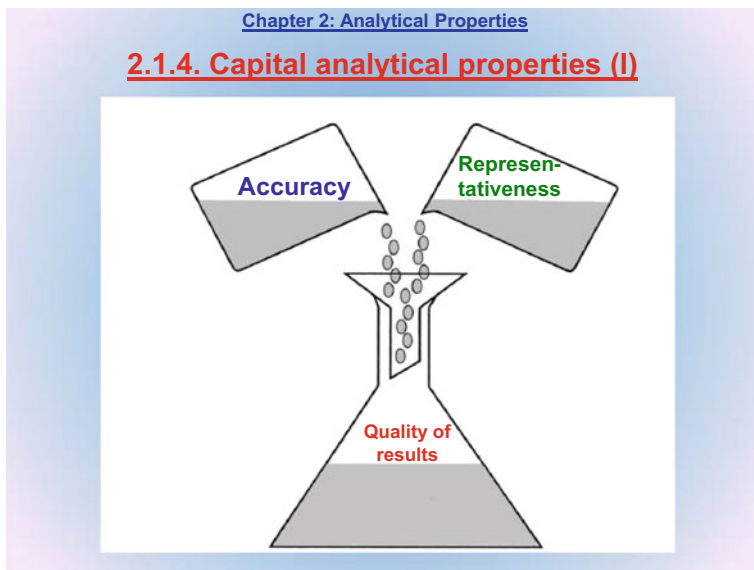


This slide compares and relates the three types of errors with accuracy and precision via four examples (methods A–D) where the same analyte was determined in identical aliquots of the same sample. The accuracy and precision are established from the errors made with each method. For this purpose, n aliquots of the same sample are independently subjected to each of the four methods and the results compared with the value held as true (\hat{X} , in red) as reference.

- *Method A* is precise but not accurate because the average result, \bar{x}_A , does not coincide with the reference value and the individual results, x_i , are highly disperse (that is, very distant from one another). Therefore, the method is subject to systematic and random errors.
- *Method B* is precise because the individual results, x_i , are tightly clustered; however, it is not accurate because the average result, \bar{x}_B , does not coincide with the reference value. The method is therefore subject to systematic errors that exceed random errors in magnitude.
- *Method C* is accurate because the average result, \bar{x}_C , coincides with the reference value; however, it is not precise because the individual results, x_i , are highly disperse. Therefore, random errors are larger than systematic errors. This is a coincidence but quite possible in practice.
- *Method D* is both accurate and precise. This is the ideal type of method for the analytical chemist because the overall result, \bar{x}_D , coincides with the reference value and the individual results, x_i , are tightly clustered, so systematic and random errors are very small.

2.1.4 Capital Analytical Properties (5 Slides)

Slide 2.13



Capital analytical properties are at the top of the hierarchy in Slide 2.4 because they characterize the results and are directly connected to analytical information. The two capital properties are accuracy and precision; both are needed to ensure analytical quality in the results.

This slide illustrates the following notion: quality in the results is achieved when both “ingredients” (accuracy and representativeness) are accomplished simultaneously. A highly accurate result that is not representative of the sample is completely useless. In fact, such a result cannot describe the sample and is hence useless to solve the analytical problem concerned (Chap. 7).

Depending on the particular analytical problem addressed, however, some analytical properties can be favoured over others provided an acceptable minimum level of quality in all is ensured (see Slides 2.56–2.61).

Slide 2.14

Chapter 2: Analytical Properties

2.1.4. Capital analytical properties (II)

Accuracy (I)

Definition

- A property of analytical results
- Degree of consistency between the result of the determination of an analyte (x_i) or the average of n results (\bar{X}) and the value held as true (\hat{X}') or, ideally, the true value (\hat{X}).

External reference

- Value held as true (\hat{X}'). Ideally, the true value (\hat{X}).

Mathematical characterization

- Systematic (or gross) error with a fixed sign (positive or negative) and expressed in an absolute or relative manner (see Slides 2-8 and 2-9).

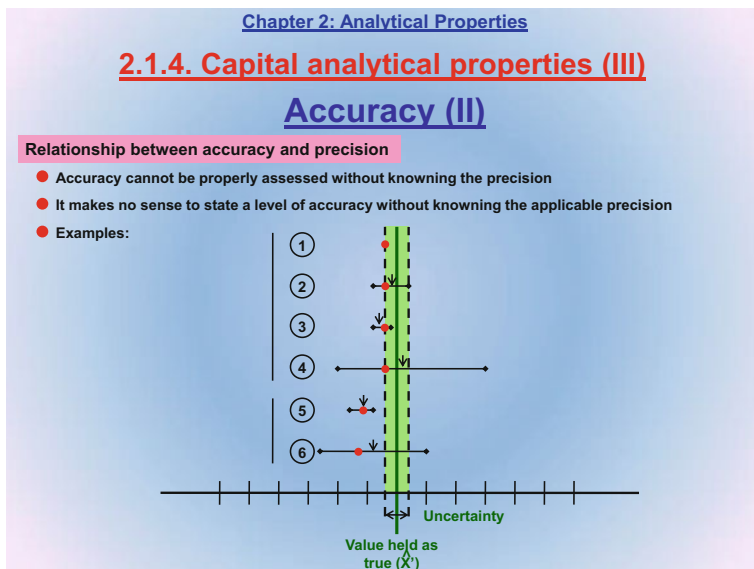
Types of errors

	Absolute value	Relative value
● Error of a result	$e_{x_i} = \pm (x_i - \hat{X}')$	$e_{x_i} \text{ rel} = \frac{\pm e_{x_i}}{\hat{X}'} (100)$
● Error of a method or "bias" (\bar{X})	$e_{\bar{x}} = \pm (\bar{X} - \hat{X}')$	$e_{\bar{x}} \text{ rel} = \frac{\pm e_{\bar{x}}}{\hat{X}'} (100)$

This slide defines accuracy and illustrates some of its features. Accuracy is a capital analytical property, a measure of consistency of results with the reference value. Accuracy can be applied to an individual result (x_i) or a body of n results. In the latter case, accuracy is used to characterize the method used to obtain the results.

The difference between a result and the reference value, \hat{X}' , is the systematic error—or gross error if exceedingly large—and can be expressed in absolute or relative terms. The slide also shows the formulae typically used to calculate errors.

Slide 2.15



There can be no accuracy without precision. In fact, it makes no sense to refer to an individual result of an analytical process, x_i , without knowing the interval within which it can fall. The slide shows six examples relating accuracy to precision and quality of a result in relation to a reference value held as true.

In the first four examples (spots in red), the result is very close to the value held as true (\hat{X}).

Example 1. The result may seem accurate because it falls within the uncertainty interval for the reference value. However, the accuracy is indefinite because the precision of the method (that is, its specific uncertainty) is unknown. For this reason, the result may be due to chance, so it lacks analytical value.

Example 2. The result is accurate because it falls within the specific uncertainty interval for the reference value. Also, it has a well-defined precision spanning an interval highly similar to that of the reference value.

Example 3. The result is accurate because it falls within the specific uncertainty interval for the reference value. Also, it has a well-defined precision which, however, spans a range that is not so similar to that for the reference value as in the previous example.

Example 4. The result cannot be deemed accurate because its specific uncertainty interval is rather broad and contains not only the values of the reference interval but also may other, widely different values.

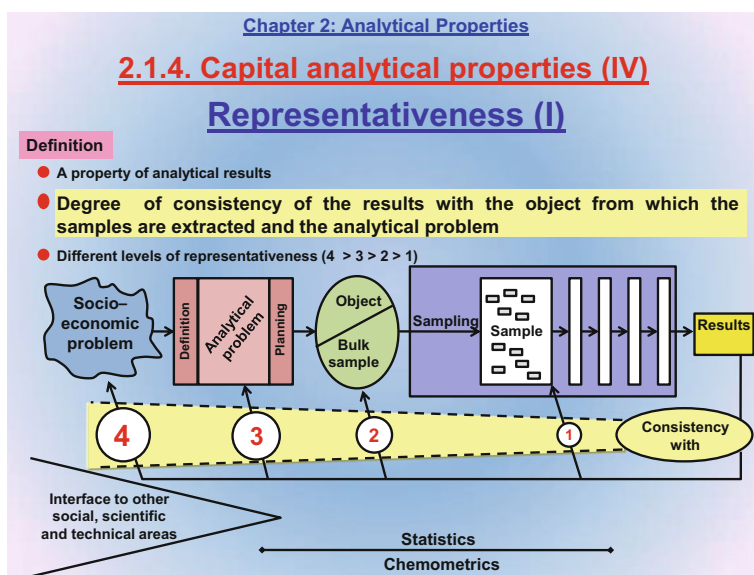
In the last two examples, the result is identical but farther from the value held as true, \hat{X}' , than in the first four.

Example 5. The result is not accurate because it does not fall in the specific uncertainty interval for the reference value. However, the method is highly precise because the uncertainty interval for the result is very narrow.

Example 6. The result is not accurate because it does not fall within the specific uncertainty interval for the reference value; also, it is not precise because the interval for the results is rather broad and contains highly disperse potential values.

It is therefore indispensable to know the precision of an analytical process in order to deem its results accurate.

Slide 2.16



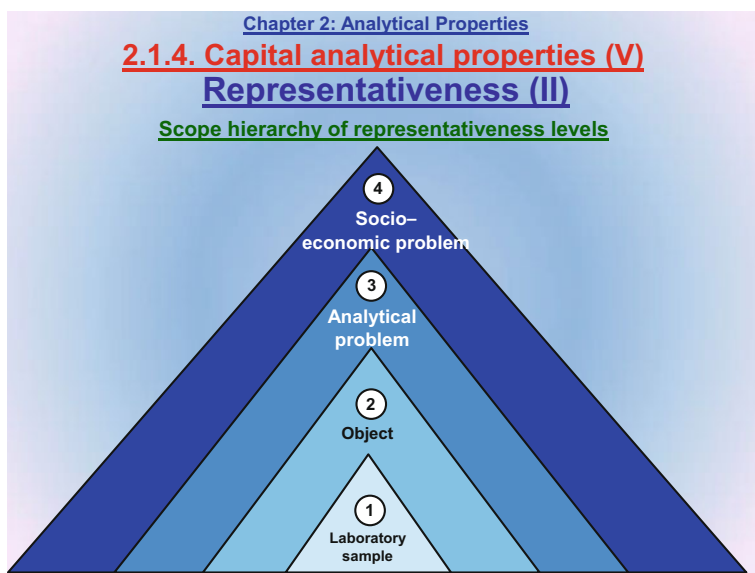
This slide defines representativeness and illustrates its importance. Representativeness increases from level 1 (lowest) to 4 (highest).

- Level 1. The results are consistent with the sample received and analysed by the laboratory; also, they provide a correct description of the sample. This level is essential because as it gives access to the others.
- Level 2. The results are consistent not only with the sample, but also with the object from which it was obtained. Representativeness is higher at this level than at the previous one because the results describe the target object in full rather than the sample alone.

- Level 3. The results should describe the object comprehensively enough to allow the analytical problem to be solved. This requires correctly interpreting the results at the previous levels.
- Level 4. At the top representativeness level, the solution to the analytical problem is applicable to the socio-economic problem from which the analysis ensued. This requires previously reaching Levels 1–3.

For the results to be representative, all links in chain (results, sample, object, analytical problem and socio-economic problem) should be traceable. Traceability is dealt with in Chap. 3, and the way the results are related to the analytical and socio-economic problem are illustrated in Slide 7.10.

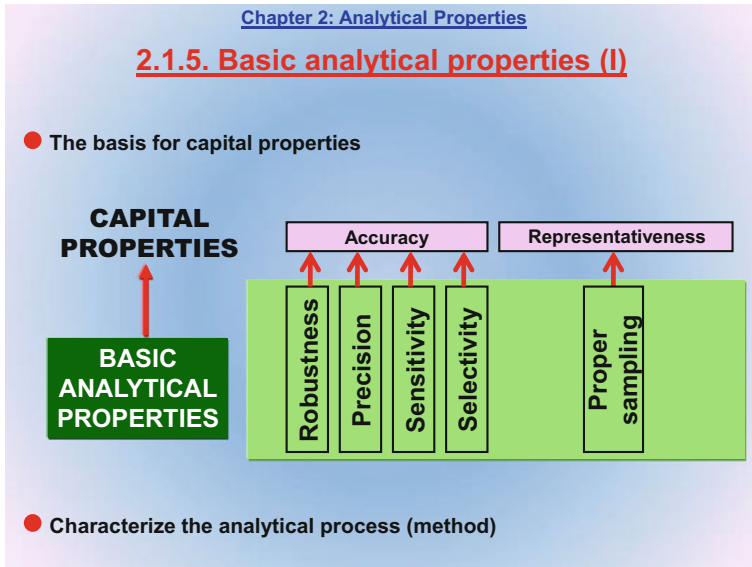
Slide 2.17



This slide ranks the different levels of representativeness described in Slide 2.16 in a scope hierarchy. Representativeness increases from level 1 to 4 here and accessing a higher level entails previously reaching the lower ones (that is, the top level includes all lower levels).

2.1.5 Basic Analytical Properties (1 Slide)

Slide 2.18



Basic analytical properties (namely, robustness, precision, sensitivity, selectivity and proper sampling) follow capital properties in the hierarchy of Slide 2.4. Proper sampling provides the basis for representativeness and the other three properties constitute the basis for accuracy (the two capital properties in Slide 2.13). All basic properties pertain to the analytical process.

2.1.5.1 Precision (13 Slides)

Slide 2.19

Chapter 2: Analytical Properties


2.1.5. Basic analytical properties (II)

Precision (I)

[1] Definition

- Degree of consistency between a set of results obtained by repeatedly and independently applying the same analytical method to the same sample in order to determine the same analyte

[2] Concepts

- Precision: - The opposite of dispersion
- Equivalent to clustering
- Characterizes the analytical process (method)
- Supports accuracy
- Related to random (indeterminate) errors (see Slide 2.9). Materializes in deviations
- Reference: arithmetic mean of a body of values obtained under identical conditions
- Parameters expressing the precision of 
 - A result: { Deviation (d)
Relative deviation
 - The result set: { Standard deviation (s)
relative standard deviation (rsd)
coefficient of variation (CV, %)
- Contradiction between precision and the mathematical expressions directly measuring precision:
The greater are d , s and CV, the lower is the precision
- A crucial aspect: the conditions under which measurements are made: - Repeatability
- Reproducibility

This slide defines precision and describes its most salient features. Precision is a basic property of the analytical process indicating how tightly clustered the body of independently obtained results of the analytical process is. Precision is essential to fully characterize accuracy as it confines the result within a well-defined confidence interval.

The parameters used to measure precision vary in the opposite direction to the property and are related to random errors. Thus, they measure dispersion or departure from a reference value (the average of the results): the greater the dispersion is, the lower will be the precision and vice versa.

Fully and properly characterizing the precision entails using well-defined experimental computation procedures (see Slides 2.21–2.23).

Slide 2.20

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (III)

Precision (II)

[3] Values characterizing precision in mathematical terms

(A) Precision of an individual result (x_i)

● Random error (due to chance): deviation from the mean (\bar{X})

Absolute	Relative
$d_{x_i} = \pm (x_i - \bar{X})$	$d_{x_i \text{ rel}} = \frac{\pm d_{x_i}}{\bar{X}} \quad (100)$

(B) Precision of a set of results ($x_1, x_2 \dots x_n$) of an analytical method

● Standard deviation (Gauss theory)

$s = \pm \sqrt{\frac{\sum (x_i - \bar{X})^2}{n - 1}}$

● Relative standard deviation (%)

$\text{r.s.d.} = \frac{\pm s}{\bar{X}}$

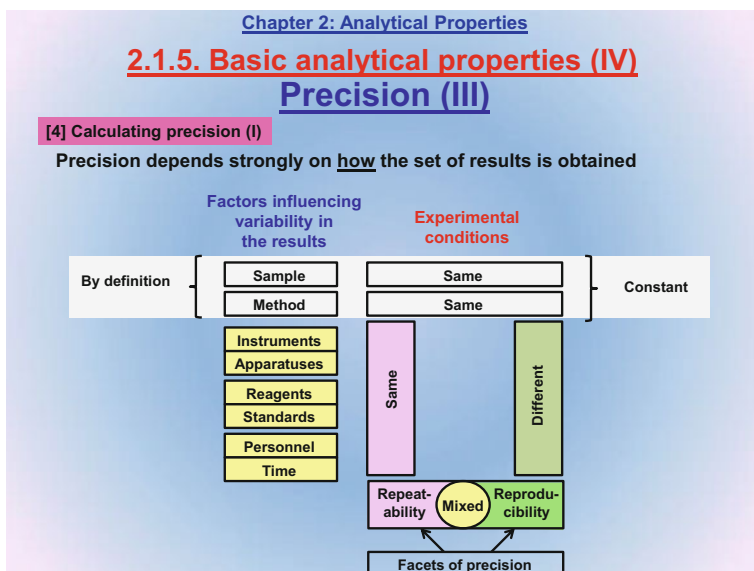
● Coefficient of variation (%)

$\text{CV} = \frac{\pm s}{\bar{X}} \cdot 100$

These are the two parameters typically used to express the degree of precision of an analytical process.

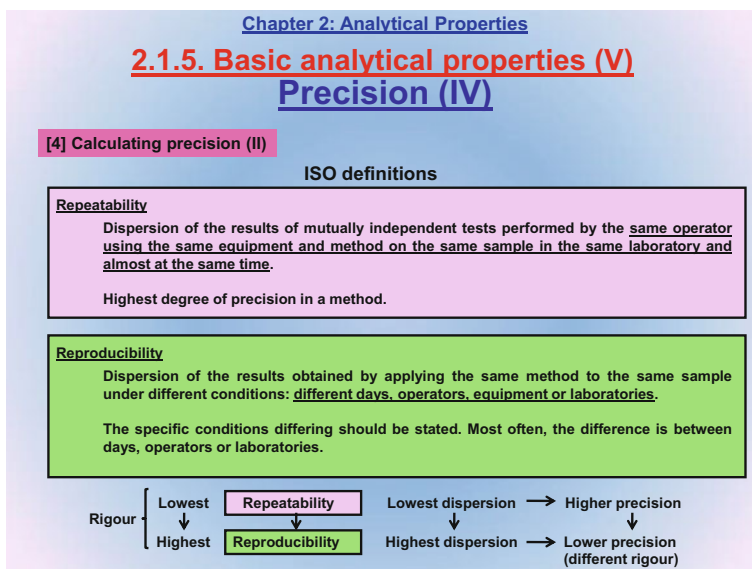
- The *precision of a result* is the individual deviation d_{x_i} of the result from the arithmetic mean for the body of results, \bar{X} , and is expressed as an interval around the result.
- The *precision of a set of results* is its so-called “standard deviation”, which represents an interval around the mean as calculated in the light of the theory of Gauss. The precision of a set of results can also be expressed as the “coefficient of variation”, a parameter ranging from 0 to 1 and a relative measure of the standard deviation with respect to the mean that allows methods to be compared in order to identify the most precise (namely, that with the lowest coefficient of variation).

Slide 2.21



Because precision is a basic property of the analytical process, it depends on how the results are obtained. Although, by definition, the method, sample and experimental conditions are maintained throughout measurements, the instruments, apparatuses, reagents, standards, operators and time need not remain unchanged as well—whether they do depends on the capabilities of the laboratory and its personnel. Precision thus has two facets: repeatability and reproducibility, which are defined in the next slide.

Slide 2.22

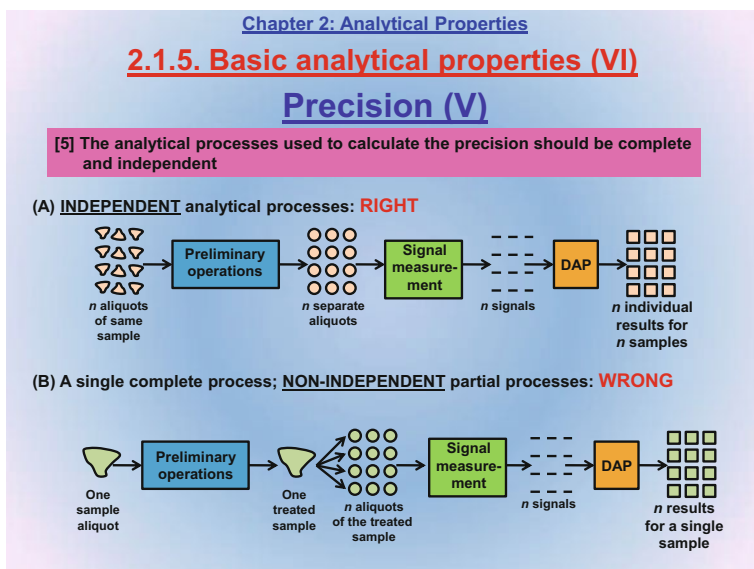


2.22.1. This slide defines the two facets of precision (repeatability and reproducibility) according to the International Organization for Standardization (ISO). Even if the instrument, time and operator differ, tests should be independently performed (that is, each sample aliquot should be individually subjected to the analytical process). The following slide exemplifies a properly conducted analytical process leading to a valid, significant precision value, as opposed to an incorrectly performed process leading to a spurious precision value.

2.22.2. The most salient difference between repeatability and reproducibility is their degree of rigour. Because repeatability is calculated with no change in the experimental conditions, it invariably leads to higher precision values (that is, to lower dispersion in the results) than does reproducibility, which is calculated with some change in the conditions. However, rigour decreases with increasing precision: although reproducibility is less precise than repeatability, it is much more rigorous because the results are reached through different pathways and hence confirmed under different experimental conditions.

In summary, precision cannot be expressed in quantitative terms without regard of the experimental conditions used to obtain the results.

Slide 2.23



One of the essential requirements to be fulfilled in order to properly calculate the precision of an analytical process is that tests should be conducted independently on each sample aliquot. The two situations shown in this slide exemplify the assessment of precision in terms of independence of the tests.

- In *situation A*, each individual aliquot is separately subjected to the analytical process (that is, preliminary operations, measurement and transducing of the analytical signal, and data acquisition and processing) to obtain as many results as aliquots are processed. The way the analyses are conducted ensures that the results will be independent of one another and hence valid for calculating the precision of the method.
- In *situation B*, the whole sample is subjected to the preliminary operations and then split into aliquots for signal measurement, and data acquisition and processing. The output is mutually dependent results because the initial treatment was applied to the sample as a whole. For this reason, the results are useless to calculate the precision of the method because part of it (specifically, its preliminary operations) was applied, only once, to the whole sample rather than to each aliquot separately.

This “trick” is sometimes used to report good precision levels which are actually not so good.

Slide 2.24

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (VII)

Precision (VI)

EXAMPLE 1: Influence of the experimental conditions on the calculation of precision

The precision of an analytical method for determining the total concentration of copper in seawater is assessed. The preliminary operations include preconcentrating the analyte on a chelating ion-exchange resin by passing a volume of 1.0 L of seawater through it. Then, retained copper is eluted with 10 mL of 2 M HCl and an aliquot of the eluate is introduced in an atomic absorption spectrometer to measure an absorbance value that is interpolated in a calibration curve in order to obtain the concentration of copper with provision for the volumes used in the analytical process.

The precision of the method is assessed by determining the analyte six times ($n = 6$) under five different experimental conditions, namely:

- ➔ 1) By preconcentrating 1 L of sample and splitting the eluate into 6 aliquots for measurement by the instrument in order to obtain 6 data and 6 results.
- ➔ 2) By preconcentrating six 1 L aliquots and measuring the analyte in each eluate by using the same facilities, reagents, ion exchanger, instrument and calibration curve on the same day (morning).
- ➔ 3) As in (2), but with the process performed on different days.
- ➔ 4) As in (3), but using different reagents, instruments and operators
- ➔ 5) By having six different laboratories analyse six 1 L aliquots of the same sample with the same method.

This slide exemplifies the contents of the previous three with the calculation of precision under different experimental conditions (five different situations that are solved in the next slide).

Slide 2.25

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (VIII)

Precision (VII)

EXAMPLE 1 (continued from the previous slide)

The table shows the results obtained in the determinations and various statistics for each set of results as calculated as described in the text.

	Study	Results (mg/L)	\bar{X} (mg/L)	s (mg/L)	CV (%)
WRONG	(1)	1.32; 1.31; 1.32; 1.33; 1.30; 1.31	1.31	0.0150	0.80
REPEATABILITY	(2)	1.34; 1.30; 1.28; 1.31; 1.33; 1.29	1.31	0.0232	1.77
REPRODUCIBILITY	(3)	1.28; 1.36; 1.30; 1.27; 1.31; 1.33	1.31	0.0331	2.53
	(4)	1.30; 1.27; 1.40; 1.37; 1.26; 1.30	1.32	0.0560	4.24
	(5)	1.35; 1.45; 1.21; 1.37; 1.30; 1.28	1.33	0.0826	6.21

The best (apparent) precision is that obtained in (1), which was incorrectly planned because the tests were not mutually independent. Precision is expressed as repeatability in (2), and as reproducibility in (3) and (4). Because changes were more marked in (4) than in (3), the former was less precise. The most precise and rigorous study was (5), the interlaboratory study, which led to the highest s and CV values.

This slide completes the example of the previous one with a table of results for each of the five situations additionally showing the precision as standard deviation and coefficient of variation. The latter parameter allows one to compare conditions because it is a relative measure referred to the mean of the results.

The solution for each situation is shown in red. It should be noted that the experimental conditions for the first situation were wrong because aliquots were not analysed in separate tests; as a result, the precision was better but incorrect. Situation 2 has to do with repeatability, whereas situations 3–5 involve reproducibility at different levels of rigour.

Slide 2.26

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (IX)

Precision (VIII)

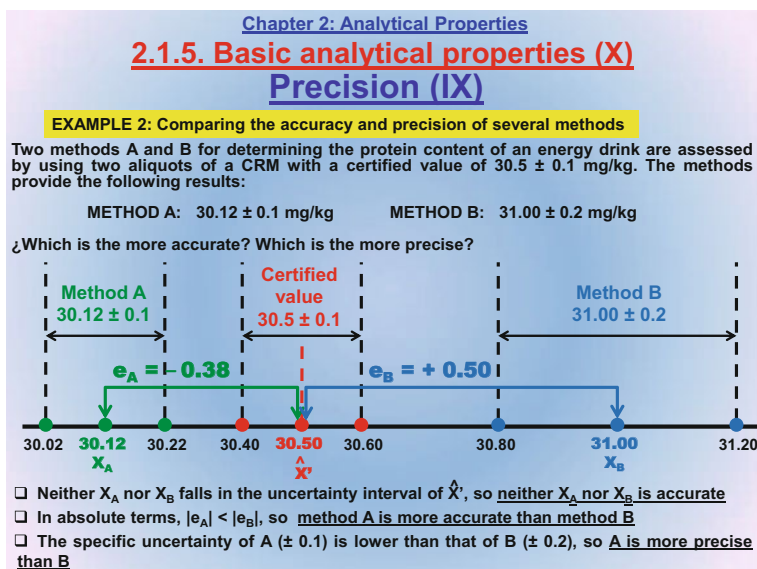
Comparing accuracy and precision

	Accuracy	Precision
Type of analytical property	Capital	Basic
A characteristic of	The results	The analytical process
Mutual dependence	Accuracy is not independent of precision	—
Reference	\hat{x} Value held as true	\bar{x} Average of the data set
Types of errors	Errors proper	Deviations
	Systematic (determinate)	Random (indeterminate)
Relationships between the concepts and their mathematical definitions	Contradictory	Contradictory
Experimental conditions	Identical	Can change. Concepts: - Repeatability - Reproducibility

This slide compares the features of accuracy, a capital property, and precision, a basic property. Their greatest difference is that accuracy is a property of the results and hence directly related to analytical information. As a consequence, it can only be assessed under unchanged conditions. On the other hand, precision is a property of the analytical process and hence dependent on the particular conditions (repeatability and reproducibility).

The references used to calculate and express errors differ, and so do the relationships between the concepts and the parameters used to express them. Also, accuracy makes no sense without precision (that is, the former can never be meaningful without the latter) (see Slides 2.4 and 2.15).

Slide 2.27



2.27.1. This is the solution to an example problem: comparing the accuracy and precision of two methods A and B by using the value for a certified reference material (CRM) and its confidence interval as reference.

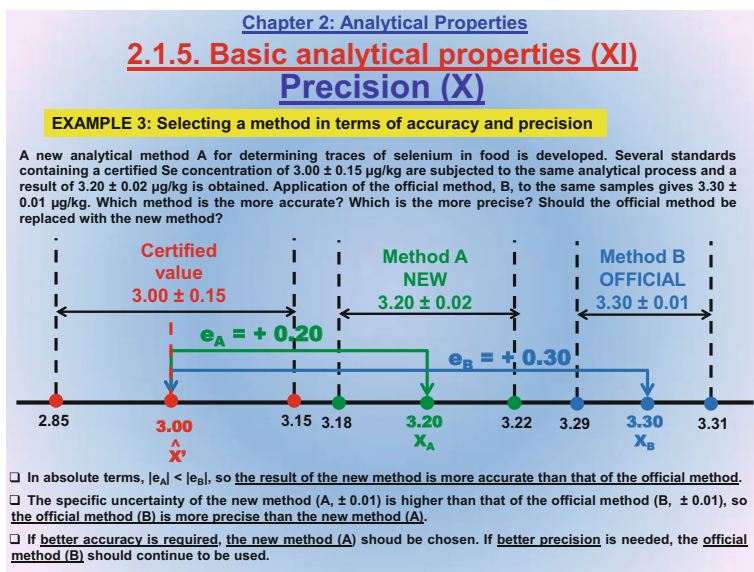
2.27.2. The first step involves placing the results of each method and the value for the CRM together with their confidence intervals in a graph. In order to find whether the results are accurate one must consider the confidence interval for the CRM and for the results of each method. If the results fall within the confidence interval for the CRM, then they will be accurate. If, on the contrary, none of the results falls within the confidence interval, then one must check if the confidence intervals for the methods share any region with that for the CRM. In the example, neither the result for method A (X_A) nor that for method B (X_B) or their respective confidence intervals fall within the confidence interval for the CRM. Therefore, as shown in the slide, neither result is accurate. As can also be seen, the result of method A is subject to a positive error and that of method B to a negative error.

2.27.3. Although neither result is accurate, the two can be compared in order to identify which is closer to the reference value. This entails calculating the absolute error e as the difference between the result of each method and the reference value. As can be seen from the graph, the result of method A is more accurate than that of method B because X_A is closer to the reference value than is X_B (0.3 vs. 0.5).

2.27.4. Identifying the more precise method entails comparing the width of the confidence intervals for the results. Since precision is inversely related to dispersion, the method exhibiting the broader interval (that is, the higher dispersion in its

results) will be the less precise. Because method A has a lower specific uncertainty than method B (0.1 vs. 0.2), the former is more precise than the latter.

Slide 2.28



2.28.1. This is the solution to a problem involving comparing a new analytical method A to an official method B in order to find whether the new method is more accurate and precise. All with regard to the value for a CRM held as reference and its confidence interval.

2.28.2. As in the previous example (Slide 2.27), the results and their confidence intervals are placed in a graph. As can be seen, both methods are subject to a positive error.

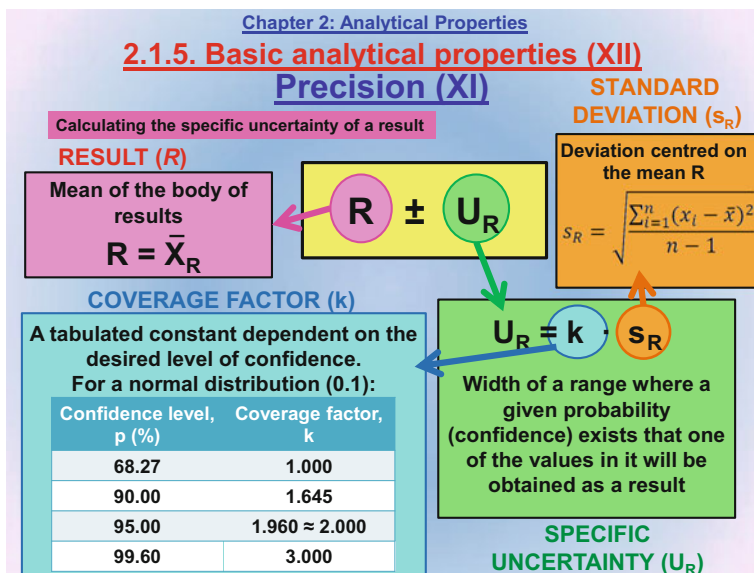
2.28.3. Identifying the method giving the most accurate results entails calculating the absolute error e as the difference between the result and the reference value. The two are compared in terms of absolute value: the result subject to the smaller error will be that falling closer to the reference value and hence the more accurate. Since $0.20 < 0.30$, the new method (A) is more accurate than the official method (B).

2.28.4. Identifying the more precise method entails comparing specific uncertainties. Since precision is inversely proportional to dispersion in the results, the method having the broader interval (that is, the higher dispersion) will be the less precise. The official method (B) is subject to less specific uncertainty than the new method (A) ($0.01 < 0.02$); therefore, the official method is more precise than the new method.

2.28.5. Which method is to be chosen depends on the preferences, conditions and aims in solving the particular analytical problem (Chap. 7). If the problem

requires more accuracy than precision, then the new method is that of choice. Conversely, if the problem requires more precision than accuracy, then the official method is to be preferred.

Slide 2.29



2.29.1. For a result to be correctly expressed, it must be accompanied by a confidence (or uncertainty) interval representing the likelihood of the result of repeating the analytical process falling in that interval with a given degree of confidence (e.g., 95%).

2.29.2. The result, R , should be the average of the n individual results x_i obtained by performing the analytical process n times on n independent aliquots.

2.29.3. The specific uncertainty, U_R , is the interval around the result where a given probability exists that of one of the values in the interval will be obtained when the analytical process is repeated. Mathematically, U_R is the product of a constant k dependent on the degree of confidence of the interval and the standard deviation s_R of a set of n results obtained from the analytical process.

2.29.4. The k values needed to calculate the specific uncertainty are tabulated. The slide shows those for a Gaussian distribution (0.1) and various levels of confidence. Obviously, k increases with increasing confidence level because increasing the probability of the results falling within the interval entails increasing its width. This is exemplified in Slide 2.31.

2.29.5. The standard deviation of the results, s_R , is calculated with the formulae of Slide 2.30; however, s_R must be used in absolute rather than relative form in the expression for the specific uncertainty.

Slide 2.30

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XIII)

Precision (XII)

Expressing a quantitative result: Number of significant figures

SIGNIFICANT FIGURES:

- Digits other than zero (e.g., 7689 → 4 figures)
- Zeros after the decimal point in a number greater than 1 (e.g., 8.00 > 1 → 3 figures)
- Zeros between two digits (e.g., 301 → 3 figures)
- Scientific notation to avoid ambiguity [e.g., 730 (2 or 3 figures?) → $7.3 \cdot 10^2$ → 2 figures]

EXPRESSING A RESULT AND ITS SPECIFIC UNCERTAINTY

Experimental data (x_i)	
1.3	1.4
1.2	1.5
1.6	1.3

SPECIFIC UNCERTAINTY (U_R) (confidence: 95%
k = 2)

Range: $U_R = s_R \times 2 = 0-294...$

s_R = standard deviation

Same number of figures as the result

ROUNDING BY EXCESS

$U_R = \pm 0.3$

RESULT (R)

$R = \bar{X} = 1.3833...$

$R = 1.4 \pm 0.3$

Bound by its specific uncertainty. **ROUNDING**

2.30.1. Properly expressing a result and its specific uncertainty entails using an appropriate number of significant figures. This slide shows the four rules to be obeyed in expressing an analytical result. As can be seen, scientific notation should be used when the results are multiples of a power of ten, whether positive or negative, in order to avoid ambiguity and facilitate interpretation.

2.30.2. In this example, a result and its specific uncertainty at the 95% confidence level are expressed in accordance with the four rules. The tabulated datum for k at the 95% confidence level in Slide 2.29, 2, is used to calculate the specific uncertainty, which is rounded by excess to the same number of significant figures as the tabulated data. The specific uncertainty is then used to calculate the mean of the results in the table, which is rounded to the same number of significant figures as the specific uncertainty (*“the specific uncertainty sets the bounds for the result”*) by applying the usual rounding rules. Finally, the result is given together with its specific uncertainty as shown in the slide.

Slide 2.31

Chapter 2: Analytical Properties
2.1.5. Basic analytical properties (XIV)
Precision (XIII)

EXAMPLE 4: Comparing specific uncertainties according to confidence level

In order to determine the amount of chromium present in wastewater, 8 aliquots of the same sample are subjected to an analytical process that provides the following results, in ppm:

3.25 3.30 3.12 3.32 3.15 3.16 3.20 3.30

Calculate the specific uncertainty at a probability level of 95% and 90%. Compare the two results

Specific uncertainty	
$P_1 = 95\%$	$P_2 = 90\%$
$k_1 = 2.00$	$k_2 = 1.65$
$U_{R1} = 2 \cdot 0.08$ $= \pm 0.16$	$U_{R2} = 1.65 \cdot 0.08$ $= \pm 0.14$
Result 3.23 ± 0.16	Result 3.23 ± 0.14

Mean
 $\bar{X} = R = 3.23 \text{ ppm}$
RESULT

Standard deviation
 $s_R = \pm 0.08 \text{ ppm}$

➔

☐ The specific uncertainty is higher at P = 95% than it is at P = 90%
☐ The result is logical because raising the confidence level entails dealing with a greater number of results and hence with a wider uncertainty interval

2.31.1. The slide shows how to solve an example problem involving calculating the specific uncertainty of a data series at two different confidence levels (95 and 90%).

2.31.2. The data are used to calculate a mean and its standard deviation as expressed in Slide 2.29 and with the number of significant figures required (see Slide 2.30).

2.31.3. The specific uncertainty at each confidence level (95 or 90%) is calculated by using the corresponding k value in the table of Slide 2.29 and expressed with the required number of significant figures, which must coincide with that of the result (R).

2.31.4. As can be seen, the specific uncertainty at the 95% confidence level is higher than that at the 90% level because increasing the probability that the result of the analytical process will fall within the confidence interval entails widening it.

2.1.5.2 Robustness (1 Slide)

Slide 2.32

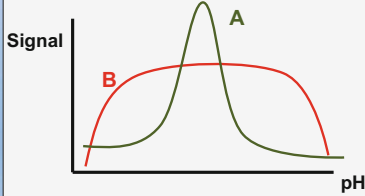
Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XV)

Robustness

- A property of analytical methods and a basis for accuracy
- **Definition**
Resistance to change of the response (result) when an analytical method is independently applied to aliquots of the same sample but under slightly different experimental conditions (pH, temperature, pressure) to introduce alterations
- **Aim**
Identifying the critical experimental conditions for a method to be reliable and transferable
- **Other features**
The result is descriptive
Assessment requires using complex chemometric techniques (univariate and multivariate methods)
Unlike precision, its calculation does not require rigorous application of the same method

Comparing the robustness of two methods A and B in terms of pH



2.32.1. This slide defines robustness and describes its most salient features. Robustness is a basic property of the analytical process ensuring that a method will operate as expected and give quality results, even if the experimental conditions are changed slightly. Robustness provides support for accuracy.

Robustness is an atypical property in that it cannot be expressed quantitatively. Rather, it has to do with “reliability” (the resistance to change of the results by effect of changes in the experimental conditions, which is essential for a method to be reliable and transferable). Robustness is similar to precision but is calculated in a rather different manner.

2.32.2. The example in the box compares the final signals (results) obtained with method A or B depending on the pH at which the analytical process is performed. Note that, because method A is strongly dependent on pH, its results change abruptly with a change in this experimental variable; as a consequence, it is more sensitive to pH changes than method B. By contrast, method B is less markedly dependent on pH, so its results are very similar—virtually identical—even if the pH is altered; as a consequence, it is much more robust than method A.

2.1.5.3 Sensitivity (16 Slides)

Slide 2.33

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XVI)

Sensitivity (I)

● A property of an analytical method and a basis for accuracy

Many complementary definitions

A. The ability to detect and quantify small amounts or concentrations of the analyte

B. The ability to discriminate similar amounts or concentrations of the analyte →

C. **IUPAC**

- A signal/concentration ratio
- Variation of the analytical signal (Δx) with the analyte concentration (Δc) coinciding with the slope of the signal-concentration curve (so-called "calibration curve")

$$S = \frac{\delta_x}{\delta_c} = \frac{\Delta x}{\Delta c}$$

Parameters used to quantify the sensitivity of a method

S Sensitivity (IUPAC)	C_{LOD} Limit of detection	C_{LOQ} Limit of quantification
------------------------------------	---	--

Relationship to sensitivity ... DIRECT INVERSE INVERSE

2-33

This slide shows three complementary definitions of the word “sensitivity”. The first (A) is the most general and obvious; the second (B) is exemplified in the next slide; and the third (C) is IUPAC’s definition, which is dealt with in detail in Slides 2.35–2.37 and in the Questions section.

Sensitivity is a basic analytical property also supporting accuracy and characterizing the analytical process. The sensitivity of a method can be expressed in three different ways, namely: as sensitivity proper (S), and as the limits of detection (LOD) and quantification (LOQ). The former is inversely related to the latter two: the lower is LOD or LOQ, the higher will be S . Only LOD can be used in Qualitative Analysis (Chap. 6), however.

Slide 2.34

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XVII)

Sensitivity (II)

Example of definition B

Assessing the relative sensitivity of three methods A, B and C used to determine the total hydrocarbon content of water samples by analysing two standards with a known content: 0.12 and 0.11 $\mu\text{g/L}$

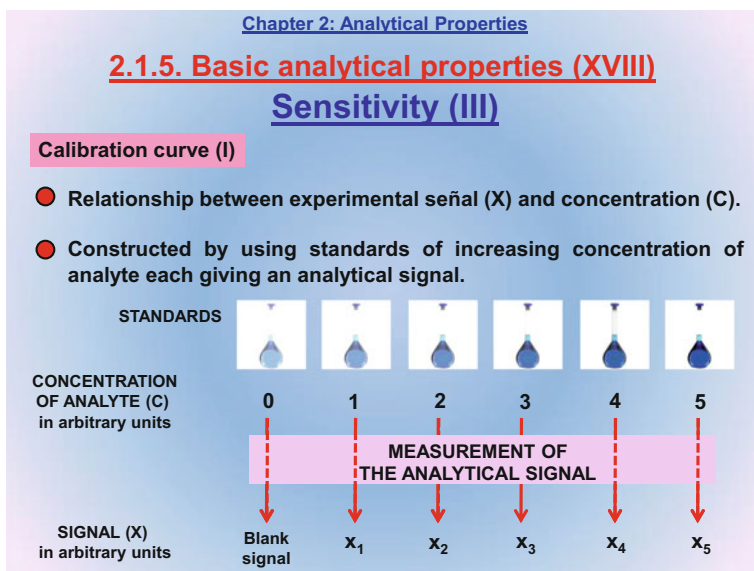
- Method A: Neither sample contains hydrocarbons
- Method B: Both contain the same amount of hydrocarbons (0.11 $\mu\text{g/L}$)
- Method C: Both contain hydrocarbons but in different amounts (0.125 and 0.116 $\mu\text{g/L}$).

Which is the most sensitive (reliable) method?

2.34.1. This is an example illustrating the second definition of sensitivity (B) in the previous slide. A sample of water containing hydrocarbons was analysed with three methods differing in sensitivity that gave different results in the separate determination of the analytes.

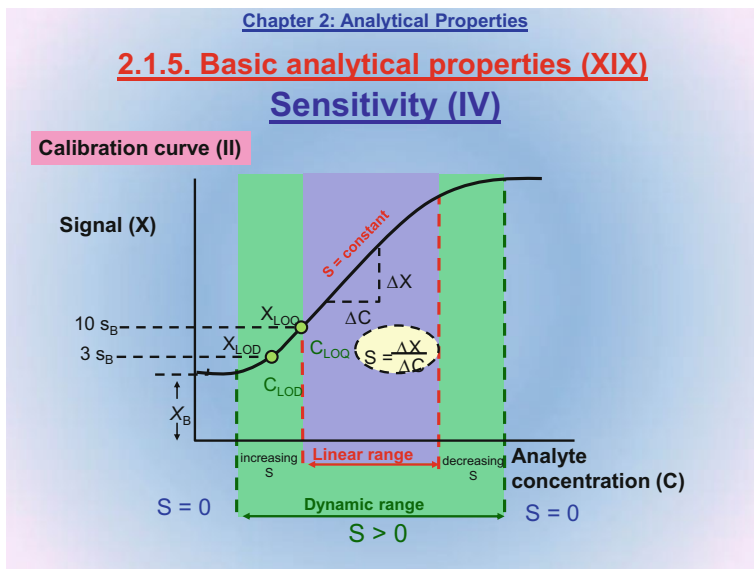
2.34.2. The most reliable method (that is, the most sensitive) will be that best discriminating hydrocarbons in the sample and most accurately quantifying them. Accordingly, method A is not sensitive enough for the intended purpose because it cannot detect the presence of the hydrocarbons. Method B is somewhat more sensitive than method B because it detects the hydrocarbons; however, it cannot discriminate them. Finally, method C is the most sensitive because it can both detect and discriminate (distinguish) them. This is one way of defining sensitivity: the ability of a method to discriminate analytes and determine their amounts (that is, to both detect and quantify the analytes).

Slide 2.35



As per IUPAC's definition, the sensitivity of a method (Slide 2.33) is the signal change per unit analyte concentration, that is, the slope of an analyte signal (X) versus concentration (C) graph. The graph is experimentally constructed by measuring the signals for a series of standards of known concentration including a blank (that is, a sample containing no analyte). The graph (Slide 2.36) exhibits various zones allowing not only the sensitivity, but also other detection-related parameters, to be quantified.

Slide 2.36



2.36.1. Plotting the signal for a standard against the analyte concentration gives a curve such as the one in this slide for the data shown in an arbitrary manner in the previous slide. The smallest possible signal (lower limit of the curve) is that produced by the instrument in response to a blank (a sample containing no analyte) and the outset, x_B , of the curve. The largest possible signal (upper limit of the curve) corresponds to the analyte saturation level, beyond which the instrument cannot detect any greater amounts.

2.36.2. The *dynamic range* is the concentration range where the signal departs from the blank signal (lower limit) and saturation signal (upper limit). The lower limit is called the “limit of detection” (x_{LOD}) because it coincides with the point beyond which the analyte can be distinguished from the blank. It is defined and calculated in Slides 2.40 and 2.42.

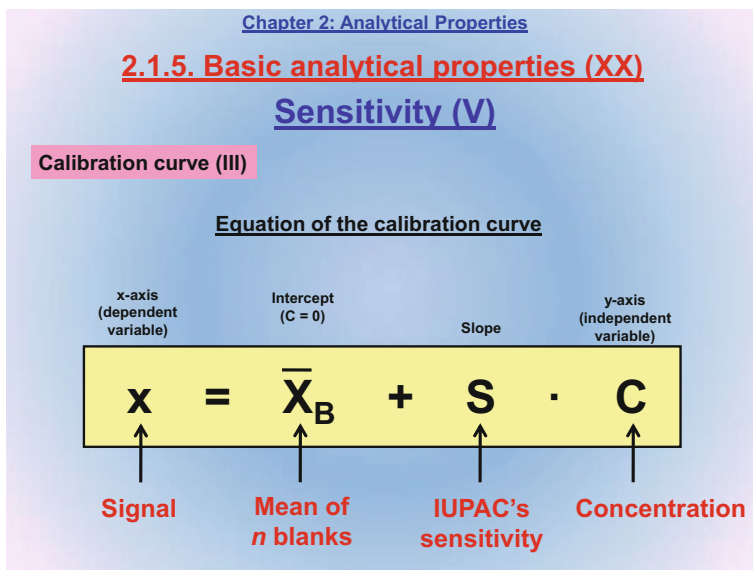
2.36.3. The *linear range* is the concentration range where the signal–concentration (X – C) graph is linear, that is, where the signal varies linearly with the concentration along a straight line—and hence in accordance with the first-order equation in Slide 2.37. The lower limit of this interval is called the “limit of quantification” (x_{LOQ}) because it is the point beyond which the amount of analyte in the sample can be determined from a simple signal–concentration relation. The limit of quantification is defined and calculated in Slides 2.41 and 2.42.

2.36.4. Based on IUPAC’s definition (Slide 2.33), the sensitivity (S) can be calculated as the slope of the signal (X)–concentration (C) curve (Slide 2.33).

At analyte concentrations within the dynamic range, $S > 0$ because the instrument is capable of detecting and discriminating concentration differences, so the

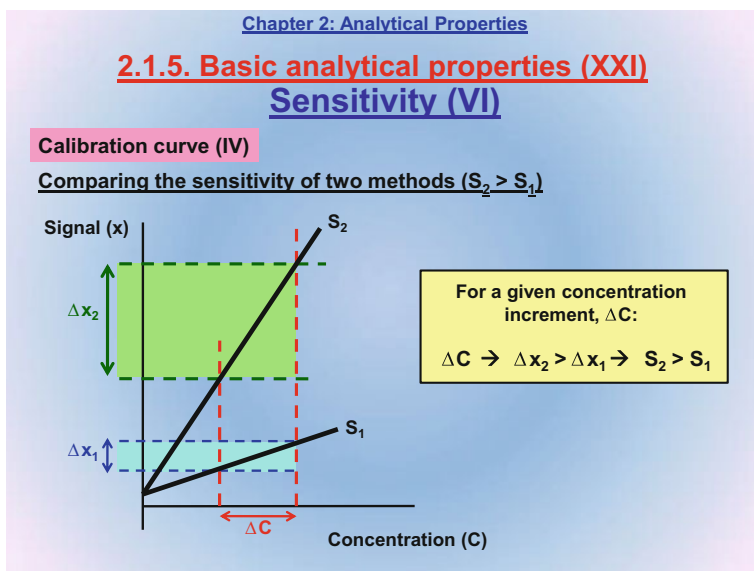
slope of the curve is invariably positive. Within the linear range, the signal changes slightly with the analytical concentration in accordance with a first-order law over the linear range (Slide 2.37); hence, the slope and the sensitivity are constant and equivalent. Finally, at concentrations outside the dynamic range—and hence also outside the linear range—the signal does not change with the analyte concentration because the instrument saturates in response to a sample with an exceedingly high concentration; as a result, the slope of the curve is constant and $S = 0$.

Slide 2.37



The calibration curve (Slide 2.36) is often a straight line conforming to a first-order equation as in this slide. Although at high dilutions the variation of the analytical signal with the analyte concentration is not a straight line, the curve can be approximated to one provided no concentrations near that of the blank are used. With this provision, the calibration curve can be defined in terms of a first-order equation where the intercept coincides with the blank signal (or the average signal if more than one blank is used) and the slope coincides with the sensitivity of the method as defined by IUPAC (Slide 2.33). This slide shows the general expression of the calibration curve and states the meaning of each parameter in it.

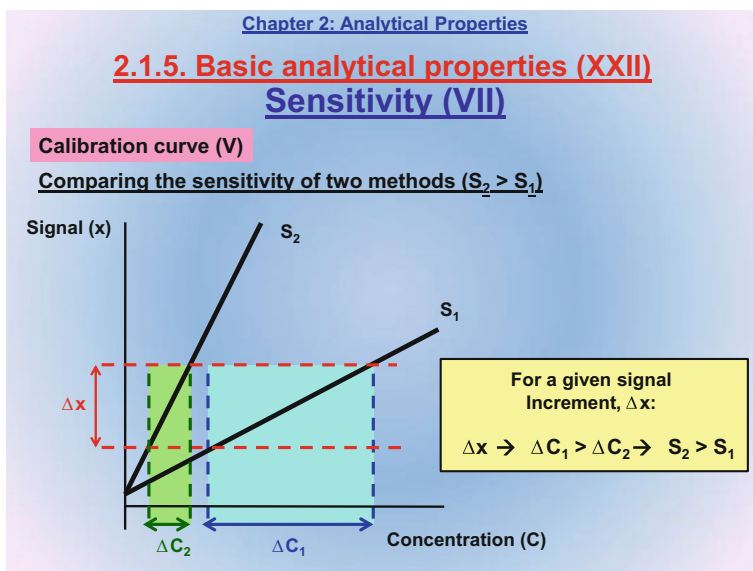
Slide 2.38



This slide and the next compare the sensitivity of two methods 1 and 2 according to two different criteria.

For an *identical concentration range*, the sensitivity increases with increasing change in the signal over the range because a given concentration range will lead to a more marked change in the signal. Because method 2 exhibits a greater signal change over the same concentration range, it is more sensitive than method 1. This is confirmed by IUPAC's definition of sensitivity (Slides 2.33 and 2.37): the calibration curve for method 2 has a higher slope than that for method 1.

Slide 2.39



In a given *signal range*, the sensitivity of a method will increase with decreasing concentration change over the range because a small change in analyte concentration will result in a more marked change in signal. In this example, method 2 is more sensitive because concentration changes are smaller than in method 1. The same conclusion is reached by comparing their sensitivity as defined by IUPAC (Slides 2.33 and 2.37): the slope of the calibration curve for method 2 is higher than that for method 1.

Slide 2.40

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXIII)

Sensitivity (VIII)

Limit of detection

Definition

- The analyte concentration C_{LOD} giving a signal x_{LOD} that can be clearly distinguished from that of an analytical blank
 \bar{x}_B : mean of n blank signals, s_B : standard deviation of n blank signals
- Mathematical approximation *by convention*

Definition $x_{\text{LOD}} = \bar{x}_B + 3 \cdot s_B$

Calibration curve $x_{\text{LOD}} = \bar{x}_B + S \cdot C_{\text{LOD}}$
signal intercept slope concentration

(1)

(2)

Relationship to IUPAC's sensitivity (S)

(1) = (2) $\bar{x}_B + 3 \cdot s_B = \bar{x}_B + S \cdot C_{\text{LOD}}$ \longrightarrow

Relationship between sensitivity concepts

$$C_{\text{LOD}} = \frac{3 \cdot s_B}{S}$$

- Its computation requires examining the blank signals and calculating the mean, \bar{x}_B , and its standard deviation, s_B

This slide defines *limit of detection* (LOD) and relates it to the calibration curve and to sensitivity as defined by IUPAC (Slide 2.33).

The limit of detection is the lower limit of the dynamic range (Slide 2.36), that is, the point where the sensitivity departs from zero to a positive value. Above LOD, the analyte can be discriminated from the blank (that is, the instrument becomes “sensitive” to the analyte). As can be seen, LOD is computed from the signal associated to the concentration in question and used to relate the analyte concentration to the sensitivity of the method via the equation of the calibration curve.

Slide 2.41

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXIV)

Sensitivity (IX)

Limit of quantification

Definition

- The analyte concentration C_{LOQ} giving a signal x_{LOQ} that coincides with the lower limit of the calibration curve
- Mathematical approximation *by convention*

Definition $x_{LOQ} = \bar{X}_B + 10 \cdot s_B$ (1)

Calibration curve $x_{LOQ} = \bar{X}_B + S \cdot C_{LOQ}$ (2)

Relationship between sensitivity concepts

Relationship to IUPAC's sensitivity (S)

(1) = (2) $\bar{X}_B + 10 \cdot s_B = \bar{X}_B + S \cdot C_{LOQ} \longrightarrow C_{LC} = \frac{10 \cdot s_B}{S}$

- Its computation requires examining the blank signals and calculating the mean, \bar{X}_B , and its standard deviation, s_B

This slide defines *limit of quantification* (LOQ) and relates it to the calibration curve and to sensitivity as defined by IUPAC (Slide 2.33).

The limit of quantification is the lower limit of the linear range (Slide 2.36), that is, the point where the sensitivity becomes constant and the signal depends linearly on the concentration. Above LOQ, the instrument can discriminate between different amounts (concentrations) of analyte (or, in other words, the analyte is “visible” to the instrument and can be quantified with it). LOQ is computed from the signal associated to the concentration concerned and can be used to relate the analyte concentration to the sensitivity via the equation of the calibration curve.

It should be noted that the definition by convention of the limits of detection (x_{LOD} , Slide 2.40) and quantification (x_{LOQ}) requires the prior knowledge of the blank signal (the average) and its standard deviation (s_B) as the limits are assumed to be 3 and 10 times greater, respectively, than the blank signal (see the definition of Slide 2.40 and that in this slide above).

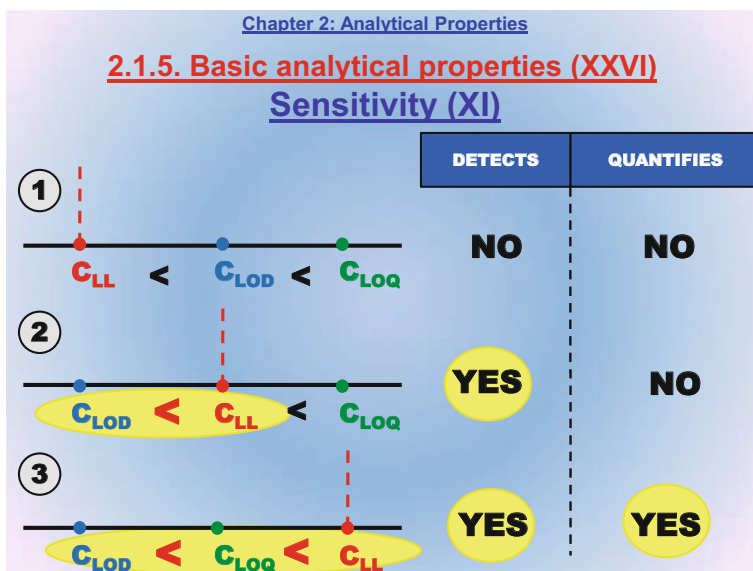
Slide 2.42

Chapter 2: Analytical Properties			
2.1.5. Basic analytical properties (XXV)			
Sensitivity (X)			
LIMIT	SYMBOL	DEFINITION	MATHEMATICAL FORMULA
LIMIT OF DETECTION	$C_{LOD}^{(*)}$	<ul style="list-style-type: none"> Lowest concentration giving a signal different from that for the blank Lower limit of the dynamic range 	$C_{LOD} = \frac{3 \cdot s_B}{S}$
LIMIT OF QUANTIFICATION	$C_{LOQ}^{(*)}$	<ul style="list-style-type: none"> Lowest concentration that can be quantified Lower limit of the linear range 	$C_{LOQ} = \frac{10 \cdot s_B}{S}$
LEGAL LIMIT	C_{LL}	A threshold bounding two concentration regions (e.g., toxic and non-toxic)	Imposed by the client or an organization
(*) The ratio of the limits of detection and quantification is			$\frac{C_{LOQ}}{C_{LOD}} = 3.33...$

This slide summarizes the limits defined in the previous two and introduces a new concept: the legal limit (C_{LL}), which is a function of the particular analytical problem addressed and of the client or organization imposing it (see Slides 7.8 and 7.15). This is possibly the most important limit because it is used as a reference to validate analytical methods and confirm whether the limits of detection and quantification are adequate to solve the particular analytical problem.

The slide also shows the mathematical relation between the concentrations at the limits of detection (C_{LOD}) and quantification (C_{LOQ}).

Slide 2.43



2.43.1. This slide illustrates three different situations regarding the limits defined in the previous one by comparing LOD and LOQ with the legal limit on a scale of increasing analyte concentrations in each.

2.43.2. In *situation 1*, LOD and LOQ are both greater than the legal limit. Because the instrument can only detect and quantify the analyte at concentrations above c_{LOD} and c_{LOQ} , respectively, the method is useful to neither detect nor quantify the analyte. In fact, the legal limit falls below both limits, so concentrations equal or similar to c_{LL} cannot be “seen” or quantified with the method in question.

2.43.3. In *situation 2*, the legal limit is higher than LOD but lower than LOQ. As a result, the method can only be used to detect the analyte ($c_{LOD} < c_{LL}$), that is, it allows the analyte to be identified but cannot be used to determine the amount present in the sample.

2.43.4. In *situation 3*, LOD and LOQ are both lower than the legal limit. As a result, the method can be used to both detect and quantify the analyte ($c_{LOD} < c_{LL}$ and $c_{LOQ} < c_{LL}$), that is, to identify it and to know the amount present in the sample.

Slide 2.44

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXVII)

Sensitivity (XII)

EXAMPLE 5.1: Solving sensitivity and precision problems

An analytical method for determining copper traces in feed is characterized by performing the following experiments:

A) Standard samples containing increasing concentrations of the analyte are subjected to the analytical process and the following results obtained:

[Cu²⁺] (ppb)	0.0	1.0	2.0	3.0	4.0	5.0
Signal (AU)	0.005	0.050	0.102	0.149	0.201	0.250

B) Five aliquots of a standard with a certified analyte concentration of 3.30 ± 0.1 ppb are subjected to the analytical process and the following results, in ppb, obtained: 3.40, 3.39, 3.50, 3.27 and 3.35.

- A provides the calibration curve, whose slope will be the sensitivity (S)
- B provides the precision of the method and the accuracy of the mean result

2.44.1. This problem illustrates the concepts behind the basic analytical properties precision (Slide 2.19) and sensitivity (Slide 2.33).

2.44.2. Section A shows the measured absorbance at the copper concentration in each standard, which can be used to construct a signal (AU) versus concentration (ppb) calibration curve in order to calculate the sensitivity of the method according to IUPAC's definition (Slide 2.33).

2.44.3. Section B shows the results obtained by subjecting a certified reference material five times to the analytical process, which can be used to assess the precision (from 5 results) and the accuracy of the result (by comparison with the certified value).

Slides 2.45–2.49 answer several questions arising from this example.

Slide 2.45

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXVIII)

Sensitivity (XIII)

EXAMPLE 5.2: Solving sensitivity and precision problems

▫ A gives the calibration curve, whose slope is the sensitivity (S)

[Cu²⁺] (ppb)	0.0	1.0	2.0	3.0	4.0	5.0
Signal (AU)	0.005	0.050	0.102	0.149	0.201	0.250

$$S = \frac{\Delta \text{Signal (X)}}{\Delta \text{Concentration (C)}} = \frac{(0.050 - 0.005) \text{ AU}}{(1.0 - 0.0) \text{ ppb}} = 0.045 \text{ AU} \cdot \text{ppb}^{-1}$$

▫ B gives the precision of the method and the accuracy of the mean result

Results for the CRM
 3.40 3.39
 3.50 3.27
 3.35

$\bar{X} = 3.38 \text{ ppb}$
 $R \text{ (certified)} = 3.30 \text{ ppb}$
 $s_x = \pm 0.08 \text{ ppb}$

$e = (3.38 - 3.30) \text{ ppb}$
 $= + 0.08 \text{ ppb (positive)}$

2.45.1. The data in the table of Section A in the previous slide can be used to calculate the sensitivity of the method according to IUPAC (Slide 2.33), that is, as the ratio of a signal change to a concentration change.

2.45.2. For example, the two data pairs highlighted in the table can be computed to calculate the sensitivity, S , in $\text{AU} \cdot \text{ppb}^{-1}$. Using other data pairs leads to very similar results.

The most accurate way of calculating the sensitivity is by plotting the data in the table to construct a regression curve. Although this procedure is simple and provides an acceptable solution, it is advisable to use two or three more pairs in order to check that the differences are small enough.

2.45.3. The five results obtained by subjecting the certified reference material to the analytical process, and its certified value, can be used to calculate the precision of the method and the accuracy of the result.

Since no confidence level is stated, the specific uncertainty (Slides 2.7 and 2.29) is assumed to coincide with the standard deviation of the method, which is taken to be its precision

2.45.4. The standard deviation can be easily calculated from the equation in Slide 2.20 and the accuracy from the absolute error (see Slide 2.14). The results are expressed in accordance with rules for the number of significant figures in Slide 2.30.

Slide 2.46

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXIX)

Sensitivity (XIV)

EXAMPLE 5.3: Solving sensitivity and precision problems

a) What is the blank signal? In what units should it be expressed?

[Cu²⁺] (ppb)	0.0	1.0	2.0	3.0	4.0	5.0
Signal (AU)	0.005	0.050	0.102	0.149	0.201	0.250

$X = X_B + S \cdot C$

Solving for the unknown

↓

$S = 0.045 \text{ AU} \cdot \text{ppb}^{-1}$
(obtained from A)

$$X_B = X - S \cdot C = (0.005 - 0.045 \cdot 0) \text{ AU}$$

$$X_B = 0.005 \text{ AU}$$

2.46.1. The sensitivity, precision and accuracy values calculated in the previous slide can be used to solve the different parts of the problem. Part (a) can be easily solved by using the equation for the calibration curve in Slide 2.37.

2.46.2. The calibration curve allows one to determine the sensitivity, S , which was calculated in the previous slide. The table gives the average of the blanks—a single value here because only one blank was analysed—and the blank concentration.

2.46.3. The data are substituted into the equation and the equation is solved for the unknown. By definition (Slide 2.35), the analyte concentration C in the blank is zero; therefore, the sensitivity, S , is also zero and the blank signal corresponds to the tabulated signal.

Again, the blank signal can be more accurately determined by constructing a regression curve from the tabulated data and calculating the intercept (that is, the signal at a zero concentration). However, the straightforward, approximate procedure used here suffices to obtain an acceptable value.

Slide 2.47

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXX)

Sensitivity (XV)

EXAMPLE 5.4: Solving sensitivity and precision problems

b) What is the signal corresponding to the certified copper concentration in he standard?

[Cu²⁺] (ppb)	0.0	1.0	2.0	3.0	4.0	5.0
Signal (AU)	0.005	0.050	0.102	0.149	0.201	0.250

1.0 ppb \longrightarrow 0.050 AU
 R (certified) = 3.30 ppb \longrightarrow X (certified)

$$X \text{ (certified)} = \frac{0.050 \text{ AU}}{1.0 \text{ ppb}} \cdot 3.30 \text{ ppb} = \mathbf{0.165 \text{ AU}}$$

2.47.1. Part (b) of the problem requires determining the signal that would be produced by the certified concentration if the analytical process were applied to the CRM in order to measure the absorbance.

2.47.2. The signal, in AU, for the certified samples can be easily computed from the certified concentration and a couple of tabulated values.

Again, the result is only approximate and could be more accurately obtained by substituting the certified concentration in the equation of the regression curve, established from the slope (S) and intercept (blank average) of the curve.

Slide 2.48

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXXI)

Sensitivity (XVI)

EXAMPLE 5.5: Solving sensitivity and precision problems

c) Can the precision of the method be calculated? Why? What is it?

◦ It can because a set of results obtained by analysing a CRM is available. It corresponds to $s_x = \pm 0.083$ ppb, calculated in B)

3.40	3.39
3.50	3.27
3.35	

➔

$s_x = \pm 0.08 \text{ ppb}$

d) Can the accuracy of the mean result, \bar{X} , be calculated? Why? What is it?

◦ It can because the certified value for the standard used is available. The mean result is subject to a positive error $e = + 0.082$ as calculated in B)

$\bar{X} = 3.38 \text{ ppb}$ $R \text{ (certified)} = 3.30 \text{ ppb}$
--

➔

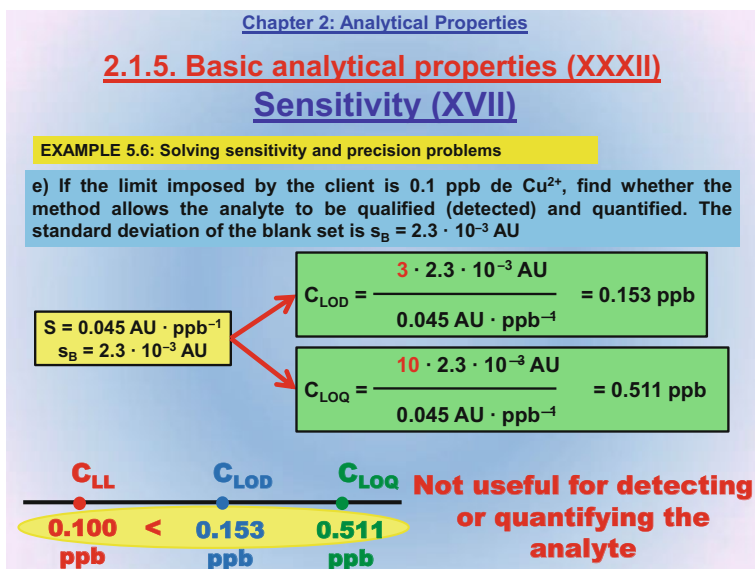
$e = (3.38 - 3.30) \text{ ppb}$
 $= + 0.08 \text{ (positive)}$

2.48.1. The solution to Part (c) of the problem is the precision of the method as calculated in Slide 2.45, B. Here, the precision is assumed to be identical with the standard deviation for the body of results obtained by analysing a certified reference material (CRM). Determining the specific uncertainty at a given confidence level requires using the procedures described in Slides 2.29 and 2.31.

It should be noted that the precision for the blanks cannot be extrapolated to the method but can be used as an approximation.

2.48.2. The solution to Part (d) of the problem is the absolute error as calculated in Slide 2.45, B.

Slide 2.49



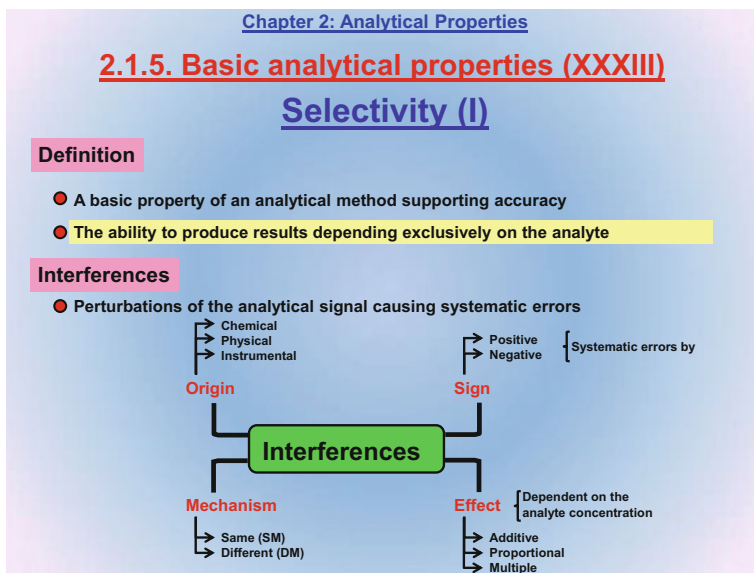
2.49.1. Part (e) of the problem involves validating the method for a given legal limit provided the sensitivity is known and the standard deviation for a set of blanks given.

2.49.2. Validating the method requires calculating the concentrations corresponding to the limits of detection and quantification from the equations in Slide 2.42.

2.49.3. Once calculated, the three limits are plotted on a scale of increasing concentrations of analyte. A comparison with the different cases illustrated in Slide 2.43 reveals that the method cannot be used detect or quantify the analyte, so it is useless for the analytical problem posed by the client's needs.

2.1.5.4 Selectivity (4 Slides)

Slide 2.50



The slide defines another basic analytical property: selectivity. An analytical method is said to be selective when it gives signals and results exclusively dependent on the target analyte (that is, when it only responds to the presence of the analyte).

An ideal method is one that is unique for a specific analyte. In practice, however, this ideal situation is precluded by interferences. In this context, an interference is anything preventing a method from being exclusively selective for an analyte (that is, something altering the analyte signal and leading to systematic errors in the result). This slide depicts various types of interferences with analytical methods.

Slide 2.51

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXXIV)

Selectivity (II)

Example of selectivity (1). Interferences with the photometric determination of Fe in wine

$$\text{Fe}^{3+} + \text{reductant} \longrightarrow \text{Fe}^{2+}$$

$$\text{Fe}^{2+} + 3 \text{ L} \longrightarrow \text{FeL}_3^{2+}$$

Coloured
chelate

The method involves adding a reductant such as ascorbic acid or hydroxylamine to an aliquot of wine in order to reduce Fe^{3+} to Fe^{2+} , adjusting the pH by adding a buffer and adding a ligand such as 1,10-phenanthroline to form a strongly coloured soluble chelate (FeL_3^{2+}) an aliquot of which is used to measure the absorbance at 510 nm.

This colorimetric method for determining the amount of iron in wines involves a preliminary operation by which Fe^{3+} is reduced to Fe^{2+} ; then, ferrous ion forms a coloured chelate L that is detected and quantified with a photometer.

Slide 2.52

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXXV)

Selectivity (III)

Example of selectivity (2). Interferences with the photometric determination of Fe in wine

	Source	Type of interference according to			
		Origin	Mechanism	Sign	Effect
1	Base colour of the wine	Chemical	Same	Positive	Additive
2	Presence of Cu^{2+} ions forming a coloured chelate (CuL^+)	Chemical	Same	Positive	Additive
3	Presence of F^- ions forming colourless chelates (FeF^{2+}) with the analyte and competing with the analytical reaction	Chemical	Different	Negative	Proportional

The determination of Fe^{2+} in wine by formation of a coloured chelate (Slide 2.51) may be interfered with by three different factors:

- (1) The typical colour of red wine, which may increase the absorbance readings of the photometer and lead to positive errors by effect of the instrument measuring a *colour excess* (e.g., one suggesting the presence of tannins in red wine). Although chemical in nature, this phenomenon arises from the presence of certain substances in the wine rather than from a chemical reaction (chelation) of Fe^{2+} or other ions in it (via a different mechanism).
- (2) The formation of coloured chelates with Cu^{2+} resulting from an unwanted reaction of the ligand with Cu^{2+} ions in the wine may be a source of interference if the cuprous chelates are visible at the measured wavelength and lead to a positive error from a *colour excess*. This interference is of chemical nature and arises from the same mechanism used to determine Fe^{2+} : the formation of coloured chelates.
- (3) The formation of colourless chelates of Fe^{2+} with fluoride ions prevents all ferrous ion from being chelated by the ligand (L) and becoming “visible” to the photometer. This leads to a negative error (“*a colour deficiency*”). This interference is also chemical in nature and arises from the same mechanism used to determine the analyte: the formation of coloured chelates.

Slide 2.53

Chapter 2: Analytical Properties

2.1.5. Basic analytical properties (XXXVI)

Selectivity (IV)

Parameters used to measure selectivity

● **Maximum tolerated ratio** (for each potential interferent)
The concentration ratio of interferent (C_{int}) to analyte (C_{anal}) causing a positive or negative error that leads to a result falling outside the limits of the interference-free result with its uncertainty ($R \pm U_R$):

$$(TR)_{\text{max}} = \frac{C_{\text{interferent}}}{C_{\text{analyte}}}$$

A slightly higher concentration of interferent, C_{int} , will cause a positive or negative perturbation

● **Other parameters:**

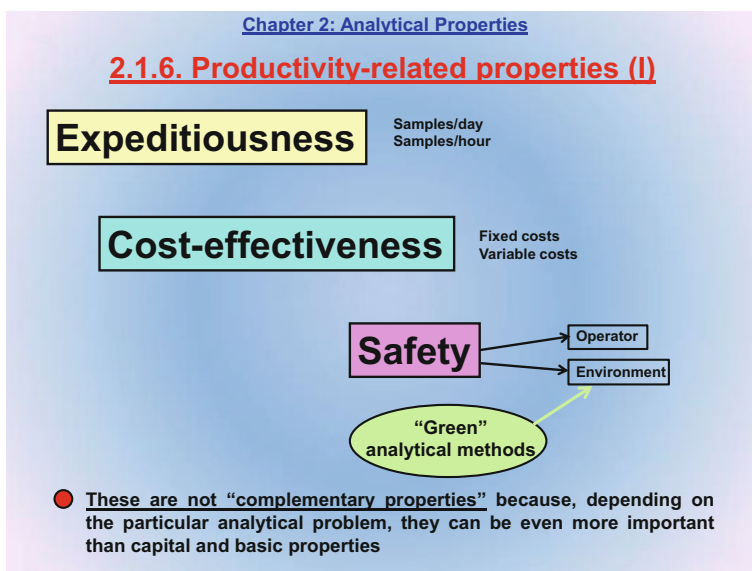
- Sensitivity ratio
- Selectivity factor
- Kaiser's parameter

These are different ways of expressing the selectivity of an analytical process or method.

- The *maximum tolerated ratio* (TR_{\max}) is the interferent-to-analyte concentration ratio giving a result coinciding with the lower or upper limit of the uncertainty interval for a result obtained in the absence of interferences. As a consequence, in the presence of the same amount of analyte, a greater amount of interferent will cause the results to depart markedly in either direction from the ideal result in the absence of interferences and to fall outside the uncertainty interval.
- The *sensitivity ratio* is the analyte-to-interferent sensitivity ratio. The more sensitive to the analyte an instrument is, the higher will be the ratio and the selectivity for the analyte.
- The *selectivity factor* is the TR_{\max} ratio for two methods used to determine the same analyte in the presence of the same interferent. This factor is used to compare methods in terms of selectivity.
- *Kaiser's selectivity parameter* is defined in terms of a complex matrix containing the sensitivity for each analyte to be determined. This parameter is used with complex samples containing more than one target analyte.

2.1.6 Productivity-Related Analytical Properties (2 Slides)

Slide 2.54



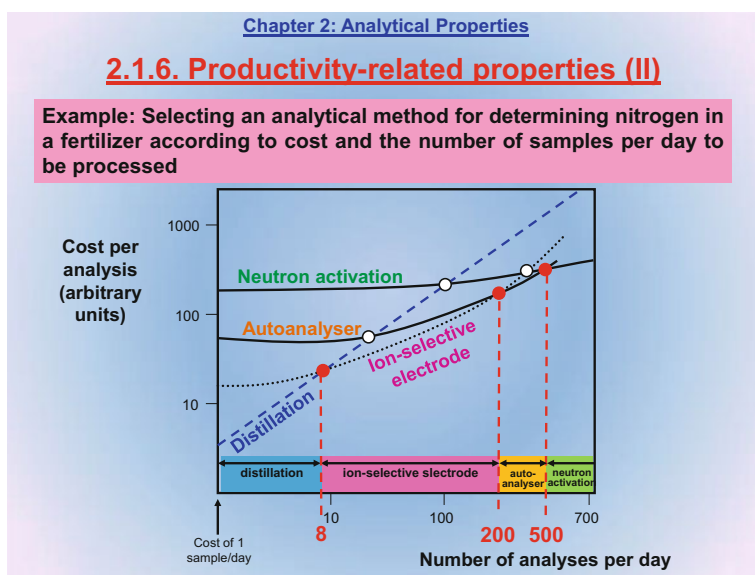
2.54.1. Productivity-related analytical properties are those relating to the development of the analytical process, and to the operators and laboratory

performing it. This slide shows the most salient of all: expeditiousness, cost-effectiveness and personnel-related factors. Expeditiousness, cost-effectiveness and personnel-related factors are related to sample analysis time, cost per analysis and safety (or risks) in the analytical process, respectively.

Although productivity-related properties are at the bottom of the hierarchy of analytical properties in Slide 2.4, they can be crucial with a view to properly solving an analytical problem and even more important than capital and basic properties. The next section of this chapter (2.1.7) is devoted to their integration with capital and basic properties, and to the need to favour some over others depending on the particular analytical problem.

2.54.2. At present, the productivity-related property “environmental safety” is being boosted by developing *green analytical methods*, that is, non-polluting methods causing no harm to the environment (see Slide 9.26).

Slide 2.55



2.55.1. This slide exemplifies the selection of an analytical method in terms of throughput and cost. Four different methods are represented on a log–log scale of cost versus number of analyses per day. Each method exhibits a different pattern of cost growth that is linear in the distillation method but curved to a different extent in those using the ion-selective electrode, autoanalyser or neutron activation instrument.

2.55.2. The most inexpensive method for a workload of less than 8 analysis per day is distillation. For more than 8, the curve for distillation intersects that for the ion-selective electrode, which becomes the more economical choice. Therefore,

either method is cost-effective for 8 analyses per day but the electrode is to be preferred for a higher throughput.

2.55.3. The ion-selective electrode is the best choice for 8–200 analyses per day. At 200, however, its curve intersects that for the autoanalyser, which thus becomes more cost-effective.

2.55.4. The autoanalyser is to be preferred for a daily workload of 200–500 analyses. However, at 500 its curve intersects that of the neutron activation instrument. Consequently, the latter is the most cost-effective choice for more than 500 analyses per day.

2.1.7 Relationships Among Analytical Properties (6 Slides)

Slide 2.56

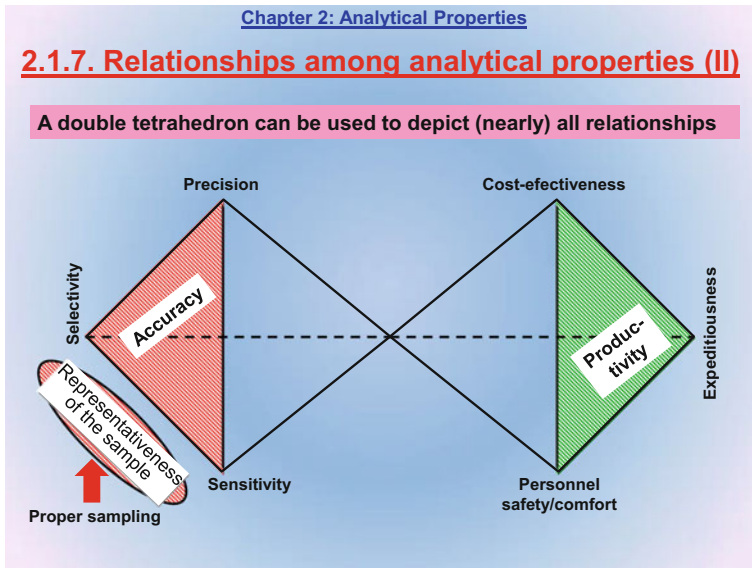
Chapter 2: Analytical Properties

2.1.7. Relationships among analytical properties (I)

- Should be dealt with jointly (holistically)
- A crucial point: their mutual relationships can be as important as or even more so than the properties themselves
- Types of relationships:
 - [1] Foundation: Capital properties are based on basic properties
 - [2] Hierarchical: Relative significance according to problem
 - [3] Contradictory: Increasing a property decreases others
 - [4] Complementary: Increasing a property increases others

The mutual dependence and relationships among analytical properties probably constitute one of the most important topics of this chapter. This slide shows various ways of associating and comparing the properties (namely, foundation, hierarchical, contradictory and complementary relationships). The relationships are illustrated in the next five slides.

Slide 2.57

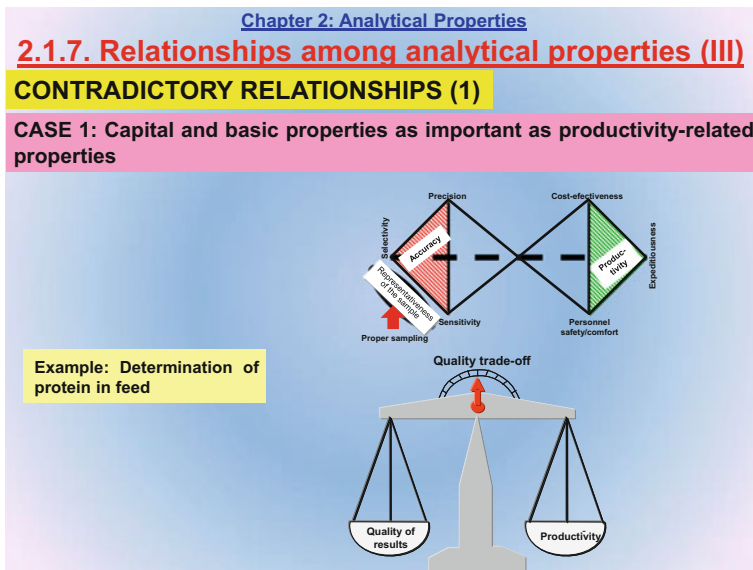


Virtually all possible relationships between the three types of analytical properties (capital, basic and productivity-related) can be depicted by connecting two tetrahedra via a common apex.

- The basic properties define and support the capital property accuracy in the tetrahedron on the left. Representativeness falls outside the tetrahedron because it supports proper sampling.
- The productivity-related properties define productivity and are in the tetrahedron on the right. “Personnel safety/comfort” is equivalent to “safety” in Slide 2.54.

Depicting analytical properties in tetrahedra facilitates relating sensitivity and selectivity or sensitivity and precision (Slide 2.61), for example. The apices in each tetrahedron can be connected to each of the apices in the other to establish a variety of relationships. Thus, accuracy can be related to expeditioness (Slides 2.59 and 2.60), precision and accuracy to cost-effectiveness, and selectivity to safety, for example.

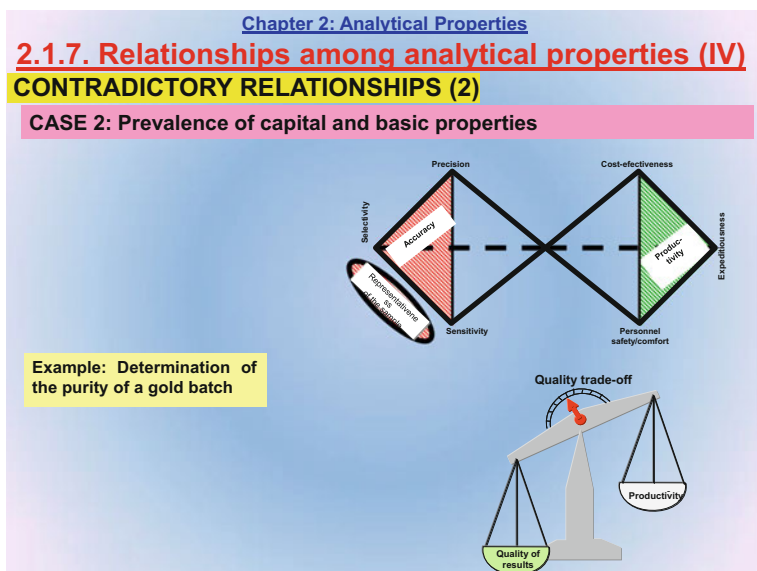
Slide 2.58



This slide and the next two illustrate contradictory relationships of capital and basic analytical properties to productivity-related properties. Which property in each pair is to be favoured depends on the particular information requirements and analytical process (see Chap. 7).

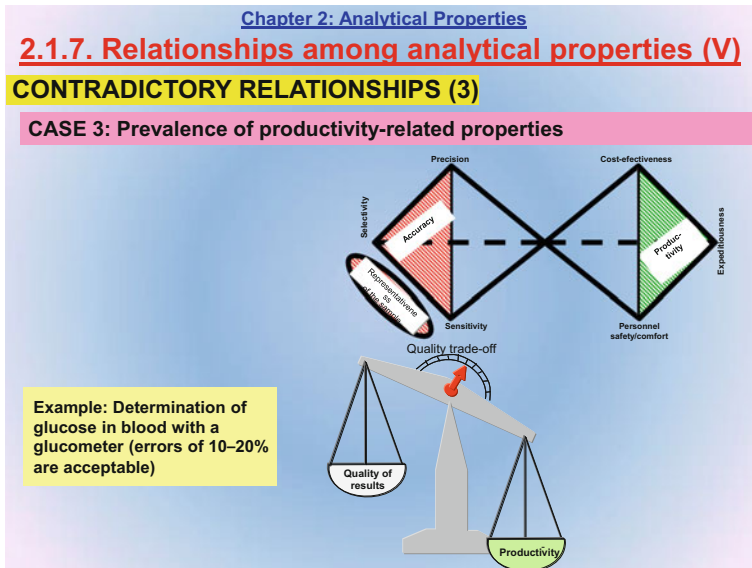
This slide depicts a situation where productivity-related properties are as important as basic and capital properties. The example involves the determination of protein in feed. This determination is subject to no time pressure because feed does not deteriorate easily with time. Also, its analysis is fairly inexpensive and hazard-free, and requires no specially high accuracy, precision or representativeness—rather, it is intended to provide information for rating the product in terms of quality. Therefore, all types of properties are similarly important here.

Slide 2.59



This slide illustrates the second type of contradictory relationship of capital and basic properties to productivity-related properties with a case where the former two must be favoured over the latter: increased accuracy and precision are sought even at the expense of slower, more expensive or even more complicated—and hazardous—analyses. The situation is illustrated with the determination of the purity of a gold batch. On the gold market, each decimal figure in the result counts because it can lead to substantial gains or losses of money. This calls for especially accurate and precise measurements even if making them requires investing more time or money. Therefore, capital and basic properties are favoured over productivity-related properties.

Slide 2.60



This slide presents the last example of a contradictory relationship of the capital and basic properties to productivity-related properties. In this case, the latter (expeditiousness, cost-effectiveness and personnel-related factors) are favoured over the former two (accuracy and precision). The example is the determination of glucose in blood with a portable meter. The portability and ease of operation of the meter, and the expeditiousness of the measurement method, allow the operator to know the patient's blood glucose level almost immediately and act as required in response. Even if the result is not accurate or precise, the result is quite acceptable because it is obtained very rapidly (that is, because productivity-related properties are favoured over capital and basic analytical properties).

Slide 2.61

Chapter 2: Analytical Properties

2.1.7. Relationships among analytical properties (VI)

COMPLEMENTARY RELATIONSHIPS

CASE 1: Relationship between sensitivity and precision

The limits of detection (C_{LOD}) and quantification (C_{LOQ}), which are used to assess sensitivity, are defined in terms of the standard deviation of the blanks, s_B :

$$C_{LOD} = \frac{3 s_B}{S} \quad C_{LOQ} = \frac{10 s_B}{S}$$

CASE 2: Relationship between sensitivity and selectivity

A) The more sensitive a method is, the higher will be the dilution needed by the sample and the lower the concentration of interferences as a result.

B) Using an analytical separation technique (Chapter 4) based on mass transfer from a phase to a lower volume of another allows two aims to be fulfilled:

- 1) Sample clean-up by effect of interferences being reduced, which increases the selectivity in an indirect manner.
- 2) Analyte preconcentration, which also increases the sensitivity indirectly.

The two cases illustrated in this slide exemplify complementary relationships among analytical properties.

- *Case 1.* The relationship between sensitivity and precision is given by the equations for the limits of detection and quantification used to calculate them (Slide 2.42). The precision of a method can be estimated from the standard deviation for a set of blanks. Because LOD and LOQ are related to the standard deviation of the blanks, the sensitivity is connected with the precision of the blanks. This relationship is complementary: the higher is the standard deviation of the blanks, the higher will be both limits, and the lower the precision and sensitivity as a result. Conversely, the lower is the standard deviation, the lower will be the limits, and the higher the precision and sensitivity.
- *Case 2.* The relationship between sensitivity and selectivity can be approached in two different ways.

In one (A), the sensitivity is related to the selectivity through the degree of dilution of the sample. The more sensitive the analytical method is, the smaller the amounts of analyte it will be able to detect; therefore, diluting the sample to an appropriate extent may even avoid saturation of the measuring instrument. In addition, dilution can reduce the effects of interferences and increases the selectivity of the analytical method for the target analyte.

In the other (B), the sensitivity is related to the selectivity through a preliminary operation: transfer of the analyte between two phases in an analytical separation

system (ASS, Slides 4.26–4.31) in order to remove interferents (for increased selectivity) and simultaneously preconcentrate the analyte (for increased sensitivity).

2.2 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 is an abridged version of Chap. 2 in the book, entitled “Analytical Properties”, which, however, has been expanded with new contents, and a number of examples and problems. Valcárcel’s book can be used to go deeper into the contents of this chapter.

Statistics and Chemometrics for Analytical Chemistry

James N. Miller & Jane C. Miller

Pearson Education, 2010.

This is an elementary handbook of statistics whose contents are especially important and useful for analytical chemists. It is intended to facilitate calculation of analytical results and extraction of information from them.

Although this chapter is inspired by some of the book contents, we have strived to simplify the computation of the parameters used to quantify the analytical properties and illustrated it with examples intended to facilitate their mathematical and statistical understanding. The book can be used by students to both expand their knowledge of the parameters dealt with in this chapter and be introduced to others also used in Analytical Chemistry at present.

2.3 Questions on the Topic (Solved in Annex 2)

2.1. Tick the correct statements in relation to the dynamic range of a calibration curve obtained in the photometric determination of iron in wines:

- ☐ The sensitivity remains constant
- ☐ The lower limit coincides with the limit of detection
- ☐ The sensitivity is always greater than zero

☐ The lower limit coincides with the limit of quantification

2.2. To which analytical properties are the following concepts directly related?

TRACEABILITY	<input type="checkbox"/> Precision	<input type="checkbox"/> Accuracy	<input type="checkbox"/> Sensitivity
ROBUSTNESS	<input type="checkbox"/> Expeditiousness	<input type="checkbox"/> Precision	<input type="checkbox"/> Sensitivity
PRODUCTIVITY	<input type="checkbox"/> Expeditiousness	<input type="checkbox"/> Cost-effectiveness	<input type="checkbox"/> Representativeness

2.3. Distinguish dynamic range from linear range in a calibration curve.

2.4. State whether the following statements are true (T) or false (F):

- ☐ Precision decreases with increasing standard deviation
- ☐ Accuracy decreases with decreasing relative error
- ☐ Sensitivity increases with decreasing limit of detection and quantification
- ☐ Selectivity increases with increasing interference

2.5. Define the analytical property robustness.

2.6. Define “bias” in relation to errors in Analytical Chemistry.

2.7. Tick the correct statements in the dynamic concentration range of the calibration curve for the photometric determination of calcium in milk:

- ☐ The sensitivity remains constant
- ☐ The sensitivity is always non-zero
- ☐ The sensitivity is not always the same
- ☐ The sensitivity decreases at the end of the range

2.8. Which datum is needed to assess the accuracy of an analytical result?

- ☐ The mean of n results
- ☐ The value held as true
- ☐ The standard deviation

2.9. State whether the following statements are true (T) or false (F).

- ☐ Selectivity increases with decreasing interference
- ☐ Sensitivity increases with decreasing slope of the calibration curve
- ☐ Accuracy increases with increasing precision
- ☐ Precision increases with increasing standard deviation

2.10. Distinguish generic and specific uncertainty.

2.11. What are the differences between “repeatability” and “reproducibility”?

2.12. What kind of reference is used to calculate (a) the accuracy of the result for a sample and (b) the precision of a method?

2.13. State whether the following statements about accuracy and precision are true (T) or false (F).

- ☐ Both analytical properties can be ascribed to results
- ☐ The two are unrelated
- ☐ Good precision can only be obtained with good accuracy
- ☐ Good accuracy can only be obtained with good precision

2.14. Name the four types of relationships between analytical properties.

2.15. What are the similarities and differences between systematic and gross errors?

2.16. Two methods A and B are used to determine the same analyte in aliquots of a sample with a certified value of 1.23 ± 0.05 mg/L. The experimental result is 1.27 ± 0.03 mg/L with method A and 1.29 ± 0.01 mg/L with method B. Which method is the more accurate? Which is the more precise? Why?

2.17. Why stating the accuracy of a result is meaningless if its precision is unknown?

2.18. Can productivity-related properties be more important than capital and basic properties?

2.19. What is a “blank”? What is the “blank signal”?

2.20. Which are the references needed to define the following analytical properties in mathematical and conceptual terms? Tick the correct choices.

	Set of blanks	Value held as true	Mean of n results	Interferences from other systems
Accuracy				
Precision				
Limit of detection				
Selectivity				

2.21. State whether the following statements as regards accuracy and precision are true (T) or false (F).

- ☐ Both analytical properties can be assigned to results
- ☐ The two are mutually related
- ☐ Good precision cannot be obtained without good accuracy
- ☐ Good accuracy cannot be obtained without good precision

2.22. Why does accuracy rest on precision?

2.23. Tick the correct boxes in this comparison of precision and robustness.

	Same sample aliquot	Same method	Supports accuracy	Basic analytical property
Robustness				
Precision				

- 2.24. How are the facets of sensitivity related?
- 2.25. Two methods A and B for determining aflatoxins in milk are compared in terms of sensitivity by analysing two different certified reference materials with certified values of 0.25 ± 0.01 and 0.28 ± 0.01 ppb. Based on method A, both CRMs contain aflatoxins. Based on method B, both CRMs contain aflatoxins and the second CRM contains a slightly greater amount than the first. Which is the more sensitive method? Why?
- 2.26. What is the lower limit of the linear range of the calibration curve?
- 2.27. What is the “maximum tolerated ratio”? To which analytical property does it relate?
- 2.28. Give an example of analysis (state the sample and analyte) where accuracy is to be favoured over productivity-related properties?
- 2.29. Is it correct to assign accuracy to an analytical process? Why?
- 2.30. The sensitivity of a method is 1.02×10^{-3} UA mL ng⁻¹. What are the units for the following parameters?

Blank signal
 Standard deviation of the blank
 Limit of detection
 Limit of quantification
 Analyte concentration

- 2.31. Complete the following table comparing the analytical properties “accuracy” and “precision”.

	Accuracy	Precision
Type of analytical property		
A typical property of		
Parameters used to measure it		
An indispensable numerical reference for calculating the parameters		
Mutually dependent		

- 2.32. (1) Discuss the ideal situation and (2) describe the real situation in independently subjecting n aliquots of sample to an analytical process in order to obtain n results.
- 2.33. Classify errors in Analytical Chemistry according to (1) form of expression; (2) direction; and (3) sources, references and magnitude.
- 2.34. A method provides accurate results. May it not be precise?
- 2.35. Define a parameter representing the analytical property “selectivity”.
- 2.36. Solve the different parts of the following problems.

– Problem A

An analytical method for determining copper traces in feed is characterized as follows:

- (1) Using the method to analyse standards of increasing concentrations of analytes provides the following results:

[Cu ²⁺], ppb	0.0	1.0	2.0	3.0	4.0	5.0
Signal, AU	0.030	0.050	0.102	0.149	0.201	0.250

- (2) Independently subjecting 5 aliquots of a reference standard with a certified concentration of 3.30 ± 0.10 ppb gives the following results, in ppb: 3.40, 3.39, 3.50, 3.27 and 3.35.

Questions:

- What is the blank signal? What are its units?
- What is the signal corresponding to the certified copper concentration in the standard?
- Can the precision of the method be calculated? Why? If it can, what is it?
- Can the accuracy of the result be calculated? Why? If it can, what is it?
- If the client's imposed limit is 0.1 ppb copper, is the method suitable for qualifying (detecting) and quantifying the analyte if the deviation of the blank signal is 2.3×10^{-3} AU?

– Problem B

An analytical process for determining pesticides (P) in water is applied through the following tests:

- (1) Subjecting a total of 10 blanks to the process gives the following results in absorbance units (AU):

0.031	0.033	0.041	0.029	0.035	0.037	0.040	0.032	0.030	0.037
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- (2) A calibration curve is constructed from a set of standards of increasing hydrocarbon concentrations. The equation for the curve is

$$\text{Signal}(AU) = 0.035 + 1.07[P]$$

where $[P]$ is the pesticide concentration in ng/mL.

Questions:

- Can the precision of the method be calculated? Why? Explain your answer.
- Express the sensitivity of the method through three different parameters.
- If the legal limit for pesticides in water is 2 ng/mL, is the method useful for their detection and quantification?

– *Problem C*

The precision of an analytical process for determining copper traces in seawater is assessed in three tests involving different experimental conditions, namely:

- (1) Processing a single aliquot of sample and introducing six portions of the treated aliquot into the measuring instrument.
- (2) Independently processing six aliquots of the same sample and introducing them into the measuring instrument on the same day.
- (3) As in (2), but having six different analysts perform the analytical process on different days.

The results obtained are as follows:

Test	Results (mg/L)					
1	1.32	1.31	1.32	1.33	1.30	1.31
2	1.28	1.36	1.30	1.27	1.31	1.33
3	1.35	1.45	1.21	1.37	1.30	1.28

Calculate the specific uncertainty at the 95% confidence level for each test and plot it. Use the uncertainty values to discuss the precision achieved in each case, and identify the facet that can be characterized with each test.

2.4 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 18 slides (30% of all) can be omitted for this purpose:

- Section 2.1.3: Slide 2.12
- Section 2.1.4: Slides 2.15 and 2.17
- Section 2.1.5: Slides 2.24, 2.25, 2.27, 2.28, 2.31, 2.34, 3.38, 2.39, 2.44, 2.45, 2.46, 2.47, 2.48, 2.49 and 2.53

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2018, XVII, 487 p. 346 illus., 345 illus. in color. With
online files/update., Hardcover

ISBN: 978-3-319-62871-4