Microwave-Assisted Sample Preparation for Trace Element Determination

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Preface

Since the first use of microwaves in chemical laboratories, almost 30 years ago, many applications have been proposed with important improvements in several fields of chemistry. Especially for analytical chemistry, the use of microwaves has increased with major concern for sample preparation. In this sense, nowadays it is well established that sample preparation is one of the most relevant steps in analytical sequence in order to achieve reliable results. Currently, analytical equipments allow very low detection capability for trace elements (e.g., inductively coupled plasma mass spectrometers), but most of them can routinely work with digested or diluted solutions. Several interferences have been reported due to problems in sample preparation step and it has been even considered by some researchers as the Achilles' heel in analytical sequence.

The use of microwaves for sample preparation related to trace analysis has been already presented in some specific books. One of them was published some years ago by Dr H. M. (Skip) Kingston (Duquesne University, USA). Other recent and important contributions were provided in the books edited by Dr M. A. Z. Arruda (Unicamp, Brazil), Dr Z. Mester, Dr R. E. Sturgeon (NRCC, Canada), and also by Dr F. J. Krug (CENA-USP, Brazil; this one in Portuguese language).

Considering the recent advances in sample preparation field using microwaves, the present book was conceived to provide additional information to previously published books. Classical methods were revised and recent applications involving microwaves for sample preparation are presented. It includes an introductory text on sample preparation and basic concepts of microwave heating and instrumentation. New applications for speciation analysis and biomolecules determination were also covered. A final chapter was included regarding safety aspects, quality control, and quality assurance for microwave-assisted sample preparation systems. Taking into account the green chemistry recommendations, special focus was given to greener digestion methods avoiding the use of concentrated reagents and the consequent effluents generation (microwave-induced combustion, microwave-assisted extraction, microwave ultraviolet-assisted digestion, oxygen-pressurized digestion, and flow digestion systems).

The editor and authors hope that this book will be useful for graduation and postgraduation students but also for people involved in routine analysis or even for experts working in new developments or applications using microwaves.

An acknowledgment must be given to my colleagues in Chemistry Department of Universidade Federal de Santa Maria, Brazil and also for the dedicated work of all the contributing authors that made possible to prepare this

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Chapter 1

Introduction to Sample Preparation for Trace Element Determination

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1.1. INTRODUCTION

The evolution of the atomic and mass spectrometry techniques, such as atomic absorption spectrophotometry and inductively coupled plasma spectrometry, has allowed the convenient determination of numerous chemical elements at low concentrations (e.g., micrograms per kilogram or picograms per kilogram). These advances have contributed to the development and characterization of new materials such as semiconductor reagents and nanomaterials, and applications in the areas of toxicology, agriculture, medicine, biology, and forensic chemistry, among others. However, these techniques generally involve the introduction of samples as aqueous solutions to the flame, furnace or plasma. This characteristic highlights a limitation of the modern spectrometry, because, although the simultaneous determination of numerous elements is possible with excellent sensitivity in <1 min, the conversion of a solid sample into a representative solution can take from 5 min to two days or more, depending on the matrix complexity. These treatments may involve a substantial transformation of the sought chemical species into a suitable form for the selected determination method. Sample preparation depends on the nature of the sample, the analytes to be determined and their concentrations, and on the desired determination precision and trueness (accuracy). Recently, after many advances in commercial instrumentation, the consensus persists that the sample preparation

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steps are time consuming, expensive, and responsible for a major source of errors in the analytical sequence. In this chapter, the role of sample preparation in trace element analysis, including the sequence of analytical steps, systematic errors, preliminary treatments such as drying and milling, and conventional wet-chemical digestions by using open and closed vessel systems will be discussed.

The set of operations between the sample and the results it provides is known as the "chemical measurement process" (CMP) and includes four steps with samples and measurement standards as inputs and information about the samples as outputs [1]. In the first step, the sample is made ready for the analytical measurement usually by a variety of preliminary operations and substeps. These preliminary operations (i.e. sampling; sample preparation/treatment, such as drying, sieving, and homogenization; solid/liquid/gas treatment; separations; analytical/nonanalytical reactions including dissolution and disaggregating; volume/mass measurements; transfer to instrument) connect the uncollected, unmeasured, and untreated sample to the measurement step. The second step is the measurement and transduction of the treated sample into the analytical signal, while in the third step the results sought are obtained by acquiring the transduced signals and processing of data. Calibration operations constitute the fourth step. These CMPs, especially the preliminary operations, for trace analyses are the focus of this chapter.

A systematic protocol to approach and solve analytical problems, which will be examined in this chapter for trace analyses, comprises five sequential, cyclic steps [1] that include the following: (1) Defining (and confirming) the information needed; (2) translating the information needed into the required chemical information; (3) planning the analytical approach; (4) monitoring, evaluating, and validating the results generated by the analytical process (CMP); and (5) implementing corrective actions when the results fail to meet the requirements of the original analytical problem (Figure 1.1).

1.2. THE ANALYTICAL SEQUENCE

A mission of analytical chemistry is to propose and develop fit-for-intended-purpose methods aimed at the determination of one or more chemical species (e.g., molecules, elements, and oxidation states) in different materials, and the approach usually involves an unsolved problem by analyzing one or more samples by a validated method [2].

Chemical analysis is a complex multistage investigation that may be summarized by a series of subtasks (steps, operations) or analysis sequence [2,3]. This sequence (Figure 1.1) will be described in this chapter. Various analytical sequences have been represented in the literature [1–3], and the one proposed by Anderson [3] will be highlighted. Although an analysis sometimes is outlined as a linear sequence, the measurement is often an iterative process rather than a linear series of steps.

The in situ direct analysis of solids (e.g., X-ray fluorescence (XRF), laser-induced breakdown spectroscopy, and spark emission spectroscopy) is often

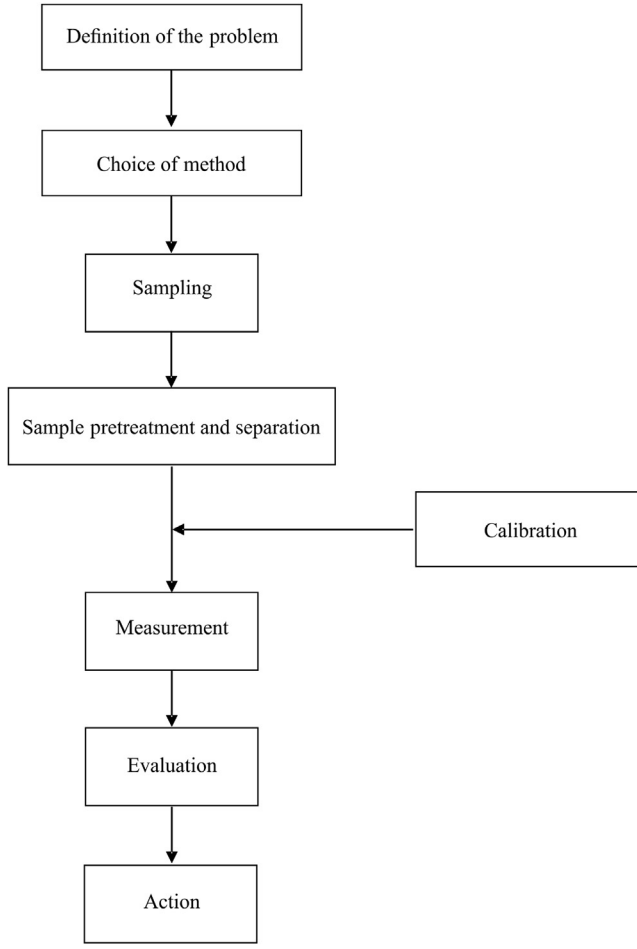

FIGURE 1.1 The analytical sequence.

close to ideal, because in some cases, the determination of the analytes can be accomplished directly without extensive sample preparation and/or in the field, and the analytical sequence will be restricted to a few steps. Few instruments (e.g., pH meters and hand-held Raman spectrometers) have been designed for measurements in the field, but in spite of their good performance for many applications, they may not be appropriate for the general determination of all chemical species in all types of samples. Among the most successful commercially available instruments for in situ analysis are portable spectrometers based on XRF spectrometry, spark optical emission spectrometry, Raman spectrometry, and laser-induced breakdown spectrometry (LIBS). However, to analyze the samples in situ is not always possible. Consequently, a field sampling procedure is necessary, and subsequently, the sampled material is analyzed in

the laboratory. Some possibilities for the direct analysis of solids for trace and ultratrace constituents exist in the laboratory, but generally methods require the transformation of the test sample into a solution.

In the laboratory, the sample must be subjected to appropriate treatment before the determination of analytes (i.e., the preliminary processes of the CMP) [1]. This treatment can be a simple sample-surface polishing or the complete transformation of a solid sample into a solution compatible with the method of determination. The way to decompose the sample for analysis depends on its nature, the elements to be determined and their concentrations, and, in some cases, the ratio between the test sample mass and volume of solution must be flexible, so that sample dilution does not impair the relative detection limit of the method. The treatment of the sample may involve a substantial transformation of sought chemical species into a form that is suitable for implementing the chosen determination method.

Before proceeding to a detailed description of pretreatment of samples, the steps that an analyst should consider for chemical analysis are reviewed. These tasks are arranged in a sequence, some of which are discussed in this chapter.

According to the Guide to Quality in Analytical Chemistry from Cooperation for International Traceability in Analytical Chemistry (CITAC)/EURACHEM [2], a chemical analysis is a complex, multistage process, which may be summarized by a series of subtasks (steps). Of course, all steps are not always mandatory. In fact, not every step will be required each time a routine measurement is performed, and that, in reality, the measurement is often an iterative process rather than a linear series of steps. These recommended steps are listed below, and some of them, marked with "*" are of more significance for nonroutine analysis than for routine analysis:

- Specification of requirements
- Information review *
- Creative thought *
- Study plan *
- Sampling
- Sample preparation
- Preliminary analysis *
- Identification/confirmation of the chemical composition
- Quantitative analysis
- Data collection and review
- Data interpretation/problem solving
- Reporting/advice

In this chapter some recommendations of this Guide edited by CITAC and EURACHEM [2] will be considered in the analytical sequence suggested by Anderson in a comprehensive monograph [3]. The main steps in the analytical sequence given by Anderson [3] are as follows:

1.2.1. Definition of the Problem

This should be the first step when planning an analysis; it establishes "what analytical information is desired?" Defining the problem establishes the qualitative, quantitative, and/or structural or temporal objectives of the analysis task.

This can be a simple question dealing with, for example, the lead content in a food product to check if it meets the *Codex Alimentarius*, or a more complex question aiming at plant nutrition diagnosis, for which the information required is the content of N, P, K, Ca, Mg, S, Fe, Cu, Mn, Zn, Ni, B, Mo, and Cl in selected plant leaves of a specific plant species.

1.2.2. Choice of the Method

Once the analytical problem is defined, then the next step is to decide on an appropriate approach (method and technique) suitable to provide the desired information. The choice of a suitable method for the determination of the desired analyte(s) is always necessary. The choice can be based on various criteria, but, ideally, the method selected must be validated or, in simple words, must fit the intended purpose. Before the method can be used, a representative sample must be obtained. Then, a sample preparation method should be selected that is consistent with the characteristics of the possible determination method. When dealing with the direct analysis of solids, the quality of sample preparation will depend primarily on the grinding method, and a possible comminution step, which is needed to produce a sufficiently homogeneous test sample. If the determination method allows the analysis of only solutions, the decomposition method should transform the sample into a solution compatible with the determination.

Thus, the method of determination should be chosen a priori to define the most appropriate strategy for obtaining analytical results that allow solving the problem. Based on this choice, the sampling method and sample preparation technique(s) also can be defined. This choice requires a knowledge of the difficulties that may limit the performance of the determination method. In fact, numerous instances exist where the determination method is chosen a priori without having a knowledge of how samples should be prepared. Anyway, by knowing exactly what information is desired, how it will be obtained can be decided in detail. Some tips for choosing the determination method are listed below:

- The analytical method should be efficient and, if possible, simple and fast.
- The method should not result in damage to materials in which the samples are processed and/or analyzed.
- The method should not be subjected to systematic errors (e.g., losses of analytes by volatilization or adsorption, contaminations).
- The selectivity of the method must be previously known.
- If possible, the method should be used with minimal manipulation.
- All operations must be carried out under maximum safety conditions.

Ideally, the choice should be based on a validated method. The analyst must assure that the procedure measures what the analyst says it measures for a specific type of sample. The validation of a method establishes from systematic studies performed in one or more laboratories if the method has characteristics to produce results for solving the problem. In analytical chemistry, validation is a process that establishes the performance characteristics and limitations of a method. It allows the identification of the factors that can affect the performance characteristics. Thus, the validation process establishes which analytes can be determined in which matrix or matrices and gives information about the risks of potential interferences. Moreover, under these established conditions, it is possible to predict if the expected precision and trueness are appropriate. Validation also should provide confidence to the analyst to know in advance if the conditions of the selected method are appropriate to obtain results for solving the analytical problem. In the case of solid samples, the fact that the preparation method is valid for the samples of interest should be clear. Furthermore, the conditions should indicate if the samples need to be dried (and under what conditions) and ground appropriately (i.e., type and characteristics of the mill, degree of comminution of the particles, minimum time of grinding), the minimum mass to be sampled, the required air quality standard of the laboratory, and/or in the sample handling environment, if humidity (e.g., use of desiccators) and temperature control during sample storage is necessary. If samples are digested, validation should indicate that the digestion method is suitable for the method of analyte determination. In this aspect, it is implied that the method of determination is part of the validation process. In choosing the method, the analyst should also consider the following points:

- Time;
- Cost;
- The need for traceability;
- Uncertainty of results;
- Quality control and quality assurance.

1.2.3. Sampling

Sampling is the process of selecting and removing from the uncollected, unmeasured, and untreated material under study a small and representative test portion (aliquot) from which the analysis is made. The term “representative” sample is subjective, and in many cases, it can be replaced and better understood as “appropriate”. See, for example, the comprehensive text by Ramsey [4], in which the answer for this key question when dealing with sampling in the environment is discussed. According to Ramsey, a more rational approach may be to make samples “representative enough”, or appropriate, with known acceptable levels of measurement uncertainty, for the stated purpose and/or decision.

Sampling is not an easy operation, and proper sampling requires overcoming numerous potential problems that make it one of the most difficult operations

of the CMP. The main sources of sampling uncertainties include (1) definition of the sampling objectives, (2) characteristics of the sample (e.g., heterogeneity, aggregation state, composition, stability, availability, and distance from the laboratory), and (3) experimental protocol including the availability of sampling tools; sample preservation and transport; location, number, and size of samples; and type of laboratory or on-site analysis [1]. A verified sampling plan with well-defined procedures for selection, collection, storage, transport, and preparation of the sample is essential. Sampling is outside the scope of this chapter, and the reader should consult expert resources for details [3].

In general, the terminology related to the sampling procedure may confuse the reader, since some terms do not have the same meaning in different applications. To avoid confusion, the general recommendation is that sampling terms in any document must be clearly defined. In particular, the authors of this chapter will follow the recommendation of the International Union of Pure and Applied Chemistry (IUPAC) proposed by Horwitz [5], from which some recommended terms are shown below:

- *Sample*: a portion that represents the whole. The sample represents the entire population of interest. It can be collected from a single location or it can be a composite sample. A composite sample is obtained from combining several samples collected at different locations within the population of interest.
- *Subsample*: When the sample is homogenized and divided among different laboratories, or when the sample is large and only a portion is taken to the laboratory for analysis it is a "subsample".
- *Laboratory sample*: The sample or subsample delivered to the laboratory.

NOTES:

  - When the laboratory sample is further prepared by subdividing, mixing, grinding, or by combinations of these operations, the result is the test sample (described below). When no preparation of the laboratory sample is required, the laboratory sample is the test sample itself.
  - The laboratory sample is the final sample from the point of view of sample collection, but it is the initial sample from the point of view of the laboratory analysis.
  - Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

- *Test sample*: Sample prepared from the laboratory sample, from which test portions are removed for testing or for analysis. While the term "sample preparation" is appropriate to describe this stage of sampling, the preparation might involve other treatments.
- *Test portion*: This refers to the actual material weighed or measured for the analysis. The test portion may be taken from the primary sample or directly from the laboratory sample. Usually, the test portion is taken from the test sample.

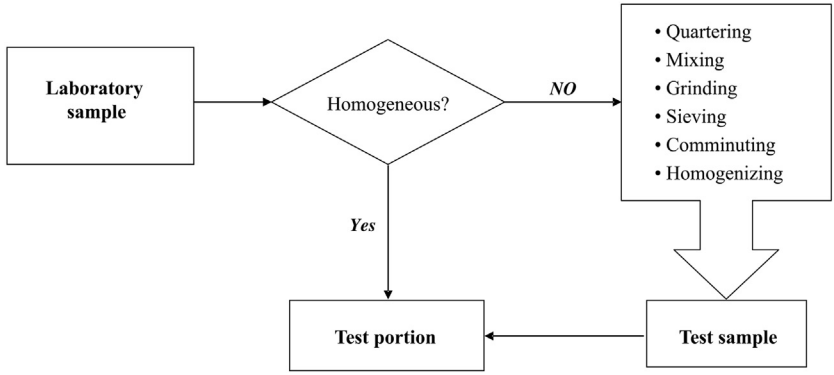

FIGURE 1.2 Diagram of the test portion sampling in the laboratory.

According to CITAC/EURACHEM [2], the analytical operations can begin by aliquoting a test portion directly from the laboratory sample, or from a test sample obtained after one or more pretreatments as shown in the diagram of Figure 1.2.

If the test portion is not representative, relating the analytical result to the original material will not be possible. This consequence does not depend on the quality of the method and/or the care taken for the analytes determination. Thus, it is important to notice that even by applying a validated analytical procedure carefully, an analytical problem will be solved only when the test samples are appropriate.

The sampling process always contributes to the uncertainty of the results, because the sampling process always introduces some error. The sampling process requires experience and knowledge regarding the problem and the chemistry related to sample preparation. If the result of the analysis is very relevant, a specialist with a knowledge of the entire analytical sequence must make the selection of one or more samples from the material of interest. When no specialist is available, the laboratory should enable the interested person to search for technical support to make the sampling as appropriate as possible. With the improvement in determination methods, which permit or require the use of smaller test portions, the uncertainty as a result of sampling becomes more important, since errors from inhomogeneities and sample transfer tend to increase, and this may increase the overall uncertainty of results. In the context of this chapter, the sample term can refer to either the laboratory sample or to the test portion that will be selected (weighed) for the chosen decomposition procedure. In this way, it should also be understood that

- the test portion should represent the laboratory sample;
- the test portion is homogeneous; thus, in some cases, it will be necessary to reduce the particle size (comminution), which is done using a suitable milling method;
- there should be no segregation of the constituents of the test sample during the selection of the test portion;
- the contamination risks must be predictable.

Guidelines and strategies for sampling freshwater [6], groundwater [7], wastewater [8], soils [9], sediments [10], and plants in terrestrial, semiterrestrial and aquatic environments [11], and an overview of the techniques commonly used for taking many different kinds of environmental samples for trace element analysis can be found elsewhere [12].

Additional information regarding general principles of sampling design and sample preservation for trace element analysis with considerations about sampling variability, sampling strategies, types of samples (judgment, random and systematic samples), and more are discussed by Kratochvil [13] in a reference book on sample preparation for trace element analysis edited by Mester and Sturgeon.

Generally, the sample should be converted into a suitable form for the sought chemical species before the determination. Only in few cases can the sample be analyzed without any pretreatment, which may or may not include some form of separation. In the analytical sequence presented by CITAC/EURACHEM [2], the operations begin by taking a test portion from the laboratory sample or the test sample. This is the situation prevailing in this book, and field sampling is treated elsewhere [4]. In many cases, the pretreatment is a separation method. The digestion (decomposition) of an organic material, for example, is a method that permits the separation of the organic fraction, keeping the analytes in a solution. In other cases, the analyte may be separated from the matrix by evaporation.

Anyway, the analyst must make sure that the signal attributed to the analyte in the measurement step is due only to the analyte and not to the presence of something that is chemically or physically similar to the analyte. This means a confirmation of the identity of the analyte. The possibility of interference by another chemical species occurring depends on the efficiency of the separation method and the selectivity/specificity of the measurement step. One aim of most separation steps during sample preparation is to remove interferences, and another is to concentrate the analyte. The analyst also should ensure that artifacts produced during sample handling do not generate a measured signal.

Selectivity and specificity are figures of merit that assess the reliability of the measurements in the presence of interferences. Although there is no universal consensus, a method is considered specific when it is 100% selective for the analyte. From a practical standpoint, it is necessary to check if the determination method can be used in the presence of concomitants (any chemical species other than the analyte present in the sample or in the sample solution) and specify the amount (concentration or mass) that may cause interferences. In the chosen determination method, this information must be clearly specified. Otherwise, it is necessary to validate or re-validate the method based on the selectivity/specificity. In this validation, the analytical chemist decides what the potential interferences are and tests them according to their occurrence in the samples.

1.2.4. Measurements

The analytical result is the final value of the concentration or amount of analyte in the sample. In general, this result is obtained from digital readings of a detector

that provides a measurement of a physical quantity such as emission intensity (atomic or molecular emission spectrometry, fluorescence, or phosphorescence spectroscopy) or absorption (atomic or molecular absorption spectrometry) at a specific wavelength. The physical quantity that contains information about the analyte concentration is termed the "analytical signal". The analytical signal is then converted to the analyte concentration through a calibration function. Data reduction of the analytical signal to a numerical answer is followed by data evaluation including statistical analysis.

1.2.5. Calibration

The conventional way to obtain a calibration for a chemical analysis is to submit known amounts of the analyte to a determination method and monitor the measurements obtained. In the analytical sequence, the functional relationship between measurements made from a series of properly prepared (solutions or solids) calibration standards is known as the calibration curve (or function). In atomic spectrometry, for example, the standard solutions are also known as reference solutions from which the calibration curve with signal intensity (background corrected) plotted as a function of concentration is prepared. A reference solution is one containing the analyte in the same solvent of the sample solution. For a matrix-matched standard solution, the standard solution contains some concomitant with the same concentrations as that of the sample. A blank solution is a solution that ideally does not contain the analyte of interest, but which has, if possible, the same matrix composition as that of the sample solution. A solvent blank contains only the solvent. The quality of the calibration depends on (1) the repeatability of the measurement, (2) the trueness of the standards, and (3) the validity of the comparison. Calibrations can be limited by poor signal reproducibility and/or uncertainties in the concentrations of the standards. These uncertainties are practically expressed as statistical confidence bands of the calibration function. Reducing the analytical signal to a numerical concentration value should include confidence limits reflecting the calibration uncertainties. This calibration approach is known as "external" calibration.

Certified reference materials and reference materials (RMs) with assigned quantity values can also be used for calibration and accuracy evaluation. These materials can be essential for the direct analysis of solids depending on the technique used. Figure 1.3 shows an analytical sequence, where one can observe the role of calibration and the tasks for method validation and quality control. The recovery tests (analyte addition), the use of appropriate RMs (consistent with the sample matrix), and other materials (secondary standards) are activities used in quality control, including the analytical blank, which is employed to estimate the detection limits.

Another calibration mode is internal calibration, in which a substance similar in chemical behavior and analytical response to the analyte is added to the sample and all standards. All measurements are ratios to the response of this "internal standard" (or "internal reference"). Selecting a suitable internal reference

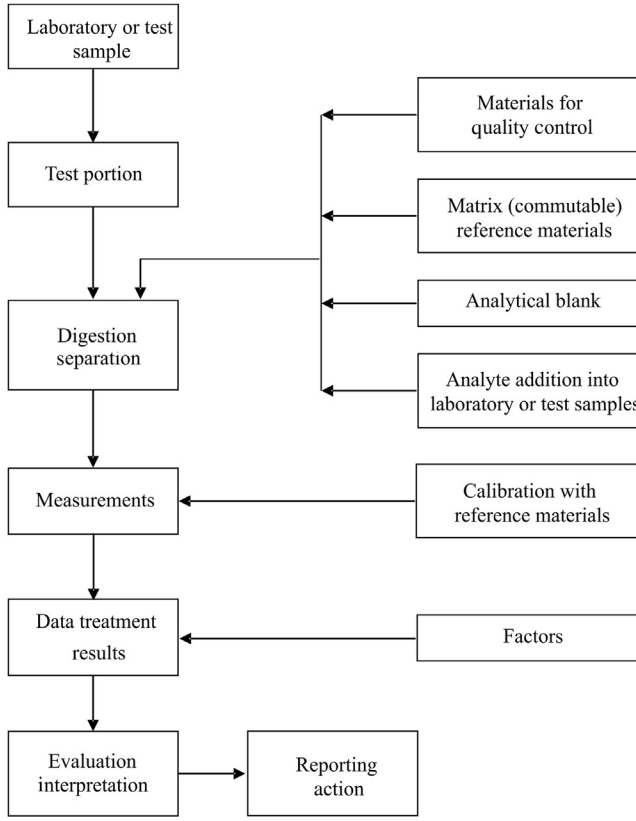

FIGURE 1.3 Diagram of an analytical sequence indicating the role of calibration and the steps or tasks to achieve results with metrological reliability. *Adapted from CITAC/EURACHEM [2].*

that behaves similarly to the analyte is a critical decision. This approach is applied when the analytical procedure is variable from measurement to measurement. For example, in flame or inductively coupled plasma (ICP) atomic and mass spectrometry, an internal standard can compensate for the variation in the sample viscosity or acid content after sample digestions.

The method of additions (analyte additions) is a calibration approach that utilizes the sample and its matrix as the base for calibration. A series of samples is prepared with known additions of analytes spiked to the sample. This series is determined, and the signal intensity plotted as a function of the known spike concentrations. The unknown sample concentration is calculated from the intensity of the unspiked sample signal intensity and the calibration function. The technique assumes that the unspiked sample signal is corrected for any background (blank) signal. The analyte addition approach is employed typically when the sample matrix is too complex to match with conventional standard solutions (e.g., petroleum sample analysis).

Another calibration protocol is isotope dilution. Here, a spike of a known amount but with a different isotopic composition is homogeneously mixed with the sample before the analytical procedure. The isotopic compositions of the initial (unspiked) and spike samples are determined typically by mass spectrometry, and the absolute analyte concentration is calculated. This very accurate approach compensates for analyte losses in the analytical procedure, and is invaluable in quantifying changes in speciation during sample processing. The technique is limited by the availability of isotopes, chemical state of the spike identical to the native substance, equilibration of isotopes during mixing, absence of contamination, and accuracy of the amount added.

1.2.6. Data Evaluation

Evaluation and interpretation of analytical data are critical steps in solving the initial analytical problem. Typically, result concentrations are obtained from calibration functions. Interpretation of results must be based on measurements from the corresponding test portions (digests in the context of this book) and from the series of calibration standards. Measurements from the analytical blanks, RMs, and other materials used for quality control are of key importance for appropriate data evaluation. For absolute methods like isotope dilution, titrimetry, gravimetry, and coulometry, calibration functions are unnecessary. However, all results should be verified by alternative measurements, analysis of RMs, or spiked additions recovery.

Statistical analysis provides numerical answers with error limits. Statistical tests help us to evaluate how well the numerical results obtained are related to the analytical objective. Furthermore, based on results, some steps in the analytical sequence may have to be repeated or changed owing to some unforeseen difficulty. Sometimes, a series of results is examined by chemometric techniques to reveal correlations and deal with large amounts of data, for example, for multielement determinations by inductively coupled plasma optical emission spectrometry (ICP OES) and ICP mass spectrometry (ICP-MS). Methods for processing multivariate data, grouping or clustering data, and classifying information require chemometric techniques. Chemometrics is the science of extracting information from chemical systems by data-driven means, such as multivariate statistics, including, for example, principal components analysis and partial least-squares. Chemometric techniques include multivariate calibration, classification, pattern recognition, clustering, including multivariate discriminant analysis, logistic regression, neural networks, regression/classification trees, and multivariate curve resolution, among others. Chemometrics is applied to solve both descriptive and predictive problems in experimental sciences, especially in chemistry [14–16].

1.2.7. Reporting/Advice

The analytical results will be used for a decision with respect to the original problem. In this sense, it is important that the analyst can interpret the results

generated during the sample analysis using a validated method and generate answers that are related to the analytical problem. The performance characteristics of the method, established during the validation process, will contribute to achieve a sound decision. The repeatability and reproducibility of measurements may be used to establish if the differences between the results are significant. The quality control, based on the validation data, can be used to confirm that the method is under control and produces reliable results. The estimation of the uncertainty of the measurements, in agreement with the method performance, allows the expression of results within a range of values, in which the most probable value (considered the true value) may be accepted with a certain level of confidence (e.g., 95%).

Remarks:

1. In routine analysis the problem and the choice of the method should be known in advance, noting that the method should be well established (validated).
2. Often the sampling is not done by the analyst, but by another qualified professional. Ideally, the analyst should always participate in the sampling process, and when this is impossible, he/she should participate in developing the sampling plan with a detailed description of the materials used.
3. The analyst will always have to provide the analytical results but is not always required and/or instructed to decide with respect to the definition of the analytical problem. In some cases, the uncertainties inherent in the method chosen may prevent or impair the decision making.
4. In many cases, the sampling process, the sample pretreatment steps, separation of the constituents of interest, quality control with RM, and the interpretation of results can be automated. An action can also be automated in an instrument of automatic process control.
5. Some analytical methods are absolute, such as the gravimetric and volumetric techniques, for example, which may dispense with the use of standards or calibration curves involving standard solutions or RMs.
6. Preliminary operations constitute the most severe bottleneck of the CMP, and a large portion of an analysis is spent preparing the sample for measurement [1], and sample treatment is quiet slow relative to the measurement and data process steps.
7. Preliminary operations are generally the largest sources of systematic and random errors that often arise from nonrepresentative samples, inappropriate sample storage conditions, incomplete removal of interferences, contamination and/or losses of trace analytes [1].

It is worth noting that among all analytical steps, the pretreatment of laboratory samples is the most critical. In general, this step is the most time consuming, costly, and where most of the mistakes occur. Therefore, the sample pretreatment procedure must always be carefully considered.

1.3. ANALYTICAL EFFICIENCY AND ROBUSTNESS

According to Anderson [3], essentially every analytical method includes some type of sample pretreatment, and most often, this step is the major part of the analytical work. Thus, when a method is evaluated to establish if its performance is adequate for analytical purposes, the pretreatment steps should be carefully considered. In summary, sample pretreatment significantly influences the following method characteristics:

- precision (repeatability and reproducibility of results);
- the trueness of the results;
- the total time, cost, and effort involved in the analysis.

In general, the selected method must be performed with the smallest possible number of pretreatment steps. However, this depends on the capacity of a method to provide analytical results with the appropriate metrological reliability. Several modern methods such as XRF, instrumental neutron activation analysis, laser ablation coupled to inductively coupled plasma mass spectrometry(ICP-MS), spark optical emission spectrometry, LIBS, solid sampling graphite furnace atomic absorption spectrometry (SS-GFAAS), eliminate or require reduced sample pretreatment compared to other method based solution samples.

One way to assess how effective an analytical method performs is to verify how its performance can be affected by varying factors that might change the quality of the results. These factors are generally identified during the development of the method, and their influence on the performance is evaluated using testing robustness. These factors should be carefully selected in order to evaluate the robustness, so that it is possible to identify the variables that can significantly affect the operation of the method. It is also necessary to ensure that these variables are under control during the application of the method. Generally, robustness tests are used to assess the effects on the precision and accuracy of the measurements, but other figures of merit such as the sensitivity and detection limit can be evaluated [17].

All these aspects show the complexity of the successive tasks typically involved in a chemical analysis. Moreover, it demonstrates the degree of expertise required to plan and run the analyte determination with an adequate degree of reliability. We recommend reading the guide edited by CITAC/EURACHEM [2], which aims for the best practice of the analytical operations in the laboratory. The guide also assists in the implementation of Quality Assurance, explaining the meaning of quality requirements for accreditation, certification, or laboratory's commitment. We do also recommend another important guide from EURACHEM [17] for more information on method validation.

1.4. SYSTEMATIC ERRORS IN SAMPLE PREPARATION

According to Tölg and Tschöpel [18], systematic errors are mainly due to the insufficient qualification of the analysts and/or to inadequate laboratory's