

## METROLOGY IN CHEMICAL ANALYSIS

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### Contents

1. Introduction
  2. Metrological characteristics of methods and procedures in chemical analysis
  3. Analytical signal: Conducting of a measurement
  4. Errors in chemical analysis: Data treatment
    - 4.1. Systematic errors
    - 4.2. Random errors
  5. Sensitivity factor, detection limit, and Dynamic range
  6. Analysis of variance, correlation and regression analysis (a general overview)
- Bibliography  
Biographical Sketches

### Summary

This chapter deals with the main aspects of the application of metrology to chemical analysis. Parts of the material are given in detail so that a reader could use the text in data treatment, for example, in the determination of a certain analyte or in the calculation of a detection limit or linear dynamic range. Some other metrological issues (such as metrological characteristics of methods and procedures) are discussed in less detail. And finally, a number of issues (analysis of variance, correlation and regression analyses) are given only at the level of general ideas in order to show what an investigator is able to obtain applying this knowledge in the field of metrology to solve concrete problems of chemical analysis. Bibliography provides the reader with the monographs wherein a more detailed consideration of all the topics described is given.

### 1. Introduction

Chemical analysis is a sort of human activity aimed at obtaining information on the chemical composition of samples. The constituents of chemical analysis are analytical chemistry and analytical service.

Analytical chemistry is a field of science concerned with the determination of chemical composition of samples and (to some extent) of their chemical structure. It serves as the basic foundation for chemical analysis. Analytical service covers all those daily and even hourly analyses of particular samples performed by using procedures recommended by analytical chemistry. That is to say that analytical chemistry is a

science providing theoretical foundation and methods suited to detect and determine the amounts of chemical substances and establish their chemical structure. Metrological basis of chemical analysis is a constituent of the theoretical foundation of analytical chemistry.

Chemical analysis is a complex multi-stage process. The following stages can be considered in the analysis of any sample: selection of a method and procedure; sampling; sample pre-treatment; signal measurement; data processing. It is important to note that this division is conventional since each stage while being interconnected with the others may be relatively complex itself and may consist of multiple separate stages.

While choosing an analytical method the chemist has to clearly conceive the purpose of analysis, the tasks to be solved, and evaluate the advantages and drawbacks of available analytical methods and techniques, *i.e.* their metrological characteristics.

## 2. Metrological Characteristics of Methods and Procedures in Chemical Analysis

The purposes and tasks solved by analytical chemists are diverse. Depending on the ultimate goal (to disclose what elements or molecules the sample consists of, or what functional groups or isotopes form it, or what phases contain the analyte) they distinguish elemental, molecular, functional, isotope, and phase analysis. While conducting an analytical procedure, an analytical chemist often has to solve a number of additional problems: to determine very low amounts, to carry out the analysis very rapidly and with high precision, to find sample composition without its destruction, to perform local or remote analysis.

Now let us discuss the concepts of “method” and “procedure” (or “protocol”). Method is a set of principles forming the foundation of analysis irrespective of a particular sample and analyte. Procedure is a detailed protocol of every condition and operation to be done for the analysis of a particular sample for a definite analyte.

For instance, gravimetric method is based on the determination of a compound mass that contains (or loses) the analyte. However, a procedure (protocol) for the gravimetric determination of a component by mass of its poorly soluble compound includes: the description of this insoluble compound precipitation conditions (pH and temperature of the solution, amount and manner of precipitating agent addition, time of precipitate aging); the mode of precipitate separation from solution; its washing; transformation of the precipitate into the form convenient for weighing etc. In cases when the analyses of particular samples are done, the procedure includes also the description of sampling and sample treatment (for example, dissolution of the sample in an appropriate solvent and elimination of the effects of the components interfering with the gravimetric determination).

Let us consider the main factors to be taken into account while selecting analytical method and procedure.

*Sensitivity of the method.* When choosing a method of analysis it is necessary to keep in mind the analyte content. In doing this, it is important to know not merely an

approximate per cent quantity of the analyte in the sample or its concentration in solution but also the sample amount available for analysis. The analytical method selection is thus determined by the total amount of the analyte.

The concentrations of the analytes as well as available sample amounts may vary widely. For example, the content of metal ions such as copper, nickel, and chromium may measure dozens per cent in their alloys, and 0.1 or even 0.01% in minerals, ores, and alloys of other metals. At the same time, the content of these metal ions in plants, living organisms, and food has been determined at levels as low as  $10^{-7}$ –  $10^{-5}$  % and in special purity substances – down to  $10^{-8}$ –  $10^{-6}$  %. The sample amount may be not limited in one case while in the others (analysis of interspersed minerals, human blood, biomasses, space objects, etc.) it may be extremely small (milligrams or even less).

Taking into account the analyte content, methods featuring different sensitivity should be chosen. The sensitivity of a method or procedure is determined by that minimum amount of the analyte which may be detected or determined by this method using this procedure. A more strict definition of this notion and its quantitative expression will be given later.

Having compared the sensitivity of various methods and evaluated the approximate content of the analyte in the sample, the analytical chemist selects this or another method of analysis. For example, for the determination of sodium in silicate rocks a gravimetric method is used which enables to determine milligram and higher amounts of sodium; at the same time, the determination of microgram amounts of this element in biological samples of live origin is done with a flame photometry method, while nano- and picogram amounts of sodium in specially purified water are determined with laser spectrometry or atomic emission spectrometry with inductively coupled plasma (ICP).

*Selectivity of the method.* While performing analyses, we encounter samples of various origins: food and agriculture reprocessing products, environmental samples and biomasses, space samples, arts and forensic samples, etc. It is natural that the choice of a method and analytical procedure is dictated not only by the analytical task but also by the sample properties. It is necessary to take into account physical properties of the sample: its aggregate state, volatility, hygroscopic properties, mechanical, structural, etc. However, chemical properties of the sample have decisive importance in the selection of an analytical method. While choosing a method one should take into account the chemical properties of the sample matrix, qualitative chemical composition of the sample, chemical properties of the analyte and accompanying impurities.

Being given the chemical properties of the matrix and all the components of the sample to be analyzed, and having evaluated possible interferences with the analysis, the chemist chooses the most *selective* method. Methods are recognized as selective when they allow for the determination (or qualitative detection) of the analytes with no interferences from other components. If a method or procedure allow us to determine just one component, they are referred to as *specific* ones. That is to say, specificity is the highest degree of selectivity.

Sometimes selectivity is characterized by the value of selectivity factor (or tolerance ratio) which equals the ratio of the interfering component amount to the amount of the analyte.

It is possible to separately consider the selectivity of a method, a procedure, or a single reaction which the analyte determination procedure is based on. For instance, highly selective are such *methods* as potentiometry, atomic absorption and enzyme methods. Many *reactions* forming the foundation of various techniques are also highly selective, for example, the reactions of metal ion complexes formation with organic ligands, enzyme and electrochemical reactions. Some reactions are specific: interaction of iodine with starch, reaction of ammonia salts with alkali used for ammonium ion detection.

While considering the selectivity of methods and procedures it is worth saying a few words about their *versatility* understood as ability to detect or determine a number of analytes. Especially valuable is the feasibility of the determination of many components using one sample (i.e. to conduct analyses of multi-component mixtures). High selectivity and high versatility of the method do not contradict each other; many multi-purpose analytical methods feature high selectivity in the determination of specific analytes. Those are, for instance, chromatography, some sorts of voltammetry and atomic absorption spectrometry. Atomic emission spectrometry with inductively coupled plasma and quantometers allow us to determine 25-30 different elements from one sample without separation.

*Errors in analysis.* One of the important factors to be kept in mind while selecting an analytical method is accuracy of the determination and therefore accuracy of the method itself. They distinguish *accuracy per se*, which reflects the proximity of the method systematic error to zero, and *precision*, or *repeatability*, which characterizes the closeness of the analytical results to their mean value. The results of a determination are *accurate* if the mean analyte amount or concentration obtained is close to its real value (which in its turn might be known beforehand if a standard sample was analyzed or established by a different wittingly accurate method). The analytical results are *precise* if single measurements are but slightly scattered around their mean value (which supplies no information of how this mean value itself is close to the real value, i.e. how accurate is the determination).

Requirements for accuracy and precision may vary depending usually upon the purposes and aims of analysis and the character of the sample. It is quite unnecessary to always strive for high accuracy and/or precision. For example, in routine control of many metallurgic and chemical production processes the analysis may be done with an error of 10-15 per cent. In the case when it is important to know the content of the matrix and, especially, of hazardous impurities with a lower error (such as in pharmaceutical or food industry), the accuracy and precision requirements reach as low as 0.1-1 per cent. For semiconductors the error in the determination of main components must be not lower than 0.1 and, if possible, 0.01 per cent since physical properties of these materials soundly depend on how strict their stoichiometry is kept.

Fairly accurate and precise are gravimetric and volumetric methods whose error falls usually within 0.05-0.2 and 0.1-0.5 per cent, respectively. The most precise of all the

modern methods is coulometry which enables for the determination of analytes with an error of the order of 0.01 per cent.

As a rule, the analytical requirements are dictated by the clients: technologists, geologists, physicians, physicists, etc. But analytical chemists should have their own understanding of the need in gaining higher or lower accuracy and precision of the ongoing analysis. Unjustified requirement of high accuracy usually lengthens the analysis and raises its cost. For instance, a decrease in the analyte determination error from 2 down to 0.2 per cent increases the analysis time by over 20 times. Too high accuracy requirements often result in a need in expensive sophisticated instrumentation. By other words, a researcher has to obtain a sober approach to the choice of a more or less accurate method, especially for the analysis of numerous samples.

*Rapidity of analysis.* The requirement for an analysis to be rapid, i.e. consuming little time, often governs the selection of a method or a procedure. Of course, any analysis favors a quick rather than a time-consuming procedure. However, analytical tasks sometimes call for a choice of an especially rapid method. Let us consider two examples from different areas of human activities. In the case for steel converter fusion which lasts for 15-20 min a number of elements are to be determined, and each analysis must be completed in a few minutes. While making surgical operations a necessity arises to determine the concentration or concentration change of some biologically active compounds (urea, glucose, medications, etc.) in patient's blood or tissues.

There are methods allowing chemical analyses to be conducted very rapidly. In the first of the above given examples the methods of atomic emission spectrometry with the use of quantometers are utilized which makes it feasible to determine many (15-20) elements in a few seconds; another way to solve this task is the use of potentiometry with various ion-selective (including enzyme) electrodes whose response time is 0.5-1 min.

While discussing the rapidity of the methods it is worthwhile noticing that in most methods and procedures the measurement of signal which is related to analyte content is basically a relatively short stage. Most of chemical analysis time is spent for sample pre-treatment. In order to reduce analysis time, one should choose more selective analytical methods and procedures, requiring no special pretreatment, other conditions being equal.

*Cost of analysis.* This often plays a great role, especially for serial analyses of many samples. Analysis cost includes the cost of the equipment and reagents used, of the analyst working time, and sometimes the cost of sample itself. The cheapest are titrimetric, gravimetric, and potentiometric methods. Higher cost equipment is used, for example, in voltammetry, spectrophotometry, luminescent and atomic absorption analyses. The highest equipment cost is characteristic of neutron activation method, mass spectrometry, electron spin resonance and nuclear magnetic resonance spectrometry, and atomic emission spectrometry with inductively coupled plasma.

Estimating the expenditures for an analysis, they take into account also the cost and availability of reagents; time required for the detection and determination of a single

component; the amount of sample, especially in cases when its material itself is expensive (such as alloys and ingots of platinum metals, gold etc.).

Other conditions being equal, the cheapest method and procedure would be preferable in solving an analytical problem put up before a chemist.

The metrological characteristics described above are the basic ones to be used while choosing the method and procedure for chemical analysis. However, there might be a need in taking into account such specific factors as the feasibility of automation, of conducting local analysis, remote analysis, non-destructive analysis, etc.

A great number of factors needed to be evaluated and accounted for in selecting an analytical method and an optimal procedure for detection or determination of an analyte make this step of chemical analysis fairly complicated. In this regard, an analytical chemist can obtain some help from computer modeling.

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## Bibliography

### Annotation

This article covers different aspects of metrology in chemical analysis. Metrological characteristics of an analytical method and analytical procedure are considered: sensitivity, selectivity, precision, accuracy, rapidity and cost-efficiency. Methods for the determination of an unknown concentration by use of a signal - analyte concentration dependence are discussed in detail. The basic notions such as precision, accuracy, systematic and random errors, and sensitivity are given. Level of the presentation of chemical analysis data processing given in this article enables it to be a manual for the evaluation of analytical results obtained by the reader. The basics and application areas of variance, correlation and regression analyses are supplied. A list of references for a deeper study of the topic is given at the end of the article.

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## Biographical Sketch

Dr. Dolmanova, Inga F. is the head of the Laboratory of Kinetic Methods of Analysis at the Department of Chemistry, M.V. Lomonosov Moscow State University, dozent, Ph.D. The area of her scientific interests is analytical chemistry; she gives the main lecture course in analytical chemistry for undergraduate students of the named University. Dr. Dolmanova and her students do research in the field

of catalytic and enzymatic methods of analysis. Over 20 Ph.D. dissertations have been defended under her supervision. She has over 200 scientific papers and 20 patents in the area of developing of theoretical basics of catalytic and enzyme methods of analysis, procedures for the determination of physiologically active metal ions and organic compounds in biomasses and environmental samples. Dr. Dolmanova is a co-author of a textbook “The Basics of Analytical Chemistry”, now widely used in Russia.

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