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1 Sample Preparation for Inorganic Trace Element Analysis

1.1 Introduction

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Many modern instrumental techniques require complete sample dissolution prior to an analysis. In other words, these techniques generally involve the introduction of samples as aqueous solutions to the flame, furnace, or plasma. A variety of techniques are employed from ambient pressure were digestion in a beaker on a hot plate (or hot block) to specialized high-pressure, high-temperature microwave heating. Although the concentrations of the trace elements in the bulk of the sample are still mainly of interest, data on their distribution of the surface of the sample, in microregions, or phase boundaries, have become increasingly important. Further speciation analysis is also required.

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In this chapter, the role of sample preparation in trace element analysis, including the sequence of analytical steps, systematic errors, preliminary treatments, wet and dry decomposition, and combustion and fusion decompositions prior to main spectroscopic methods of analysis, will be discussed. Within the general area of inorganic trace analysis, the coverage will be restricted to environmental, bioinorganic, forensic chemistry, and industrial trace element analysis.

In modern trace analysis, the term **sample preparation** cannot be exactly defined and covers a very broad field. It starts with mechanical pretreatment of the sample, for example, cleaning, drying, grinding, sieving, and filtering prior to instrumental methods of analysis, and extends to chemical methods, for example, digestion, decomposition, extraction approaches, separation, and enrichment required for a wet chemical procedure in which the solid, liquid, or gaseous samples are prepared and passed onto the real determination step.

Sample preparation depends on the nature of the sample, the analyte to be determined and their concentrations/amounts, and on the desired determination precision and accuracy. Sample preparation, is, however, inherently expensive and time consuming, and is responsible for the major source of errors in the various stages of an analytical procedure.

We will therefore discuss, in this chapter, mainly the physical and chemical operations that precede the real determination step of the multistage combined procedure.

1.2 Aspects of sampling and sample preservation

The importance of adequate sampling was recognized by leading authorities a considerable time ago, yet it would appear that the level of practice among many

investigators left much to be desired. Thus, the warning issued by Thiers in 1957 [1] that "unless the complete history of any sample is known with certainty, the analyst is well advised not to spend his time analyzing it" was largely ignored for several years. No universally accepted definition for this term or other nomenclature in this area exists. Sampling can mean one thing to a statistician and have some other connotation to a technician collecting a sample, an analyst examining a sample, or an administrator determining whether a sample meets the requirements of a law or a contract. Definitions of terms have always been a matter of concern in sampling, and efforts are being made to clarify the situation. For example, the International Union of Pure and Applied Chemistry has prepared a document proposed by Horwitz [2] intended to furnish concepts, terms, and definitions in the field of sampling relevant to analytical chemistry and that are generally applicable regardless of what sampling objective, commodity, location, quality, or form is involved.

Sampling for subsequent trace analysis is without doubt by far the most crucial step in an analytical procedure and is the last step of the preanalytical phase that can possibly affect the accuracy of the analytical results via interference factors. If not properly planned and practically performed by using appropriate sampling tools with the utmost care and expertise, total, systematic, as well as random, errors for sampling can range from a small percentage to several orders of magnitude.

The purpose of sampling is to extract a representative amount of material from a **lot** – **the sampling target**. According to CITAC/EURACHEM [3], 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. A verified sampling plan with well-defined procedures for selection, collection, storage, transport, and preparation of the sample is essential, and the reader should consult expert resources for details [4, 5]. It is clear, in trace analysis, that sampling must always be followed by an appropriate stabilization (preservation) step, with due regard for the nature of the matrix and the analyte and can only be optimized before analysis. It is shown how nonrepresentative sampling processes will always result in an invalid aliquot for measurement uncertainty (MU) characterization [6].

A specific sampling process can either be **representative** (in some cases, it can be replaced and better understood as **appropriate**) or not. If sampling is not representative, we have only undefined, mass-reduced lumps of material without provenance that are not actually worth analyzing. Only representative aliquots reduce the MU of the full sampling and analysis process to its desired minimum; and it is only such MU estimates that are valid. Sampling **correctness** and representatives are essential elements of the sampling process. Representativeness implies both correctness and a sufficient small sampling reproducibility (sampling variance).

The starting point of every measurement process is the primary lot. The lot (also termed the sampling target or decision unit) refers both to the physical, geometrical form and size and the material characteristics of the material being subject to sampling. All lots are characterized by significant material heterogeneity – a concept

only fully acknowledged and defined by the theory of sampling (TOS) – where it is crucially subdivided into constitutional heterogeneity and distributional heterogeneity. Heterogeneity is the prime characterization of all naturally occurring materials, including industrial lots. Heterogeneity manifests itself at all scales related to sampling for nearly all lot and material types. The heterogeneity concept is introduced and discussed in complete detail in the pertinent literature [7, 8]. The full pathway from **lot to analytical aliquot** is complex and is subject to many types of uncertainty contributions in addition to analysis. TOS focuses on the conceptual and practical active steps needed to minimize all sampling contributions to MU.

According to the available information regarding the candidate test site and the requested sampling station network resolution, quite a number of sampling approaches have been developed, a few of which are mentioned here, such as random sampling, systematic sampling, representative sampling, and subsampling. All approaches have their merits, and the selection of the most appropriate sampling mode depends on a number of boundary conditions.

1.2.1 Sample

This is a correctly extracted material from the lot, which can only originate from an unbiased, representative sampling process. The term sample should always only be used in this qualified sense of "representative." If there is doubt as to this characteristic, the term "specimen" should be used instead.

1.2.2 Specimen

This is a "sample" that cannot be documented to be the end result of a bona fide representative sampling process. It is not possible to ascertain the representatives status of any isolated small part of a sampling target by itself. It is only the **sampling process** that can be termed representative or not.

1.2.3 Random sampling

Random sampling is the arbitrary collection of samples within defined boundaries of the area of concern and is directed at obtaining an extreme value, such as the best or worst case. The selection of sampling points must be performed in a way that gives all locations within the boundary of the test area the same chance to be selected. The basic assumption for choosing the random sampling approach is that the test area is homogeneous with respect to the pollutants to be monitored. The higher the heterogeneity of the area is, the lesser the random sampling approach shall produce the correct information needed for the complete future cleanout of the area. This means

that progressive information with regard to the pollutants of concern is needed prior to sampling, which is usually not the case.

In random sampling of an entire lot of bulk material, the material is divided into a number of real or imaginary segments. Because of its simplicity, sampling at evenly spaced intervals over the bulk is often used instead of random sampling, although results must be closely monitored to prevent errors from periodicity in the material.

1.2.4 Systematic sampling

Each sample collected systematically and analyzed to reflect or test some systematic hypothesis, such as changes in composition with time, temperature, or spatial locations, should be considered representative of a separate, discrete population under the existing conditions. However, the results may still be statistically tested for the significance of any apparent differences.

A carefully designed sampling plan includes the possibility of unanticipated events of phenomena that could prejudice the analyses. For example, measurements at timed intervals are sometimes made with random start or other superimposed random time element. The less known about a given process, the more randomness is merited. Conversely, the more fully a process is understood, the more efficient is a systematic approach to date acquisition.

1.2.5 Representative sampling

Representative sample frequently connotes a single sample of a universe or population expected to exhibit average properties of the population. It is not possible to select such a sample by a random process or to verify whether it is representative. A truly representative sample seems valid only if the sample is defined *a priori* as representing a specific purpose.

Although it may reduce costs, measurement of samples defined as representative yields information not equaling that from valid random samples of the population, except when the population is homogenized before sampling to produce a number of similar subsamples. A properly designated and executed random sampling plan provides sample mean and variation between members, neither of which can be obtained by analysis of one **representative sample**.

1.2.6 Composite sampling

Until here, single-sample approaches have been considered. For a number of good reasons, composite sampling schemes might be preferred, one and not the least of the reasons being identified in analysis cost.

A composite sample may be considered a special type of representative sample. A composite sample represents **physical averaging**, as opposed to arithmetic averaging of analytical results from individual increments. Many sampling procedures assume that only average composition is desired, such as bulk, time-weighted, or flow-proportional averages, and specify collection or preparation of a suitable composite. Elaborate crushing, grinding, mixing, and blending procedures have been developed and standardized for preparing solid composites.

Analysis of individual samples permits determination of the average (at the expense of additional analytical effort), of the distribution of samples within the population (between-sample variability), and of within-sample variability (if replicate analyses are conducted). Composite samples provide limited information, and the consequences should be carefully considered before deciding between this approach and the analysis of individual samples.

1.2.7 Subsampling

Subsample is a correctly mass-reduced part of sample (primary, secondary, etc.). A subsample is a result from a dissociative (disaggregation) process; a composite sample is a result from an integrative process. Subsampling is necessary because the sample received by the analytical laboratory is usually larger than that required for a single measurement. Test portions taken for replicate measurements of different constituents by several techniques must be sufficiently alike so that results are compatible. The effort necessary to reduce particle size, mix, or otherwise process the laboratory sample before withdrawing portions (subsamples) for analysis depends on the homogeneity of the original sample.

It is obvious that a major requirement for trace element analysis is that specimens be taken under noncontaminating conditions and thus avoiding all kind of losses; the specimen and the sample derived from it must exactly reflect the properties of the matrix. The number and types of samples and sampling devices are too diverse to enumerate here, but some general principles and recommendations will be given for collecting samples in which trace metals are to be determined. Ideally, all sampling devices, tools, and containers should be constructed from plastics with a low content of trace metals, such as one of the Teflon, or polyethylene (PE). By removing all metals from the sampler, a major source of contamination is eliminated. Of course, there are many instances in which this is not practical or possible. In these cases, the best alternative is to select a high-purity material that will produce no consequential contamination. In general, for trace analysis, sampling tools made from stainless steel, such as titanium and ceramics for blades, or highly pure materials like nickel for needles should be used. In this case, there is only one element that cannot be analyzed due to high blanks. By now it is obvious that a major requirement for trace analysis is that the sample be taken under noncontaminating conditions. There are those who

will object to the cost or dispute the necessity of applying clean room conditions to all sampling operations [9]. The use of noncontaminating implements and samplers, as well as complete portable clean room facilities, has become a well-established procedure among many geochemists and oceanographers working in pristine environment. In addition to contamination by vessels and tools, samples can also be contaminated by reagents, which have to be added as stabilizers, anticoagulants, and preservatives [10], especially because they are often added in excessive amounts.

The second important step of the preanalytical phase is the storage (preservation, stabilization). In trace analysis, sampling must always be followed by an appropriate preservation and/or stabilization step, with due regard for the nature of the matrix and the analyte.

Unfortunately, many materials are not stable once they have been sampled and seldom can samples be analyzed immediately after collection; they need to be stored for a certain period. Samples may deteriorate by trace element adsorption, losses from aqueous samples, particle segregation in heterogeneous powders, dehydration or bacterial growth in biological samples, or by decomposition of the sample matrix and the formation of volatile compounds of the trace element analytes. Stabilization techniques exist for most of these problems, but they must be noncontaminating and the apparatus used for this process must be evaluated for contamination potential.

Liquid samples, such as water (drinking, surface, waste water), beverages, fruit juices, urine samples, etc., should always be acidified with mineral acids to pH < 2 (HNO_3, HCl, and $HClO_4$, all of the highest purity grade) immediately after collection for stabilization purposes to avoid losses due to wall adsorption and also inhibit bacterial growth. However, the pH should also be selected in accordance with the requirements of the subsequent analytical steps.

Losses of elements may occur through the formation of insoluble products that are strongly adsorbing to the wall of the container, co-precipitation with the main inorganic and organic constituents of the matrix, the formation of volatile compounds that penetrate the plastic, and also the formation of compounds that are unsuitable for the subsequent analytical procedure. Most of these detrimental effects are diminished or eliminated by the addition of sufficient amounts of preservative. Contamination during storage is due mainly to the material of the containers. A wide variety of sample container materials for bottles, flasks, tubes, and vials can be used, the most common being polyfluorocarbons (polytetrafluorethylene (PTFE), PFA), PE, polypropylene (PP), polyvinyl chloride (PVC), polycarbonate (PC), high-purity quartz, and borosilicate glasses.

Loss of water from aqueous matrices (e.g., tissue, fruit, vegetables, and soil samples) may occur during storage. For this reason, analytical results should always be reported in terms of dry mass to avoid false interpretations. Drying is best conducted immediately after sampling. Water removal can be accomplished by oven drying at elevated temperature, use of desiccating materials, or freeze-drying (lyophilization). Freeze-drying has been shown to be the most satisfactory procedure since it

minimizes the loss of highly volatile elements and compounds, and as at low temperatures fewer alterations of the biological material occur and the formation of insoluble substances is also decreased.

Liquid samples requiring preservatives, such as blood and urine, are preferably stored at +4 °C, provided that they will be analyzed within 2–3 weeks. If a longer storage period is necessary, however, the best way to store biological material is to maintain it at temperatures around –20 °C until analysis. In the storage of tissue, it is important to know whether the entire specimen or an aliquot sample representative of the mean value of the specimen will be submitted for analysis. In the first case, no special precaution is needed. After determination of the fresh weight and, if the specimen is dried, the dry weight, the specimen is cooled as soon as possible to –20 °C or below. At this temperature, bacterial and chemical interactions are largely diminished. During freezing and thawing, the structure of the specimen will be altered by the rapture of membranes and outflow of intracellular liquid; however, since the total specimen will be analyzed, the accuracy of the analysis will not be affected. If storage over several years is envisaged, the sample should either be dried at –18 °C or quick-frozen in liquid nitrogen at –196 °C and then stored at or below –70 °C.

Determination of an analyte in serum or plasma requires that the analyte be isolated subsequent to sampling. This is no longer possible after deep-freezing because of the hemolytic nature of blood samples. In case of elements at very low concentration, it is preferable that an investigation be conducted on serum rather than plasma. This reduces the risk of contamination because unlike blood plasma serum is recovered without addition of an anticoagulant.

The risk of contaminations persists during the entire storage period. Thus, if the biological samples cannot be analyzed immediately, they should be kept in an adequately controlled environment or hermetically sealed in a proper material, for example, plastic. So, in general, samples should be stored at low temperatures in cleaned containers made of proper materials [11, 12].

Additional information regarding general principles of sampling design and sample preservation for trace element analysis is discussed by Kratochvil [13] in a book on sample preparation for trace element analysis.

1.3 Error sources during the analytical procedure

Error (systematic error) relating to a trace element analysis may occur at all points from sampling through to the determination step. Systematic error arises whenever the actual nature of the measurement process differs from that assumed. For a measurement to be both accurate and precise, the measured value must be both accurate and precise and must be corrected for all sources of systematic error or bias, and the true value must lie within the stated level of confidence. Systematic errors as a rule become evident at the μg/g concentration range and increase enormously with

decreasing absolute amounts or concentrations of the elements to be determined. They can exceed several orders of magnitude, depending on the omnipresence and the distribution of the elements in our environment and in the laboratory. Abnormally high values in the analysis may result from the contamination by airborne dust, reagent blanks, and container material. Of course, as usually a blank value is subtracted, such errors are in principle corrected. A high blank thus primarily affects the reproducibility and the limit of detection of an analysis.

There exists no chance to discern systematic errors by statistic evaluation of the analytical data, especially because the most important condition for a statistical treatment of data, which are supposed to display a normal distribution, very often does not apply. Further, no other simple means for the detection of systematic errors are available. Systematic errors depend strongly on the element to be determined, on the matrix, on the method and procedure used, on the conditions of the laboratory, and on some other parameters.

The most important sources of systematic errors [14] are:

- inadequate sampling, sample handling and storage, in homogeneity of the sample;
- contamination of the sample and/or the sample solution by tools, apparatus, vessels, reagents, and airborne dust during the analytical procedure;
- adsorption and desorption effects at the surface of the vessels and phase boundaries (filters, columns, and precipitates);
- losses of elements (e.g., Hg, As, Se, Cd, and Zn) and/or compounds (e.g., oxides, halides, and hydrides of the elements) due to volatilization;
- unwanted or incomplete chemical reactions (e.g., change of the valence of ions, precipitation, ion exchange, formation of compounds and complexes);
- influences of the matrix on the generation of the analytical signals (incomplete atomization, overlap of peaks); and
- incorrect calibration and data evaluation as a result of incorrect standard materials, unstable standard solutions, or the use of false calibration functions or unallowed extrapolations, respectively.

A survey of systematic errors in decomposition methods [15] is given next:

- Errors resulting from contamination from
  1. the atmosphere (the air, laboratory environment), the sampling;
  2. reagent impurities; and
  3. materials (vessels, tools).
- Errors as a result of losses of elements by
  1. volatilization,
  2. adsorption on the vessel material, and
  3. reactions with the vessel material
- Errors resulting from incomplete sample decomposition or dissolution

This contribution will mainly deal with the most serious sources of systematic errors of multistage procedures: element losses due to volatilization and adsorption as well as the contamination due to the three most important blank sources: tools and vessels, reagents, and laboratory air and dust.

1.3.1 Blank

Masking of components in a sample, severe interferences with detection, uncertain qualitative analysis, and unreliable quantitative measurements are all problems in trace analysis potentially connected through a common factor, **the blank**. Few analytical techniques are free from the influence of these difficulties. Even though the threshold for measuring trace constituents has been lowered significantly with the discovery and development of techniques with high sensitivity, the full potential for measurement by spectrophotofluorometry, polarography, anodic stripping voltammetry, kinetic and spectroscopy methods, and other techniques with sensitivities sufficient for measuring elements at the nano/picogram level is precluded in many practical applications.

In the case of the inability to reproducibly control the blank at levels insignificant in comparison with the constituent being determined or where difficulties associated with quantitatively manipulating and recovering submicrogram quantities of trace elements exist, the limits at which trace elements can be measured by most techniques will be established by these restrictions. In the presence of constantly fluctuating blanks, the accuracy and precision of quantitative trace measurements are also influenced significantly. Thus, first-order improvements in the reliability of measurements at or below the ppm/ppb/ppt region depend greatly upon controlling and reducing the size of the blank and, where possible, eliminating its effects.

Contamination from particulates in air, impurities in reagents, and trace elements from containers is considered to be primarily responsible for the blank. Hazards from less conspicuous sources, including instrumental noise interpreted as a signal from a component of the sample, must be considered as well [16]. Since considerable attention by analytical chemists to these problems is necessary in trace analysis, state-of-the-art techniques for providing pure atmospheres and working conditions, for purifying and storing ultrapure reagents, and for performing routine analytical procedures under ultraclean conditions are subsequently discussed.

1.3.2 Contamination

Contamination in trace analysis is always understood as the increase in the measured amount or concentration of a component, resulting from its introduction at various stages of the analytical procedure, from several independent sources other than the sample and can occur at any point. These are the air, laboratory atmosphere and working areas, reagents, tools, and apparatus associated with sampling and sample preparation, and laboratory ware; these will be discussed in sequence.

The atmosphere of the laboratory is loaded with particulate matter from different sources such as the environment, floor, walls, ceiling (paint), furniture, equipment, clothes, analyst himself, and so on. Accordingly, various inorganic and organic compounds are present and, in principle, any element can be found, depending on the environment, the laboratory itself, and its history. Thus, the composition of the air in the laboratory will often approximate that of the surrounding atmosphere and will fluctuate with prevailing atmospheric conditions. Again the dust particles will contain relatively high concentrations of those elements that show a high abundance in the Earth's crust (e.g., Si, Al, Fe, Ca, Na, K, Mg, P). In addition, all elements of anthropogenic pollution (e.g., Mg, Cu, Cd, Pb, Ni, Co, Zn, Mn) are always present. Dust and particles brought to, and released or created in the laboratory by the activities of personnel, appear as a more abundant and critical source of contamination [17].

When the dust comes in contact with the sample, it is a severe source of contamination. Sometimes, protection may be achieved with a cheap and very simple means, such as closed vessels and apparatus or glove boxes. Ideally, trace analytical work depending on conventional techniques should be carried out in a high-class clean air laboratory. More efficient and convenient are **clean** rooms and clean benches [18], which are flushed with dust-free air. A clean room is an area that is hermetically separated from the outside atmosphere and that is only accessible through an air lock. A filter assembly provides for pure air at an overpressure against the outside atmosphere and for circulation with a turbulent flow. A clean hood also reduces particles and dust in laboratory air. A much cheaper and simpler solution for reducing blank values due to contamination from laboratory air is the use of evaporation chambers [18]. The major development for providing particulate-free air is the so-called high-efficiency particulate air (HEPA) filter [19], which has a definite pore size of 0.3 μm. The dust removal efficiency by the deposition on the filter is about 99.97–99.95 %. The quality of a clean room or clean bench is expressed by the number of particles per cubic foot having a diameter between 0.5 and 5 μm and one distinguishes between the classes 100, 10,000, and 100,000. Typical is "class 100" or "class 10," meaning less than 100 or less than 10 particles per cubic foot of air. The use of a clean bench in a clean room illustrates only one possibility. Another more expensive alternative is to keep the whole clean room as dust-free as possible. This can be achieved with the aid of a laminar air flow that enters the room through a HEPA filter installed over the whole area of one wall or the ceiling [18]. For advanced technologies, however, still much higher-purity demands now exist. For instance, the electronic industry claims a much lower dust content for the production of megabyte chips (class 10 or 1 according to the US Federal Standard). For trace analysis, however, this enormous effort to get such a high air quality is only rarely necessary.

Availability of clean air facilities, however, does not in itself guarantee dust-free conditions. The placement of equipment or containers, too high exhaust velocities, room draughts, or an operator working (the number of persons in the laboratory) near the fume-hood can distort laminar flow, cause turbulences, and dramatically affect

the performance of clean air installations. Also, the weather plays an important role; when it is raining, the air generally is essentially purer than when it is dry.

Contamination in trace analysis is comprehensively dealt with in the book by Zief and Mitchell [20] and by Mitchell [21]. It initiated extensive follow-up work, which has made an essential contribution to our understanding of the problem. Advances in contamination control are also the subject of a recent survey by Barnes et al. [22] in a book on microwave-assisted sample preparation for trace element determination edited by de Moraes Flores and Mitchell in his review paper [23]. Supplementary information on systematic errors caused mainly by contamination and losses of elements can be found in comprehensive monographs dealing with trace elemental analysis from Knapp and Schramel [24] and Hoffmann [25].

1.3.3 Reagents

Reagents used in sample preparation are another very common source of contamination. Reagents used that come into contact with the sample or standards, such as water, acids, bases, solvents, salts used as matrix modifiers, buffers, supporting electrolytes, fluxes, oxidants and reductants, chelating agents, and other reagent chemicals, must be of the highest available purity. At least as importantly, they must be stored and handled in such a way as to maintain this level of purity. Some of these needs for pure reagents have been met by commercial suppliers who have focused their attention on this problem and have introduced special lines of ultrapure, super pure, or electronic-grade reagents and metals. Because specific attention has been given to the proper handling, containing, analysis, and storage of reagents, levels of many trace elemental impurities in commercial lots of chemicals have been reduced considerably. The dynamic interplay between preparation, handling, containment, and analysis of ultrapure chemical standards and reagents for the clinical chemical laboratory is described [26]. Even though an overall improvement in the quality of several suppliers' chemicals has been accomplished, for most ultratrace analyses the analyst must still verify that the purity of any purchased reagent is sufficient for the intended analytical application. Reagent impurities capable of interfering with the analytical measurement should be so low that they give a blank value that is less than 10 % of the analyte level. Although reagents sufficiently pure for many applications are available commercially, the analytical laboratory committed to ultratrace determinations of a variety of elements must also be able to produce a wide range of pure reagent chemicals itself. For many analytical problems, the level of a specific contaminant of interest can be adequately controlled only by designing a special laboratory purification method. The basic analytical reagents can now be ultrapurified on the laboratory scale with relative ease by a number of techniques. Accordingly, in extreme trace analysis, we often have to use only those reagents that can easily be purified, such as gases and liquids [27, 28].

Ultrapure water is the most abundantly used analytical reagent, and the preparation of ultrapure water, for example, by distillation below the boiling temperature (sub-boiling, nonboiling) in a quartz [29] or PTFE [29, 30] stills or by membrane processes and its permanent quality control, is of greatest importance. The term sub-boiling distillation was coined and the first publication produced by 1972 [31]. Regarding membrane processes, three membrane processes are widely used in water purification systems: reverse osmosis, ultrafiltration, and microfiltration. A fourth process, ultramicrofiltration, is sometimes identified as lying between ultrafiltration and microfiltration. The processes are differentiated from one another by virtue of the different ranges of pore sizes found in the membranes. The reverse osmosis is a membrane separation technique using a material through which water molecules will pass but solute molecules will not. Unlike ultrafiltration, in which separation of substances is based solely on molecular size and form, reverse osmosis membranes retain ions of a size comparable to that of the water molecule. The next method of water purification is deionization (sometimes called demineralization). Most laboratory deionizers are mixed-bed cartridge units in which cation-exchange and anion-exchange resins act in concert to remove ionic contaminants (mainly inorganic salts) from the feed water. In many laboratories, it may be desirable to preprocess the deionizer feed water using a reverse osmosis unit or mixed bed ion exchanger, thus removing most of the dissolved salts before the final purification step. Normally, the purified water production must be conducted in a laboratory with appropriate air cleanliness and stored in vessels or containers free from contamination. The quality of this reagent, needed in large volumes for dissolving samples and preparing solutions, must be periodically monitored by quantitative analysis [32–36]. Since water of absolutely purity has virtually no conductance, the easiest and fasted method of measuring water purity is by measuring conductance (reciprocal of resistivity) with a meter made for this purpose [37]. Readings are expressed in μs/cm. On the other hand, a resistivity >18.2 MΩ cm is an indication of quality, but is not necessarily a certificate of high-purity water.

High-purity reagents do not always satisfy the standards required by extreme trace element determination since the control of impurities is usually restricted to only a few elements. Liquid decomposition reagents (e.g., nitric, sulfuric, hydrochloric, perchloric acids) and some organic solvents in a highly pure quality can be obtained by the so-called sub-boiling distillation [30]. The distillation made of quartz, PP, or PTFE should be used for the purification of acids (except HF) and water. The purification is based on evaporation of the liquid by infrared heating at the surface to avoid violent boiling [25]. In this way, the formation of liquid aerosols that are transported with the distillate is avoided, which in the conventional distillation technique contaminates the distillate. The residual impurities for sub-boiled liquids are at the pg/mL level, which is sufficient for most of the ultratrace procedures. The yield of such a sub-boiling still amounts to some 100 mL per day. This is sufficient for most purposes in

ultratrace analysis purposes due to unavoidable contamination during storage. Therefore, only that volume of acid required for the immediate use should be prepared. Apart from this technique, no other universal (single) purification procedure is capable of removing all metallic or cationic impurities to such a low extent. It should be noted that sub-boiling distillation ensures the separation of impurities of low vapor pressure such as metal ions, but it does not eliminate impurities having high vapor pressure such as organic compounds or some anions [30].

One means that has been used to overcome the formation of liquid aerosols that are transported with the distillate is isothermal (also called isopiestic) distillation [38–40]. In principle, if containers of volatile reagent-grade acids (HCl, HBr, CH_3COOH, HF) and NH_4OH and pure water are placed in a sealed chamber (such as large desiccators), acid vapor will be absorbed in the pure water until an equilibrium vapor pressure is reached. This isopiestic distillation is the room temperature version of the sub-boiling method (which it preceded) and produces a highly pure but medium strength product. The latter problem can be circumvented by saturating pure water or isopiestically prepared reagents with pure gaseous compounds, NH_3, HCl, and HBr, for example. The method for HF purification based on a combination of isopiestic and sub-boiling distillation resulting in increase in production rate has been reported [41]. The purity of the distilled water and purity of the container largely determine the quality of reagent produced.

Reports of quantitative determination of trace elements by electrodeposition and anodic stripping imply general utility of electrochemical methods for ultrapurification of reagent chemicals. Electrodeposition is a very interesting tool for separation of ultratrace concentrations from salt solutions as these are good electrolytes and as electrolysis techniques suffer from contamination only to a very low extent [42]. For example, the constant current electrodeposition of trace elements (Cu, Cd, Co, Fe, Ni, Pb, Zn) onto a graphite tube cathode from highly concentrated NH_4F solutions was studied. The deposition yield of >99 % was achieved in the ng/mL range (and below) so that a solution of high purity was obtained [43, 44].

Electrolysis at the mercury cathode has been recognized for decades as being potentially extremely effective for purifying aqueous solutions of various reagents [27]. In principle, any reagent soluble in water can be purified by electrolysis at the mercury cathode, provided its component ions are not electroactive at the applied cathode potential required for reduction of the impurity ion. Electrochemical inertness at the anode potential is also required. Additionally, the reagent solution must be chemically inert with respect to reaction with mercury (including dissolution of the mercury).

In general, all reagents should be checked for contamination before use by analyzing **reagent** or **sample** blanks containing all the reagents in the same concentrations as would be present in the final sample solution. Any reagent that is shown to be contaminated must be discarded; for this reason, it is often a good idea to purchase these high-purity chemicals in small quantities.

1.3.4 Materials

Materials used in the construction of buildings are known to contribute atmospheric pollutants or produce particle fallout. Calcium in trace quantities can be constantly emitted from materials commonly used in walls and ceilings. Paints containing metallic pigments are chipped, flaked, or abraded from walls and furniture. Stainless steel hoods, sinks, and other furniture, copper faucets and pipes, gas regulators, metal heating and air conditioning units, and other metallic objects usually corrode after prolonged use under normal laboratory conditions. Metallic dusts from these objects contribute significantly to particulates in the atmosphere of the laboratory.

No vessel material is absolutely resistant even to water. The vessel material in contact with the sample during the decomposition or dissolution also frequently causes systematic errors. Elements can be either dissolved from the material or desorbed from or adsorbed on the container surfaces. Therefore, all vessels used to contain samples, standards, or reagents used in the analysis should be checked and shown to be free of contamination before they are used. It is preferable to set aside a set of vessels for trace analysis only. Especially glass, which contains a number of elements as major or minor components and a lot of other elements at a very high trace level, is very impure as compared to quartz, PTFE, PP, and PE [45]. In addition, the losses of elements due to adsorption are very high. Therefore, glass vessels should not be used for element determinations in the extreme trace range.

Vitreous silica, especially artificial quartz, is the most pure material that is commercially available in different purity classes but unfortunately quartz containers (and tools) are also the most expensive ones. They definitely deliver negligible blanks (except for Si), low wall adsorption, temperature resistance up to 1,200 °C, and high resistance to most inorganic acids with the exception of HF and concentrated phosphoric acid.

Fluorinated polymers PTFE (Teflon), PFA (Teflon), and TFM (Hostaflon) are substantially less pure. Nevertheless, they are much more cheaper than quartz and therefore they are preferred in most of the routine laboratories, especially used as the digestion vessels, but exhibits very variable quality depending on its origin. The maximum digestion temperature for such vessels is about 250 °C. The advantage of these materials is their resistance against nearly all acids, and they can therefore be used for sample digestion with HF. Contamination from the vessel material is not a problem. In general, PTFE is not as good as the other two materials because of its porous structure, which arises from the sintering process used for the vessel production. TFM is a chemically modified PTFE (PTFE modified by Hoesch) and does not suffer from the porous structure of PTFE.

FEP is an excellent material for storage containers because of its dense and nonpolar surface. Losses of polar ions via adsorption effects can mostly be neglected. It is also used for liners of digestion bombs, but must not be heated above 200 °C.

The polymer FEP is purer than conventional PTFE and is thus recommended for procedures aiming at the determination of trace elements.

PE and PP are stable up to 135 °C and are successfully used for storage containers, beakers, and flasks, but they are not as good as FEP, although they are less expensive.

Glassy carbon is used for high-temperature digestion vessels. It is also resistant against most acids; however, it is not resistant to oxidation. For example, oxidizing reagents such as nitric acid significantly attack the surface at elevated temperatures. Another disadvantage is a comparatively high risk of contamination; glassy carbon is not as clean as quartz glass or fluorinated polymers.

Especially during sampling, one has to avoid the sample to come into contact with other materials causing severe contamination. Therefore, for example, rubber is not a suitable material because of its relatively high contents of Sb, As, Zn, Cr, Co, and Sc. Nylon contains Co and PVC Zn, Fe, Sb, and Cu at the higher trace level. In addition, contamination in a trace element laboratory can come from a laboratory gloves (vinyl, latex), contaminated samples by Zn and Fe [46], or, for example, from micropipette tips [47].

With regard to the vessels and tools, their bulk material is not the only source of contamination. The other contamination source is impurities at the surface. In addition to the selection of a suitable material (container, vessel, tool), an appropriate preconditioning of the material surface is necessary to minimize adsorption or desorption. To minimize or eliminate such impurities, proper cleaning procedures are necessary. The conventional cleaning technique for laboratory glassware consists of its rinsing and leaching with high-purity acids (HNO_3, HCl) and pure water. In addition, leaching can be supported by applying ultrasonic treatment. Decontaminating the surface of containers by extracting with chelating agents is recommended as well. However, leaching is very expensive and time-consuming and it requires large volumes of pure, high-purity or even ultrapure acids, which will become a waste problem because of environmental contamination. Another disadvantage is the fact that the cleaned vessels remain in contact with the acids now enriched with impurities, by which they are again contaminated. Therefore, in many cases these procedures are not effective enough so as to guarantee for residual blanks down to the lower pg/mL region.

A very effective and much less time-consuming cleaning of quartz vessels can be achieved by steaming with acid vapor described by Knapp [48]. This method can also be applied to vessels and tools made of borosilicate glass, PTFE, TFM, PFA, and glassy carbon. For purification, the vessels are continuously exposed to the hot vapor of the purifying liquid. By steaming the vessel with nitric acid or hydrochloric acid, the surface is cleaned from adsorbed matter and conditioned in such a way that adsorption phenomena are greatly reduced.

Especially during sampling and sample preparation, there is an inevitable risk of contamination by tools for cutting, drilling, milling, sieving, crushing, grinding, and pulverizing. Metal contaminations of biological tissues and fluids with Cr, Ni, Co, Fe,

Mn, Cu, and others due to use of scalpel blades and syringe needles are observed. Therefore, the use of forceps, knives, spatulas, and needles made of plastic, titanium or quartz is recommended. Tools (scalpels and knives) made of corundum single crystals (Al_2O_3) grown artificially were found to be excellent for clean preparation of biological samples [49]. Biological tissues in contact with the surface of a common surgical instruments (scalpels and knives) become contaminated with virtually all trace elements, particularly with Cr and Co, present in the instrument material [50].

The operator himself also represents a very serious source of contamination. The number of particles emitted per minute by a person amounts up to millions. They are released by the skin, hair, clothes, jewelers, cosmetics, disinfectants, talc, etc.

1.3.5 Contamination by sample handling

In spite of the fact that we have available very effective techniques for the cleaning of the vessels and equipment, for the purification of the reagents and for maintaining a clean laboratory and working place, further contamination, for example,, arising from storage of the sample solution [51], from sample handling and from the analytical procedure cannot be totally excluded. At the ppb and still much more at the ppt concentration level, even a very simple working step such as pipetting, shaking, evaporation, filtering, etc., already can increase the blanks considerably [14].

Alarming is not the real value of the blank of one single step but the fact that blanks occur even during very simple operations and accumulate during the whole analytical procedure to amounts in the ng/g range. In extreme trace analysis, the scattering of the blanks can exceed several orders of magnitude.

In principle, the various sources of systematic errors described above are present in all steps of an analytical procedure such as sampling, transport, storage, sample pretreatment, decomposition and dissolution, and separation and preconcentration. Accordingly, the general statement can be made that with decreasing absolute amounts of the elements to be determined, systematic errors increase dramatically and that they are the main problem in extreme trace analysis. Unfortunately, this fact will often not be realized in the daily work of routine laboratories and may then be the reason of wrong results with dramatic consequences with respect to economy, safety, and health.

1.3.6 Losses

Losses of elements are caused by volatilization, chemical reactions, or by reactions with the material of vessels, containers, and tools, and, finally, by adsorption or desorption processes.

Losses of elements by volatilization mainly occur at high temperatures. However, for very volatile elements, these interferences can already be remarkably high at room

temperature [52]. The analytes may be lost in the elemental form, oxides, and predominantly as halides or even as hydrides. The extent of the loss depends on the type of sample, and the variable temperature and time. Especially, mercury is well known to be extremely volatile. It can be lost during sampling, storage, and sample preparation, when aqueous solutions are stored in open vessels or in vessels made of organic polymers. Mercury losses can occur within a few hours and, in addition, elemental Hg quickly penetrates through sample containers made of plastic such as PE or PP. Therefore, samples in which Hg is to be determined should not be stored or transported in plastic containers so as to avoid Hg losses by volatilization or prevent contamination by the Hg present in the environment (ambient atmosphere).

The number of elements and compounds that can be lost as a result of volatilization increases with temperature. This must be considered when evaporating solutions or when performing decomposition procedures [53]. Volatile chlorides of Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}, Ge^{4+}, Se^{4+}, Pb^{4+}, and Te^{4-} may be lost during acid solution evaporation or during organic materials combustion.

During the dissolution of metals and alloys with nonoxidizing acids, the hydrides of elements such as S, P, As, Sb, Bi, Se, or Te may escape. Furthermore, hydrides can also be lost from alloys during the sampling step. Also, when drilling or cutting metal samples such as Al or Fe, the well-known smell of H_2S or PH_3 and other volatile hydrides often indicates the loss of these elements.

In general, volatilization can be prevented by application of closed systems (evaporation, closed vessel digestion, etc.). When closed systems are not suitable, volatilization can be reduced or prevented by reducing the temperature (storage, freeze-drying, low-temperature ashing, etc.). One also should avoid all chemical reactions by which volatile compounds can be formed (e.g., the formation of Cr_2OCl_2).

Many problems in elemental analysis are associated with the level of concentration to be determined; the concentration of the trace elements of very diluted solutions may change very quickly as a result of adsorption and desorption effects, which lead to losses or contamination. By these processes, ions or compounds of trace element are bound onto the surface of the container and may be released later on when the composition of the solution changes. The adsorption losses of elements become appreciable at concentrations $<10^{-6}$ mol/L and are of the order of 10^{-9}–10^{-12} mol/cm^2 [14].

In handling aqueous solutions containing low concentrations of ions, the researcher must consider various factors to minimize or prevent container adsorption of ions. The kind of ion and container, the period between collection and analysis, light effects, and dissolved salts are some of the aspects that need to be evaluated. Other factors, such as the sampling technique and contamination effects, must be considered in the analysis. In working with low ion concentrations, only metal-free containers may be used, and scrupulous care must be undertaken in all collection and analytical steps to avoid contamination. For field studies, PE would be preferable to glass because of its handling characteristics.

1.4 Sample treatment after the sampling process

Physical sample preparation is a very important aspect of the chemical analysis process. Methodology depends on the sample type and the reason for the trace analysis. Depending on the type of sample, most of these operations involve predominantly physical methods such as cleaning, drying, grinding, sieving, cooling or freezing, and mechanical agitation and homogenization [20].

Cleaning is most recommended for some kinds of materials, particularly parts of plants, such as roots, leaves, and fruits [53].

When the trace elements determination is carried out on aqueous matrices (e.g., tissues, fruit, vegetables, and soil samples), attention must be paid to changes in sample mass during the storage period. For this reason, analytical results should always be reported in terms of dry mass (weight) to avoid false interpretations. Drying is best conducted immediately after sampling. It is a widely used method that minimizes physical and chemical changes of samples; however, this process irreversibly alters the biological matrix because water and all volatile constituents are eliminated. Such problems are easily solved by oven drying, microwave drying, and freeze-drying (lyophilization).

Oven drying of biological material is performed at temperatures between 60 and 65 °C. The stream of hot clean air was frequently used as a drying procedure in the preparation of biological materials. It is very important to control the temperature because the biological matrix may decompose, depending upon the nature of the sample. Losses of elements during drying may occur owing to the formation of insoluble substances (e.g., aluminum oxides) and the evaporation of volatile elements or compounds of elements. Thus, a large portion of inorganic- and organic-bound mercury is lost by drying. Similar effects can be observed for arsenic, antimony, selenium, and others. On the other hand, drying at lower temperatures will reduce volatilization losses but also expose the sample to the ambient environment for longer periods of time, which serves to increase the risk of the contamination. The drying operation until constant weight is a common requirement for solid samples that contain varying amounts and unknown types of water; drying may be performed at 105 °C.

Microwave-assisted drying, a very fast drying procedure, exhibits the same problems as laboratory oven drying. An exact control of the microwave energy is necessary to prevent overheating of the sample and losses of some elements [54]. Proper equipment and optimized programs for the microwave oven were recommended to prevent losses of elements by overheating of the samples and contamination by the ambient atmosphere. Volatile elements should not be determined in samples dried in a microwave oven or in a drying oven.

Freeze-drying has been shown to be the most satisfactory procedure for trace element analysis of biological materials since it minimizes the loss of highly volatile elements and compounds. It is also known as lyophilization or vacuum drying. Freeze-drying is to be preferred over oven drying as at low temperatures fewer alterations of

the biological material occur and the formation of insoluble substances is also decreased. Losses due to evaporation are also reduced, but not excluded. Drying at a temperature as low as 120 °C can result in the loss of up to 10 % of most elements, and losses for mercury, lead, and selenium may be considerably higher (e.g., 20–65 %) with certain matrices [55]. To avoid losses of volatile elements, especially Hg, As, or Se, it is recommended that the sample be cooled during freeze-drying to <10 °C. Without cooling, the temperature of the sample will increase to room (laboratory) temperature after sublimation of the moisture and this may again lead to losses. Contaminations by drying arise mainly from the material of the drying apparatus employed. Thus, specimens for subsequent analyses for Cr, Ni, Co, or Mn should never be dried in a stainless steel oven; in such cases, aluminum is the preferred material.

To avoid systematic errors during the drying process, it is recommended that the original moist sample material be analyzed whenever possible and to correct the analytical result with the factor obtained by the separate determination of the dry mass. In this case, losses of volatile elements or contamination by dust during the drying process are inconsequential.

The homogenization process is another important process in sample preparation for solid sampling analysis, easily leading to contamination and/or losses of elements, and it is easily achieved by grinding process. Homogenization of samples is, in many cases, necessary to provide a representative sample. In solid samples, elements are normally distributed in an inhomogeneous way. Trace element determinations are usually restricted to relatively small samples, which requires that a fairly large sample be comminuted and homogenized prior to removal of an aliquot for analysis. In general, narrow particle size distributions with particles preferably below 10 µm diameter may ensure the desired analytical homogeneity [56, 57]. The choice of grinding technique can vary, depending on the properties of the sample matrix, especially on its hardness, fiber, and fat contents. To avoid possible nickel or chromium contamination from the construction material, all parts of the grinding device coming into contact with the biological materials are made of titanium or PTFE. The cryogenic grinding technique (brittle fracture technique) was introduced by Iyengar and Kasperek [58], and it relies on an increase of hardness of all tissues, the insertion of failures in the crystal structure, and use of very smooth force for the reduction to small pieces [59]. Before starting the grinding process, the whole grinding device (metering trough, mortars and balls, grinding cylinder and rods, etc.) should be cooled with liquid nitrogen for several hours. If the temperature of the components is constant at less than −190 °C, the grinding process is started without any further supply of liquid nitrogen. Therefore, for soft tissues, grinding and milling in vibrating ball mills applying PTFE or PFA containers and PTFE coated balls (made from stainless steel or tungsten, etc.), eventually under cooling with water or liquid nitrogen, are the preferred means. For hard materials, such as bone, teeth, etc., other container materials like Zr, Ti, or W and cooling under liquid nitrogen are necessary. Since then, some cryogenic grinding applications have been described [60–62].

Other mechanical mills such as mortar and pestle, blenda, ball and mortar, and disk mills have been also intensely applied to grind samples. Ball mill was successfully used in the preparation and certification of a pig liver reference material. Fish [63] and bovine liver samples [60] were also homogenized using ball mill. In both cases, good results were obtained for Cd determination in fish samples (slurry-ETAAS) and Cu and Zn determination in bovine liver samples (solid-ETAAS). In the same way, mortar and pestle was successfully used to grind fish samples for Se determination.

Comparing many IAEA and NIST environmental and biological materials ground using difference technique, including cryogenic and other mechanical mills, Fajgelj and Zeissler [64] concluded that jet air milled biological reference materials presented the lowest particle size distribution, making them suitable for small sample analysis.

However, when a representative aliquot is to be taken from the specimen, a homogenization step prior to storage is essential. The structure and composition of the biological material will be changed by both drying and freezing. Homogenization is mostly carried out in mixers with rotating knives. These instruments are one of the main sources of contamination. Often, the composition of the different materials from which the mixer is made is unknown. The most contaminating item is the knife because there will always be some abrasion. The use of mixers with stainless steel blades or knives should be avoided in trace element analysis. Therefore, the knives and/or blades must be made from materials that are of no analytical interest, for example, titanium or tantalum or special ceramic materials. High-speed mixers give rise to considerable cavitation by which water and volatile organic substances, as well as volatile elements (e.g., Hg), can be lost. Cooling during mixing is advised. The efficiency of mixing with respect to homogenization and contamination must be controlled for each new kind of specimen by analyzing samples of different size. For the homogenization of biological material with a low water content, distilled water must be added.

Comminution of the sample presents a significant opportunity for contamination. Contamination of the sample from abrasion of the comminution equipment is fundamentally unavoidable, so efforts must be made to select the best possible equipment for each particular analytical task. Equipment is preferred in which the sample comes into contact only with surfaces fabricated from such high-purity plastics as PTFE since this permits the sample to be used without restriction for the determination of a large number of elements. Friability can be increased by deep-freezing or drying the sample prior to comminution.

The sieving of fresh or previously milled samples is one of the methods most used for the evaluation and classification of the particle size distribution; by knowing the particle size distribution, it is possible to infer the homogeneity of the sample or the viability of the grinding method chosen. In general, microanalytical techniques yield better accuracy for homogeneous particle size distribution. For trace metal analysis, metal sieves can contaminate the samples. Wear-resistant plastic sieves and sieve holders are recommended for all sieving operations of samples for trace metal analysis.

AQ3

Some analytical techniques require the separation of suspended particles as a primary treatment. The oldest method of water purification is filtration. This method may be divided into adsorption filtration, such as that provided by a carbon filter, and mechanical filtration using a screen or membrane. The carbon filter is effective for removing certain organics, odors and tastes, and chlorine. Mechanical filtration does nothing more than remove undissolved particles. In the water analysis, for example, filtration through a membrane filter with a porosity of 0.20 or 0.45 µm is recommended. The fraction that passes through the filter is designated **soluble**. The use of a fiberglass prefilter with porosity of 1–5 µm is recommended in samples with high levels of suspended solids. The residue remaining on the filter can be leached or decomposed, and subsequently analyzed.

1.5 Decomposition as a sample preparation method for elemental analysis: an analytical perspective

Many modern instrumental techniques require to convert solid (or solid containing) samples to solutions prior to an analysis. The terms decomposition, destruction, digestion, acid digestion, dissolution, ashing, wet ashing, oxidative acid digestion, and mineralization all refer to this process. In this contribution, the general expression will be decomposition, which is specified to be dry or wet ashing. Mineralization refers to those procedures that result in inorganic chemical forms of the analyte only. A variety of techniques are employed from ambient pressure wet digestion in a beaker on a hot plate to specialized high-pressure microwave heating. Traditionally, decomposition of the sample in elemental analysis requires it to be mineralized in order to remove the organic content. Sample decomposition for total element determination therefore appears to be the recommended procedure on every occasion.

In general, it is required from any decomposition procedure to alter the original chemical environment of the sample into a digest, that is, a solution in which the analyte is distributed homogeneously. More specific conditions set to a decomposition technique are

- The decomposition must be complete. Inorganic materials have to be converted completely into soluble compounds, and organic materials have to be totally mineralized.
- Removal of residual matrix components that interfere in the detection; residues should be quantitatively soluble in a small volume of high-purity acid.
- The decomposition procedure has to be as simple as possible and should not require complicated apparatus.
- The decomposition must be adapted in an optimal manner to the whole analytical procedure; possibility of adjustment of the oxidation state of the analyte and, consequently, compatibility with postdecomposition chemistry.

- Preference should be given to procedures where decomposition and separation are achieved in one step.
- In order to minimize the systematic errors in the decomposition procedure (contamination, loss of elements, incomplete decomposition), clean vessels made of an inert material, and the smallest amounts of high-purity reagents should be used, and dust should be excluded. Reaction chambers should be as small as possible. Precautions should be taken so as to minimize losses of analytes (elements) due to adsorption on the vessel material (reactions with the vessel material) and volatilization.
- Execution is not hazardous or dangerous for laboratory personnel.
- The yield from the decomposition step should be checked by using radioactive tracers.

This section gives an overview of decomposition methods and recent developments and applications of the decomposition of different materials. Other sample preparation methods, such as chemical extraction and leaching, solubilization with bases, enzymatic decomposition, thermal decomposition, and anodic oxidation, are beyond the scope of this contribution and will not be discussed here.

There are numerous publications giving useful information on the decomposition of any conceivable combination of matrix and analyte. Some comprehensive books and review articles contain material pertinent to either organic [65–68] or inorganic [69–74] matrices; others, to both [75–85].

Within the scope of this section, a comprehensive discussion on decomposition techniques is not feasible. For more comprehensive information, the following reviews and books are available: books by Šulcek and Povondra [72], Bock [75], and Krakovská and Kuss [81] are dedicated solely to decomposition methods. Other books deal exclusively with a single technique: microwave-assisted sample preparation [85, 86], which has also been reviewed elsewhere [88–98]. Recommended guidelines for sample preparation (methods of digestion) of different matrices are also available from the *Encyclopedia of Analytical Chemistry* [99]. Although it is very difficult to refer to every paper published in this area, the enlisted bibliography of this chapter gives a comprehensive coverage of advance of the topic made to date, its potential application, novel developments, and progress in decomposition techniques.

1.5.1 Sample decomposition techniques

Table 1.1 gives an overview of the different decomposition methods for organic and inorganic sample material. The intent is not to present the procedural details for the various sample matrices, but rather to highlight those methods that are unique to each technique and sample.

Table 1.1: Scheme of decomposition methods.

Decomposition technique	Required reagents	Application
Wet chemical decomposition		
In open systems		
• Acid digestion (thermally convective wet decomposition)	• HNO_3, HCl, HF, H_2SO_4, $HClO_4$	• Inorganic/organic
• Microwave-assisted wet decomposition	• HNO_3, HCl, HF, H_2SO_4, $HClO_4$, H_2O_2	• Inorganic/organic • Waters, slurries
• Ultraviolet decomposition (photolysis)	• H_2O_2, $K_2S_2O_8$, HNO_3, O_3	• Inorganic
• Ultrasound-assisted acid decomposition	• H_2O_2, HNO_3	
In closed systems		
• With conventional heating (thermally convective pressure digestion)	• HNO_3, HCl, HF, H_2O_2	• Inorganic/organic
• With microwave heating	• HNO_3, HCl, HF, H_2O_2	• Inorganic/organic
In flow systems		
• With conventional heating	• HNO_3, H_2SO_4, H_2O_2, HCl	• Inorganic/organic
• With microwave heating	• HNO_3, H_2SO_4, H_2O_2, HCl	• Inorganic/organic
• Ultraviolet decomposition	• H_2O_2, $K_2S_2O_8$, HNO_3	• Waters, slurries?
Vapor-phase acid digestion		
• With conventional heating	• HNO_3, HCl, HF, H_2O_2	• Inorganic/organic
• With microwave heating	• HNO_3, HCl, HF, H_2O_2	• Inorganic/organic
Combustion		
In open systems		
• Dry ashing		• Inorganic/organic
• Low-temperature ashing (combustion in a stream of oxygen)		• Organic • Organic
• Cool plasma ashing (Wickbold combustion)		
In closed systems		
• Oxygen flask combustion (Schöniger flask)		• Organic
• Oxygen bomb combustion		• Organic • Organic
• Combustion in a dynamic system (Trace-O-Mat)		
Fusion decomposition	Fluxes	• Inorganic

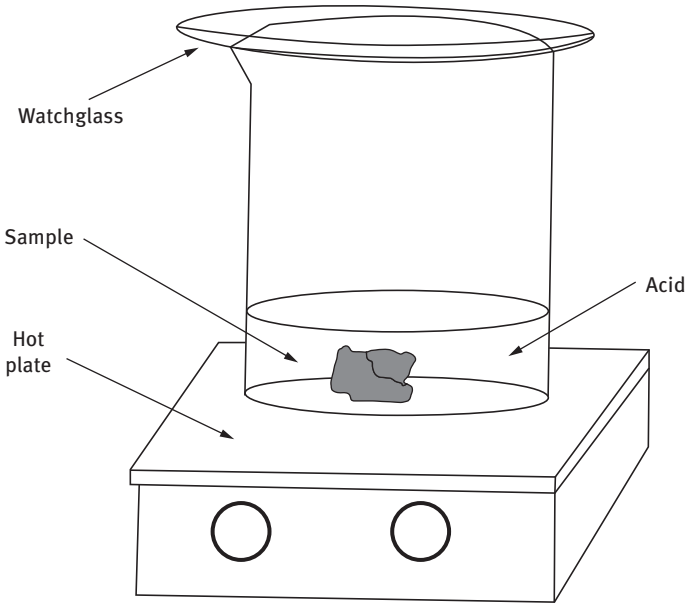

Figure 1.1: Acid decomposition in open system.

One of the oldest and simplest methods, and still most frequently used techniques, is wet decomposition in open systems (Figure 1.1). Wet decomposition can also be used in connection with closed systems.

1.5.1.1 Wet chemical decomposition

Sample wet decomposition is a method of converting the components of a matrix into simple chemical forms. This decomposition is produced by supplying energy, such as heat; by using a chemical reagent, such as an acid; or by a combination of the two methods. Where a reagent is used, its nature will depend on that of the matrix. The amount of reagent used is dictated by the sample size, which, in turn, depends on the sensitivity of the method of determination. However, the process of putting a material into solution is often the most critical step of the analytical process because there are many sources of potential errors, that is, partial decomposition of the analytes present, or some type of contamination from the vessels of chemical products used. It is beyond the scope of this contribution to discuss all possible systematic errors; therefore, further details on how to avoid systematic errors during sample decomposition that cannot be referred to in detail here are discussed in Section 1.5.

AQ4

The majority of wet decomposition methods involves the use of some combination of oxidizing acids (HNO_3, hot concentrated. $HClO_4$, hot concentrated H_2SO_4) and nonoxidizing acids (HCl, HF, H_3PO_4, dilute H_2SO_4, dilute $HClO_4$) and hydrogen peroxide. All of these acids are corrosive in nature, especially when hot and concentrated,

Table 1.2: Physical properties of common mineral acids and oxidizing agents used for wet decomposition.

Compound	Formula	Molecular weight	Concentration		Density (kg/L)	Boiling point (°C)	Comments
			w/w (%)	Molarity			
Nitric acid (V)	HNO_3	63.01	68	16	1.42	122	68 % HNO_3, azeotrope
Hydrochloric acid	HCl	36.46	36	12	1.19	110	20.4 % HCl, azeotrope
Hydrofluoric acid	HF	20.01	48	29	1.16	112	38.3 % HF, azeotrope
Perchloric acid (VII)	$HClO_4$	100.46	70	12	1.67	203	72.4 % $HClO_4$, azeotrope
Sulfuric acid (VI)	H_2SO_4	98.08	98	18	1.84	338	98.3 % H_2SO_4
Phosphoric acid	H_3PO_4	98.00	85	15	1.71	213	Decomposes to HPO_3
Hydrogen peroxide	H_2O_2	34.01	30	10	1.12	106	

and should be handled with caution to avert injury and accidents. Concentrated acids with the requisite high degree of purity are available commercially, but they can be purified further by sub-boiling distillation [31].

Wet digestion has the advantage of being effective on both inorganic and organic materials. It often destroys or removes the sample matrix, thus helping to reduce or eliminate some types of interference. The physical properties of the common mineral acids used in sample preparation are summarized in Table 1.2.

Most wet decomposition procedures are conducted under conditions that they, in terms of temperature or reagents used, must be considered as extreme. Thus, the material of which the flasks, crucibles, etc., are made must be chosen carefully according to the particular procedure to be employed. The material from which the digestion device is fabricated is also a frequent source of elevated blanks. Elements can be either dissolved from the material or they can be desorbed from the surface. Very important in this respect is the nature of the material. The suitability of materials may be estimated according to the following criteria: heat resistance and conductance, mechanical strength, resistance to acids and alkalis, surface properties, reactivity, and contamination, whereby the specific characteristics of the organic and inorganic material must be also given special consideration. Table 1.3 shows the preferred materials for decomposition vessels. The container material in contact with the sample during the decomposition also frequently causes systematic errors. Elements can be either dissolved from the material or desorbed from or adsorbed on to the container surfaces. This amount will depend on the material, contact time, and temperature. Table 1.4 summarizes the inorganic impurities likely to be encountered with various

Table 1.3: Preferred materials for wet decomposition vessels.

Material	Chemical name	Working temperature (°C)	Heat deflection temperature (°C)	Water absorption (%)	Comments
Borosilicate glass	SiO_2[a], B_2O_3[b]	<800[c]			Ordinary laboratory glass is not suitable for use in wet decomposition procedures
Quartz	SiO_2[d]	<1,200			For all procedures involving wet decomposition of organic material, quarto is the most suitable material for vessels
Glassy carbon	Graphite	<500			Glassy carbon is used in the form of crucibles and dishes for alkaline melts and as receptacles for wet decomposition procedures
PE	Polyethylene	<60			
PP	Polypropylene	<130	107	<0.02	
PTFE	Polytetrafluorethylene	<250	150	<0.03	PTFE is generally used only for decomposition vessels in pressure decomposition systems
PFA	Perfluoralkoxy	<240	166	<0.03	
FEP	Tetrafluorperethylene	<200	158	<0.01	
TFM	Tetrafluormetoxil			<0.01	

[a] SiO_2 content between 81 and 96 %.
[b] B_2O_3 content between 3 and 5 %.
[c] Softens at a temperature of 800 °C.
[d] SiO_2 99.8 %.

Table 1.4: Inorganic impurities in selected vessel materials (data in ng/g).

Element	Borosilicate glass	Quartz	Polyethylene	PTFE Teflon[a]	Glassy carbon
Al	Main	100–50,000	100–3,000		6,000
As	500–22,000	0.1–80			50
B	Main	10–100			100
Ca	10^6	100–3,000	200–2,000		80,000
Cd	1,000	0.4–10			10
Co	100	1	0.5	2	2
Cr	3,000	3–5	20–300	30	80
Cu	1,000	10–70		20	200
Fe	$2 \cdot 10^5$	200–800	1,000–6,000	10–30	2,000
Hg		1		10[b]	1
Mg	$6 \cdot 10^8$	10	100–2,000		100
Mn	6,000	10			100
Na	Main	10–1,000	200–10,000	25,000	350
Ni	2,000				500
Pb	3,000–50,000		200		400
S	Main	Main			85,000
Sb	8,000	1–2		0.4	10
Ti	3,000	100–800			12,000
Zn	3,000	50–100	100	10	300

[a] Teflon is a registered trademark of DuPont.
[b] Strongly dependent on storage conditions.

vessel materials. The borosilicate glass, which contains several major, minor, and trace elements in relatively high concentrations, is usually not suitable for element determinations in the extreme trace range. Quartz can be considered a pure material found in the market and is available in varying degrees of purity. For most sample preparation steps in trace (metal) analysis, high-purity quartz is the preferred container (and tool) material. Alternatively, high-purity synthetic polymers can be used in many decomposition applications: PE, PP (PP), PTFE, and polymers (PFA, FEP, TFM). The apparatus and containers that are used for the wet decomposition procedures must be scrupulously cleaned and tested for any possible contamination. Usually, it is sufficient to boil the flasks in concentrated nitric acid, followed by rinsing several times with ultrapure water before use. In cases where this procedure is not adequate, one of the most powerful cleaning procedures is steaming the vessels with nitric or hydrochloric acid with assembly in a microwave-heated sealed Teflon vessel [48]. This procedure is particularly recommended for quartz, borosilicate glass, and PTFE vessels.

To generalize this section, nitric acid is an almost universal decomposition reagent and the most widely used primary oxidant for the decomposition of organic matter because it does not interfere with most determinations and it is available commercially in sufficient purity. Hydrogen peroxide and hydrochloric acid can be

usefully employed in conjunction with nitric acid as a means of improving the quality of a decomposition. Hydrochloric acid and sulfuric acid may interfere with the determination of stable compounds. Mixtures with hydrochloric acid are generally used for samples containing principally inorganic matrices, and combinations with hydrofluoric acid are used to decompose silicate insoluble in the other acids. Safety considerations are particularly important when using perchloric acid.

a) Wet decomposition in open systems

Open vessel acid digestions, one of the oldest techniques, are undoubtedly the most common method of sample decomposition or dissolution of organic and inorganic sample materials used in chemical laboratories. This inexpensive technique is of inestimable value for routine analysis because it can be easily automated; all the relevant parameters (time, temperature, introduction of decomposition reagents) lend themselves to straightforward control.

The main advantage of wet decomposition over dry ashing is its speed. However, systems of this type are limited by a low maximum decomposition temperature, which cannot exceed the ambient pressure boiling point of the corresponding acid or acid mixture. For instance, the oxidizing power of nitric acid with respect to many matrices is insufficient at such low temperatures (boiling point 122 °C). One possible remedy is the addition of sulfuric acid, which significantly increases the temperature of a decomposition solution. Whether or not this expedient is practical depends on the matrix and the determination method. High-fat and high-protein samples are generally not subject to complete decomposition at atmospheric pressure. Other disadvantages relate to the risk of contamination through laboratory air, the necessarily rather large amounts of required reagents, and the danger of losses of trace elements. Losses can be kept low by using an excess of acid combined with a reflux condenser and by optimization of temperature and duration. Nevertheless, systems operated at atmospheric pressure are preferred from the standpoint of workplace safety.

Thermally convective wet decomposition. The conventional approach to wet decomposition entails a system equipped with heated conventional source (Bunsen burner, heating plate, sand bath, etc.) operating either at a fixed temperature or in response to a temperature program. Acid decompositions are often accomplished in any vessel, usually in glass or PTFE (beaker, conical flask, etc.) with or without a refluxing condenser. However, when a sample is decomposed in open wet digestion, refluxing is compulsory. The necessary apparatus has been described by Bethge [100]. Open block decomposition systems have been popular in sample analysis over the past decades, but have consistently suffered from the major drawback of their sensitivity against corrosion and subsequent risk of contamination (Figure 1.1). Therefore, block digestion systems (hotplate techniques) have not been considered state-of-the-art technology in trace and ultratrace sample preparation. Graphite block digestion systems are becoming more frequently considered. These systems overcome the deficiencies of the

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traditional systems, made from stainless steel or aluminum, because the block is manufactured from graphite and typically coated with a fluoro-polymer to prevent the possibility of metallic contamination from the surface of the system during the handling of the samples. Graphite block systems present an alternative to the current mainstream technology of open- and closed-vessel digestion systems as they allow large numbers of samples to be digested simultaneously, thus overcoming one of the major weaknesses of closed-vessel systems. Commonly employed decomposition agents include nitric acid, sulfuric acid, hydrofluoric acid, perchloric acid, and hydrogen peroxide, as well as various combinations of these. Most applications of wet decomposition involve aqueous or organic matrices, such as surface waters, waste water, biological and clinical samples, food samples, as well as soil, sediment and sewage sludge, coal, high-purity materials, and various technical materials. More recently, open systems have progressed; usual decomposition ramps consist of several vessels equipped with reflux condensers to limit possible volatilization losses of some analytes and to avoid the evaporation of the reactive mixture. Such assembling is entirely satisfactory for ensuring concurrent digestions of a large series of samples. Modern commercially available Hach Digesdahl Digestion Apparatus (Hach Comp., USA) is designed to digest organic and mineral samples for subsequent analysis.

Microwave-assisted wet decomposition. The most innovative source of energy for wet decomposition procedures is microwaves. Because the heating takes place inside the decomposition mixture, microwave decomposition is more efficient than with conventional means of heating. Using microwaves, both the speed and the efficiency of decomposition for some types of samples considered difficult to solubilize are often improved. Additionally, automation becomes possible with some instrumentation.

Since Abu-Samra et al. [101] reported on the application of microwave techniques to wet decomposition of biological samples, there has been a rapid development in microwave-assisted decomposition for elemental analysis. Recent reviews [79–85] detail the application of microwave-assisted decomposition to a wide variety of sample types, such as geological, biological, clinical, botanical, food, environmental, sludge, coal and ash, metallic, and synthetic materials and mixed samples, and present specific experimental conditions as a function of the matrix to be digested. The earliest attempts at microwave-assisted digestion were performed using home appliance microwave ovens. This was necessary because commercial devices were not available at the time. The use of domestic microwave ovens in laboratory experiments should be discouraged because of safety and performance. Microwave-assisted decomposition in open systems at atmospheric pressure is generally applicable only with simple matrices or for strictly defined objectives, and the results are reproducible only if the specified decomposition parameters are strictly observed. The performance of the focused-microwave-assisted systems and a wealth of applications have been reviewed by White and Mermet [88, 89] and very recently by Nóbrega et al. [102]. Focused-microwave-assisted sample preparation is a suitable strategy for dealing

with high masses of organic samples (up to 10 g). Losses may be encountered with mercury and possibly also with organometallic compounds. Addition of sulfuric acid is essential in order to achieve a sufficiently high decomposition temperature using atmospheric pressure equipment, where the boiling point of the acid establishes the maximum decomposition temperature, although it is important to remember that the presence of sulfate interferes with many procedures for metal determination. Although nonpressurized microwave systems are limited by a low maximum digestion temperature, which cannot exceed the ambient pressure boiling point of the acid (or the acid mixture), they provide the best option with regard to the safety of personnel because no overpressure can occur. Moreover, nonpressurized microwave-assisted digestion is suitable for online decompositions in continuous-flow systems.

Very recently, Matusiewicz [103] presented an overview of the different microwave-based systems used for solid and liquid sample pretreatment. They comprise relevant publications relating to current research, the unique instrumental approach, and the various commercially available systems including their operating parameters and accessories.

Ultraviolet decomposition. Ultraviolet (UV) decomposition is utilized mainly in conjunction with uncontaminated or slightly contaminated natural water matrices (aqueous solutions), such as sea, surface, fresh, river, lake, ground, estuarine, and costal water. Liquids or slurries of solids are decomposed by UV radiation (light) in the presence of small amounts of hydrogen peroxide, acids (mainly HNO_3), or peroxodisulfate (i.e., beverages, special industrial waste water, water of sewage treatment plants, soil extracts) [104]. Dissolved organic matter and complexes of the analyte elements are decomposed to yield free metal ions. The corresponding decomposition vessel should be placed in the closest possible proximity to the UV lamp (low or high pressure) to ensure a high photon flux. In photolysis, the decomposition mechanism can be characterized by the formation of OH^* and O_2^* radicals from both water and hydrogen peroxide that is initialized by the aid of the UV radiation [104]. These reactive radicals are able to oxidize, to carbon dioxide and water, the organic matter present in simple matrices containing up to about 100 mg L^{-1} of carbon. Complete elimination of the matrix is, of course, possible only with simple matrices or by combining photolysis with other decomposition techniques [105]. The method does not oxidize all organic components possibly present in water; chlorinated phenols, nitrophenols, hexachlorobenzene, and similar compounds are only partly oxidized. Effective cooling of the sample is essential because losses might otherwise be incurred with highly volatile elements. Hydrogen peroxide addition may need to be repeated several times to produce a clear sample solution. Modern UV decomposition systems are commercially available (see Ref. [104], Table 1.1).

Ultrasound-assisted acid decomposition. Although analytical chemists have shown little interest in the use of ultrasound, its potential usually surpasses that of the other

conventional auxiliary energies. Thus, ultrasound is of great help in the pretreatment of solid samples as it facilitates and accelerates steps such as dissolution, fusion, and decomposition, among others. An acid decomposition method that uses ultrasonic device (bath or probe) has been developed. The propagation of ultrasonic waves characterized by a minimum frequency of 16 kHz results in rapid fluid movement through compression and rarefaction: an enormous number of microscopic cavities are formed and free radicals are generated, chemical layers are dispersed and the contact between the ingredients of the reaction is accelerated. Usually, ultrasonic effects are much more intense in heterogeneous than in homogeneous chemical systems because emulsification is favored and mass heat transfer in two-phase systems is increased. These effects have been exploited for sample preparation in agriculture, biological, and environmental chemistry [106, 107].

Wet decomposition in closed systems. During the last few decades, methods of wet sample preparation using closed vessels have become widely applied. Closed systems offer the advantage that the operation is essentially isolated from the laboratory atmosphere, thereby minimizing contamination. Decomposition of the sample is essentially ensured by a common wet digestion procedure, which is performed under the synergistic effects of elevated temperature and pressure; decomposition occurs at relatively high temperature due to boiling point elevation. The pressure itself is, in fact, nothing more than an undesirable – but unavoidable – side effect. These techniques are generally much more efficient than conventional wet decomposition in open systems, the loss of volatile elements is avoided, any contribution to blank values may be reduced, and the decomposition of more difficult samples is possible. The principal argument in favor of this form of decomposition is the vast amount of relevant experience acquired in recent decades. Closed-system decomposition is particularly suitable for trace and ultratrace analysis, especially when the supply of sample is limited.

Because the oxidizing power of a decomposition reagent shows a marked dependence on temperature, an arbitrary distinction should be made between low-pressure decomposition and high-pressure decomposition. Low-pressure decomposition (<20 bar) is limited to a temperature of ca. 180 °C, whereas with high-pressure apparatus (>70 bar) the decomposition temperature may exceed 300 °C.

Thermally convective wet pressure decomposition. The decomposition of inorganic and organic substances in sealed tubes was the method first proposed for pressure digestion at the end of 19th century, and some of these applications are still difficult to replace by other digestion methods. The use of sealed glass tubes goes back to Mitscherlich [108] and Carius [109], often referred to as the Carius' technique, first described in 1980. Carius undertook digestion of organic materials with concentrated nitric acid at 250–300 °C. The sample and acid were mixed in a strong (thick)-walled quartz ampule and sealed. The ampule was transferred to a "bomb canister" and heated in what was called a "bomb oven" for several hours, after which it was cooled,

opened, and the contents analyzed. Carius tube decomposition involves the generation of internal pressure in excess of 100 bar at 240 °C. For safety, any stainless steel sleeve jacket (along with solid CO_2 pellets, to maintain equal pressure across the tube wall when heated) that is large enough to contain the Carius tube will suffice as an external pressure vessel [110].

With the development of the so-called Carius tube, the field of closed-vessel decomposition was born. Decomposition in autoclaves with metal inner reaction vessels was originally proposed in 1894 by Jannasch [111], but was not widely employed because of a number of drawbacks (such as strong corrosion of the platinum vessel).

Extensive use of pressure decomposition in analytical procedures began in 1960 as a result of the considerable technological progress in the manufacture of organic polymers. Convectively heated pressure vessel systems have proved to be the most valuable systems for guaranteeing complete, or almost complete, digestion of solid samples because they provide elevated digestion temperatures (about 200–230 °C) [112]. Most sample vessels for use in thermally convective pressure digestion are constructed from PTFE [113–115], PFA [116], or PVDF [117], although special quartz vessels with PTFE holders [118] or glassy carbon vessels [119] are available for trace analysis purposes. The sample vessel is mounted in a stainless steel pressure autoclave and then heated, usually in a laboratory drying oven, furnace or heating block, to the desired temperature (Figure 6). Because of the necessity to examine numerous samples, mechanized multisample pressure digestion systems able to process rather large sample numbers of the same matrix type were developed [120]. A cooling circuit can be fitted into the metal casing (jacket) to permit rapid manipulation of the solution formed immediately after removing the "digestion bomb" from the oven or heating block [121]. Dissolution can be also accelerated by mixing the reactants, preferable by using a stirring bar (covered with PTFE) [122]. An alternative design has been proposed by Uchida et al. [123], wherein a small screw cap vial for sample digestion is placed inside the Teflon digestion double vessel. To improve dealing with pressure–temperature evaluation and the carbon balance for some materials, a system with a Teflon-lined membrane pressure meter and a thermocouple was designed [124]. Recently, a digestion vessel for use with a convection oven was proposed [125], which has an unusual design in which the vessel consists of three nested structures: an innermost PTFE container of 30 mL capacity, an intermediate PTFE container of 100 mL capacity, and an outer stainless steel shell.

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All thermally initiated digestions have the disadvantage that a considerable amount of time is consumed in preheating and cooling the digestion solutions and sample vessel [126], the limited sample size, and the inability to visually check the progress of the digestion. The contributions of Langmyhr, Bernas, Tölg, and coworkers are worth mentioning with regard to the commercialization of the digestion vessels or "digestion bombs," as they are often called. Today, there are a number of digestion bombs covering the whole market range, including the popular Parr acid digestion bombs (Parr Instrument Company, USA), Uniseal decomposition vessels

(Unseal Decomposition Vessels Ltd, Israel), stainless steel pressure vessels with Teflon inserts (Berghof Laborprodukte GmbH, Germany), the pressure decomposition system CAL 130FEP (Cal Laborgeräte GmbH, Germany), and the pressure digestion system (PRAWOL, Germany).

To avoid the problem of loss of mechanical stability at high temperatures, vessels made of quartz are now being used in a new pressure digestion system [127, 128]. The introduction of a high-pressure ashing (HPA) technique by Knapp [127] has not only reduced the effective digestion time but also opened the way to digestion of extremely resistant materials, such as carbon, carbon fibers, and mineral oils. A perfected system of wet decomposition under high temperature (320 °C) and pressure (130 bar) developed by Knapp is commercially available, the HPA-S High Pressure Asher system (Anton Paar GmbH, Austria) [128, 129].

Very recently, again in respect to complete decomposition of organic waste materials, a potent digestion technique was developed [130] based on a prototype of an HPA device using infrared heating (IR-HP-asher). High-pressure decomposition is conducted in six quartz vessels inside a steel autoclave, with a maximum digestion temperature as high as 300 °C at a pressure of 130 bar. The novelty of this approach lies in the design of an HPA system with IR heating.

As metal autoclaves are expensive, a pressure vessel without an outer metal casing has been designed. The vessel can be sufficiently well sealed by using a screw cap [131]. Volatile components are not lost during heating and the laboratory atmosphere is thus not contaminated by acid vapors. All-Teflon thick-walled PTFE vessels (bombs) have been used in the dissolution of refractory oceanic suspended matter using HCl, HNO_3, and HF [132]. Translucent Nalgene-sealed bottles have been proposed for the "wet pressure digestion" of biological materials (fish, bird, plant tissue) using a combination of $HClO_4$ and HNO_3 [133]. A method utilizing a pressure digestion technique for real sample matrices using linear PE bottles has been proposed [134]. Vessels of PE are transparent, permitting observation of the whole digestion process and reduction of the reaction time to a minimum. A complete decomposition of fatty material with slight overpressure (<4 bar) was possible in a closed system completely made from quartz [135]. A closed PTFE bomb (30 mL capacity, screw-cap vessel machined from molded, stress-relieved Teflon-TFE rod) was designed for the digestion of materials using a conventional heating (drying) oven [136].

Microwave-assisted pressurized wet decomposition. Closed-vessel microwave-assisted decomposition technology has been acknowledged as one of the best solutions for "clean" chemistry applications and has a unique advantage over other closed-vessel technologies. The vessels used for microwave acid digestion are either low-pressure or high-pressure bombs. The current generation of microwavable-closed vessels consists of a two-piece design, liners and caps composed of high-purity Teflon or PFA with casings (outer jacket) made of polyetherimide and polyetherethereketone or other strong microwave transparent composite material. Their practical working

temperature is 260 °C (softening point of Teflon), and their pressure limit is 60–100 bar. Closed-vessel decomposition is ideal for those samples that are being dissolved in HNO_3 and/or HCl.

Microwaves only heat the liquid phase, while vapors do not absorb microwave energy. The temperature of the vapor phase is therefore lower than the temperature of the liquid phase and vapor condensation on cool vessel walls. As a result, the actual vapor pressure is lower than the predicted vapor pressure. This sort of sustained dynamic, thermal nonequilibrium is a key advantage of microwave technology as very high temperatures (and, in turn, short digestion times) can be reached at relatively low pressures.

The inspiration for pressure digestion studies came from a US Bureau of Mines report [137], which described how rapid dissolution of some mineral samples had been achieved using a microwave oven to heat samples and an acid mixture contained in PC bottles. Smith et al. [138] substituted Teflon PFA fluorocarbon resin vessels for PC because of its superior chemical and mechanical properties. Buresch et al. [139] used low-pressure-relief-type containers made of PTFE or quartz. Alvarado et al. [140] exploited modified thick-walled Pyrex glass test tubes fitted with PP screw caps as pressurizable vessels. Kojima et al. [141] modified a Teflon digestion bomb by using a double Teflon vessel with a PP jacket to permit leak-free and safe decomposition of samples. A closed-vessel microwave digestion system was described [142]. *In situ* measurement of elevated temperatures and pressures in closed Teflon PFA vessels during acid decomposition of organic samples was demonstrated; temperature and pressure monitoring permitted controlled decomposition and studies of decomposition mechanisms.

Laboratory-made all Teflon bombs, used for low- or medium-pressure work, are also appropriate for microwave-heated digestion purposes [143], some fitted with pressure-relief holes, valves, or membranes (rupture discs).

Low-volume microwave-assisted decomposition methods have found applications for studies involving small sample sizes where loss of sample in large digestion equipment is inevitable. Small quantities of tissue (5–100 mg dry weight) are decomposed in high-purity nitric acid by use of a modified Parr microwave acid digestion bomb with modified Teflon liner [144]. The use of low-volume (7 mL) Teflon-PFA closed vessels designed for the preparation of small-sized (<100 mg dry mass) biological tissues has been described [145].

In order to prevent excessive pressure rises during closed microwave acid decomposition of fairly large (1 g) samples having high organic content, an open-vessel predecomposition technique under reflux was designed to allow the escape of oxidation products, such as carbon dioxide, without incurring evaporation losses of acid or analytes. Following predecomposition, the vessels were capped and subjected to microwaves to complete the decomposition under pressure [146].

In an attempt to minimize the delay in opening Teflon pressure vessels following microwave acid digestion, and thus significantly reduce sample preparation time,

digestions with the pressure vessels immersed in liquid nitrogen and the use of liquid nitrogen as a pre- and postdigestion coolant were applied [147]. In other developments, a special type of Teflon bomb was constructed in which the vapor pressure can be maintained at a moderate level (up to 5 bar) by means of an internal quartz or Teflon cooling spiral. During operation, reflux of the condensed acid and water vapors continuously renews the liquid phase over the sample [148].

Several microwave heating configurations were presented by Pougnet et al. [149, 150] based on 500 or 1,200 W, 2.45 GHz fundamental-mode microwave waveguide cavities, which heat pressure vessels currently used in laboratories for sample decomposition and other applications.

The capsule concept was reviewed in detail by Légère and Salin [151, 152]. The sample is handled in an encapsulated form until it is in the digestion solvent. The operation of the capsule-based microwave-assisted digestion system proceeds in several steps, during which temperature and pressure are monitored.

From the previous discussion, it is clear that microwave acid digestion can be easily adapted for closed-vessel digestions; hence, its application has been limited to digestions in closed Teflon-lined vessels made of nonmetallic microwave-transparent materials operating with a maximum upper safe pressure of around 60–100 bar. In response to these limitations, Matusiewicz [153, 154] developed a focused-microwave-heated bomb that would exceed the operational capabilities of existing microwave digestion systems and permit the construction of an integrated microwave source/bomb combination, capable of being water or fluid cooled *in situ*. Another vessel configuration integrates the microwave chamber around the vessel. These consist of one or several microwave transparent vessels (Teflon, quartz), which can be sealed, enclosed in an acid-resistant stainless steel chamber [155]. The steel chamber acts as both the pressure vessel and microwave chamber. Modern systems can handle acid decompositions at temperatures up to 320 °C and pressures of 130–200 bar.

Very recently, a novel microwave-assisted high-temperature UV digestion for accelerated decomposition of dissolved organic compounds or slurries was developed [156, 157]. The technique is based on a closed, pressurized, microwave decomposition device wherein UV irradiation is generated by immersed electrodeless Cd discharge lamps (228 nm) operated by the microwave field in the oven cavity. The immersion system enables maximum reaction temperatures up to 250–280 °C, resulting in a tremendous increase of mineralization efficiency.

Today, there are a number of microwave-digestion bombs and systems available [103].

1.5.1.2 Flow systems

Discrete vessel systems, whether at elevated or atmospheric pressure, require a large amount of handling. Processes such as assembling, closing, opening, and positioning the vessel in the ordinary oven or microwave field are laborious and time consuming. Continuous flow-through thermal digestion, UV decomposition, and microwave

digestion systems were designed to overcome some of the limitations by replacing the vessels with flow-through tubing (coil). Samples are digested by pumping them through a coil containing a digestion matrix while being heated (by thermal, UV, or microwave). The continuous flow of a carrier stream through these systems washes the system, removing the need for tedious vessel clean-up procedures. These systems can handle reactions that produce sudden increases in temperature and pressure, or unstable samples. Many different designs of flow digestion systems have been published, but very few meet the prerequisites for high-performance sample decomposition.

b) Thermal heating

Many of the disadvantages of sample digestion can be overcome by automating sample preparation in an enclosed system through the use of flow technology.

A well-established digestion system was presented by Gluodenis and Tyson [158]. Here, the PTFE tubing is loosely embedded in a resistively heated oven. By using PTFE tubing, the maximum digestion temperature is restricted to ca. 210 °C. The limited mechanical strength of the material merely allows maximum working pressures of up to 35 bar. Therefore, the usual working pressure is about 10–20 bar. The potential of the system was illustrated by the decomposition of cocoa powder slurries in 10 % HNO_3 injected into the manifold and decomposed under stopped-flow, medium-pressure conditions.

In a series of papers [159–161], Berndt described development of a new high-temperature/high-pressure flow system for the continuous decomposition of biological and environmental samples. It was shown [159] that temperature up to 260 °C and pressure up to 300 bar can be reached in a flow system when an electrically heated Teflon lined HPLC tube is used as the digestion capillary. Digested biological samples (blood, liver, leaves) were collected at the outlet of the flow system. In subsequent papers [160, 161], an electrically heated Pt/Ir capillary served as a digestion tube at temperatures of 320–360 °C and pressures of about 300 bar, and withstands concentrated acids. Due to the totally glass-free environment, samples having high silicate content can be digested by the addition of hydrofluoric acid.

c) UV online decomposition

UV decomposition is a clean sample preparation method as it does not require the use of large amounts of oxidants. Furthermore, UV decomposition is effective and can be readily incorporated into flow injection manifolds. The sample flows, in the presence of H_2O_2, H_2SO_4 or HNO_3, through a tube (PTFE, quartz) coiled around a fixed UV lamp(s). A short review of such flow systems has appeared recently [162]. Analyzers of this kind are produced by SKALAR Analytical, Holland, for example.

Fernandes *et al.* [163] developed a manifold based on a two-stage online UV/thermal-induced digestion procedure for oxidation purposes. The UV digestion

apparatus consisted of a 4-m-long PTFE tube tightly wounded directly around the UV source (15 W) to form a spiral reactor. The thermal digestion apparatus consisted of a 2-m-long PTFE tube coiled in a helix and submerged in a thermostatic bath at 90 °C.

d) Microwave-assisted pressurized flow-through

Many different designs of microwave-assisted flow digestion systems have been published [89, 96, 162], which open up new possibilities, primarily in fully automated sample preparation for elemental analysis.

The earliest work reported in this field was Burguera *et al.* [164], who applied a flow injection system for online decomposition of samples and determined metals (Cu, Fe, Zn) by flame AAS. The methodology involved the synchronous merging of reagent and sample followed by decomposition of serum, blood, or plasma in a Pyrex coil located inside the microwave oven. This approach permits essentially continuous sample decomposition and drastically reduces sample processing time, and is suitable for those samples that require mild decomposition conditions (especially liquids).

According to the location of the digestion unit in the system, there are two types of manifolds described in the literature to date: before and after the injection unit. In the former arrangement, the sample is introduced into the microwave oven in a continuous flow [165] or a stopped flow mode [166]; after decomposition, the injected sample flows to the microwave oven unit together with the reagent(s) to be decomposed, and is then cooled and degassed prior to its delivery to the detector [167]. In both cases, the measurements can be performed partially or totally offline or online.

Solid samples call for more sophisticated flow systems because they need to be digested in the presence of highly concentrated acids, which rapidly destroy organic matrices. A first attempt aimed at simplifying manipulation of the digest was reported in 1988 [168]. Lyophilized, finely ground and weighed samples of liver and kidney were placed in test tubes together with mineral acids and the contents shaken before exposing them to microwave radiation to avoid violent reaction with abundant foam formation. The tubes were loaded into a covered Pyrex jar inside a domestic microwave oven operated for a specified time at a given power. Carbonell et al. [165] initiated the determination of metallic elements in solid samples using the slurry approach coupled with microwave oven digestion in a flow injection system for F-AAS determination of lead. Various natural samples (artichoke, chocolate, sewage sludge, tomato leaves), real and certified, were slurried in a mixture of HNO_3 and H_2O_2 using magnetic stirring, followed by continuous pumping around an open recirculating system, part of which (120 cm PTFE tubing) was located in a domestic oven.

A microwave-heated, flow-through digestion container (coiled Teflon tubing) was designed for a commercial (Prolabo A300) focused microwave system (instead of microwave oven) and applied to the online preparation of biological samples, including milk, blood, and urine [169].

For an extensive oxidation of organic sample constituents with nitric acid, temperature of more than 200 °C is necessary. The PTFE tubes used, however, cannot

withstand the vapor pressure of the decomposition mixture at 200 °C or more. Thus, new alternatives had to be found to overcome this limitation. One way to increase the pressure resistance of the tubes is to wrap them with a plastic tape of high mechanical strength. Results from a digestion system (CEM SpectroPrep system) equipped with such tubes have been published [170]. A CEM SpectroPrep system was used at moderate powers to perform online decomposition of slurried samples of biological tissues (0.5 % m/v) and marine sediment (1 % m/v). The pressure thresholds of this system are near 25 bar. To achieve the desired temperatures of approximately 250 °C, however, it is necessary to be able to increase the pressure in the system up to 35 bar or so. A recently developed device enables the application of such high temperatures (250 °C) by means of a new pressure equilibrium system (with a pressure of 40 bar) [171]. The pressure equilibrium system keeps the pressure inside and outside the digestion tube (PTFE or PFA) equal, even for extremely fast oxidation reactions. The system's ability to handle only up to 1 % m/v slurries and lower slurry concentrations for biological materials restricts the type of sample that can be analyzed, unless the most sensitive elemental detection devices are used, such as ICP-MS. Therefore, Mason et al. [172] modified the SpectroPrep oven and developed a wide bore continuous-flow microwave digestion system for the determination of trace metals (Cd, Cr, Mn, Ni, Pb) following *aqua regia* extraction. The described system demonstrated an ability to cope with real soil samples ground to a larger particle size (250 µm) and slurried without the use of surfactants.

Perhaps, the current fascination for using microwave heating for online digestion has led to the introduction of commercial instruments based on this hybrid technique [103].

The advantages of microwave-enhanced flow systems basically include a significant reduction in sample preparation time, the ability to accomplish reactions that would normally be too dangerous in a closed vessel because of sudden increases in temperature and pressure, and the capability to handle transient or readily decomposed samples or intermediates. However, flow-through systems are a problem area because all samples must be homogeneous and small enough to pass through the tube, and the majority of samples requires some form of processing before they can be put into the tube.

1.5.1.3 Vapor-phase acid decomposition

An alternative approach to acid digestion of the sample matrix that prevents introduction of impurities exploits gas-phase reactions. In the past four decades, several novel approaches to sample digestion procedures have been considered using inorganic acid vapor produced in one vessel to attack and dissolve material in another. A review by Matusiewicz [173] summarized analytical methods based on vapor-phase attack in promoting the dissolution and decomposition of inorganic and organic materials prior to determination of their trace element content. This approach is currently used (in

open, semi-closed, and closed systems) whenever applicable because digestion using gas-phase reagents is preferred to the solution.

The combination of hydrofluoric acid and nitric acid vapor as a digestion agent has proven effective in the preparation of samples for spectrographic determination of trace impurities in open system. Zilbershtein et al.[174] used this approach to dissolve silicon and to concentrate impurities on a PTFE sheet. The residue and PTFE sheet were transferred to a graphite electrode that subsequently served as one electrode of the dc arc for spectrographic trace analysis.

With respect to semiclosed systems, a PTFE apparatus generating HF vapor has been specifically designed to minimize contamination during trace-element determination of ultrapure silicon, quartz, and glass [175]. The sample is placed in a PTFE beaker mounted on a perforated PTFE plate that is kept above the level of liquid HF in the chamber. Thomas and Smythe [176] describe a simple all-glass apparatus for vapor-phase oxidation of up to 90 % of plant material with nitric acid. Addition of perchloric acid ensured fast and complete oxidation, and the presence of HNO_3 during the final $HClO_4$ oxidation step eliminated any danger of explosion. Klitenick et al. [177] used the same technique, with a simplified pressurized PTFE digestion vessel, for the determination of zinc in brain tissue.

Some materials may not be fully dissolved by acid digestion at atmospheric pressure. A more vigorous treatment involves bomb digestion in pressure vessels designed to incorporate the techniques of a closed pressure vessel and vapor-phase digestion in a single unit. This has the advantage of being easier to construct than the apparatus described in previous papers [174–177], and it requires considerably smaller volumes of acids. Heating can be accomplished in an ordinary oven (with conductive heating) or using a microwave field.

A predecessor of this concept of closed-vessel vapor-phase sample digestion was introduced by Woolley [178]. He described a low-temperature (up to 110 °C) and high-temperature (up to 250 °C) version of the apparatus. Each device consists of an airtight PTFE vessel containing two concentric chambers: an inner chamber that holds the sample cup and an outer chamber. Both vessels were designed for the digestion of high-purity glass using relatively impure solvent acids: a 50:50 mixture of concentrated HNO_3 and HF. A completely closed PTFE bomb or autoclave [179] has been developed with a temperature gradient for digestion of more difficult compounds, such as siliceous material. Marinescu [180] presented an interesting development in which the conventional single-sample pressure digestion bomb was converted for multisample vapor-phase digestion. A multiplace holder for field sampling was developed to fit directly into the digestion bomb. This technique has been used for organic and inorganic solid, semisolid, and liquid samples. Kojima et al. [181] modified a sealed PTFE bomb in which the dissolution of highly pure silica with HNO_3, HCl, and HF acid vapor was possible using a PTFE vial placed in a PTFE outer vessel. A laboratory-made high-pressure digestion bomb with a PTFE microsampling device was developed by Matusiewicz [182]. This simple and inexpensive apparatus was

found to be convenient for treating a small number of samples and can be easily made by modifying available PTFE bombs. It should be noted that PTFE microsampling devices can be used for both vapor-phase digestion and discrete nebulization techniques in atomic spectrometry. Vapor-phase digestion in a closed system (bomb) of high-purity materials for spectrographic determination of trace elements is a convenient and useful technique [183]. The method uses graphite electrode with an enlarged cavity and excludes the use of a collector. A technique [184] has been developed that employs the vapor-phase acid generated in the quartz vessel of a commercial high-pressure, high-temperature digestion apparatus (High Pressure Asher HPA, Anton Paar, Austria). Small biological samples (50–165 mg) were digested in a mini-quartz sample holder (3.1 mL volume). When biological standard reference materials were digested at 230 °C and 122 bar, the residual carbon content (RCC) in the digested samples was less than 1.8 %.

Despite methodologies previously proposed for closed systems with conventional heating being successful, very few attempts to employ microwave power for vapor-phase digestions have been described. An early trial with a low-pressure microwave arrangement was unsatisfactory [185], although recently an interesting variant of the digestion vessel design has been proposed for dissolution and decomposition of samples [186]. The method developed was an extension of the acid vapor-phase thermal pressure decomposition of biological materials reported previously by Matusiewicz [187]. Microwave-assisted vapor-phase acid digestion employing a special PTFE microsampling cup, suitable for 250 mg subsamples of marine biological and sediment reference materials were digested with HNO_3 and HNO_3-HF, respectively, at a maximum pressure of ca. 14 bar [186]. Very recently, several papers [188–192] discussed the further application and evaluation of this pioneering concept of Matusiewicz [187], employing either commercial pressurized microwave digestion systems and quartz sample containers [188], quartz inserts [189, 190], TFM inner vessels [191], or focused microwave ovens operating at atmospheric pressure and PTFE microsampling cups [192].

To summarize this section, use of acid vapor-phase digestion and attack of some organic and inorganic matrices as a sample preparation method is a convenient and useful technique. Closed pressure systems are the technique of choice to avoid losses of elements by volatilization while still maintaining extremely low values for the blank (by application of isopiestic distillation of the reagents and technical grade acids).

1.5.1.4 Efficiency of wet decomposition procedures

Quality control is becoming increasingly more significant in analytical chemistry. However, it is presently applied primarily to measurement techniques and not to sample preparation. For quality control in sample decomposition, it is necessary to measure and record certain parameters exactly to be able to subsequently trace the course of the decomposition process.

In spite of that, complete decomposition of the sample is required to achieve reproducible and accurate elemental results by instrumental analytical methods. This is particularly the case for all voltammetric and polarographic determinations [193–196]. Interferences caused by incomplete decomposed organic compounds also occur, to a certain degree, when using atomic spectrometric methods such as AAS [197, 198], ICP-OES [199, 200], and ICP-MS [201, 202]. As noted earlier, nitric acid is the most frequently utilized sample dissolution medium. Unfortunately, the carbon contained in organic materials is only partly converted to CO_2 by HNO_3 at temperatures of up to 200 °C [14]. In these cases, extending the digestion time and increasing the quantity of nitric acid does not improve the extent of decomposition. In principle, temperature and digestion time ultimately determine the effectiveness of a digestion, with RCC serving as a useful measure of quantitative assessment [123, 203]; in other words, the highest temperatures are required to achieve a decomposition as complete as possible [204, 205]. It should be noted here that the usefulness of the decomposition technique should be judged not from a visual point of view because it often happens that a clear, colorless solution, indistinguishable from water still contains significant amounts of carbon. In closed systems, the pressure depends not only on the temperature but also on the type and quantity of the sample, the size of the vessel, and the nature and quantity of the decomposition reagent. This pressure is not responsible for the determination quality, but nevertheless it should be controlled automatically. Würfels et al. [206–209] described the extremely strong impact from residual organic compounds on elemental determinations by means of inverse voltammetry and demonstrated that a temperature of 300–320 °C is necessary for pressurized sample decomposition with pure nitric acid to obtain a solution containing less than 0.1 % carbon. Otherwise, trace elements cannot be determined with inverse voltammetry. This was confirmed by Wasilewska et al. [210], who showed that for complete oxidation of organic compounds with nitric acid, the decomposition temperature should be raised to 300 °C. The influence of the digestion equipment (either thermal or microwave) is negligible if the digestion time employed is long enough to reach the steady-state temperature. Sample digestion with nitric acid between 220 and 250 °C leads to RCCs in the low-percentage range.

The mode of heating of the digestion vessels is more and more supplanted by microwave technology; therefore, microwave-assisted wet decomposition is a frequently used sample preparation technique for trace element determinations in organic materials. Studies of the RCC as a measure of decomposition efficiency have been undertaken [185, 211–215]. Using gas chromatography, Stoeppler et al. [123] quantified the ashing ability of conventional pressurized decomposition. Differences between the carbon content in the original sample and the carbon converted to CO_2 showed that the investigated biological and environmental samples were not completely ashed with nitric acid. Würfels and Jackwerth [216] determined the residual carbon in samples decomposed under pressure or evaporated with HNO_3. In most cases, microwave decomposition of biological material was incomplete. Subsequently, the undigested

compounds were identified [207]. Parallel to Würfels and Jackwerth's studies [216], the residual organic species in nitric acid digests of bovine liver were identified by Pratt et al. [217]. Kingston and Jassie [218] evaluated the decomposition of several biological and botanical samples wet decomposed with HNO_3. Free amino acid concentrations of human urine samples were typically reduced by a factor of 10^5. This reflects the comparative efficiency of protein hydrolysis, and is not necessarily equivalent to the total carbon oxidation efficiency. Nakashima et al. [213] investigated the digestion efficiency of HNO_3–$HClO_4$ mixtures. The total RCC in a number of decomposed marine biological reference material (NRCC TORT-1) solutions was determined and used as a relative measure of the efficiency of various decomposition schemes. Two-stage microwave-assisted decomposition was superior to single-stage decompositions. However, even the two-stage procedures were not complete and 24 % carbon remained. The determination of residual carbon in digests of biological material with simultaneous ICP-OES analysis was described by Hee and Boyle [214] and Krushevska et al. [215]. The oxidation efficiencies of different dry and wet ashing procedures for milk samples were compared by Krushevska et al. [219], who noted that the residual carbon concentrations obtained with medium-pressure microwave-assisted decompositions varied between 5 and 15 %. Oxidizing mixtures of H_2O_2 or H_2SO_4 with HNO_3 applied in a medium pressure (11 bar) microwave system did not yield a decomposition efficiency higher than that for pure nitric acid. However, with the high-pressure/temperature-focused-microwave-heated TFM-Teflon bomb device, organic material is totally oxidized with nitric acid in a single-step procedure [153, 155]. Matusiewicz and Sturgeon [220] critically evaluated online and high-pressure/temperature closed-vessel techniques with regard to efficiency of decomposition. The completeness of destruction of biological materials (standard and certified reference materials) was characterized in terms of their RCC in the solution following digestion. Pressurized decomposition in a TFM-Teflon vessel was the most effective procedure (organic material was totally oxidized with nitric acid in a single-step procedure), whereas urine and sewage plant effluent were incompletely decomposed (between 56 and 72 %) with online microwave-heated decomposition using nitric acid, nitric acid and hydrogen peroxide, and peroxydisulfate oxidation. Very recently, the residual weight of a bottom antireflective coating (BARC) sample was successfully used as an indicator to evaluate the decomposition kinetics [221]. The weight degradation rate was independent of the sample weight under various temperatures, but strongly dependent on the digestion acid volume and the digestion temperature. Mathematical modeling for prediction of decomposition efficiency for the BARC sample was achieved by employing decomposition kinetics as the backbone.

Hydrogen peroxide is a very popular oxidizing reagent as it is converted to water and oxygen during the oxidation of biological material [185, 222–224]. However, an experiments with HNO_3–H_2O_2 mixtures conducted by Matusiewicz et al. [222] showed that all versions of pressurized microwave-assisted digestion with HNO_3 and H_2O_2gave an incomplete decomposition. No significant improvement in the efficiency

was achieved with 50 % H_2O_2. The extension of this observation to medium-pressure and high-temperature microwave heating provided verification of this observation [225]. Nitric acid digestion with the addition of H_2O_2 did not enhance decomposition efficiency in this study compared to the use of only HNO_3. Thus, an alternative oxidizing reagent is desirable to completely and safely decompose organic carbon residues. It was found that ozone is very effective in destroying natural organic compounds [226–228] and has the potential to be used as an additional decomposition and/or finishing reagent [229].

A single digestion procedure is often insufficient for the complete decomposition of a complex matrix, leading some authors to recommend a combination of two or more techniques. Two examples will suffice to illustrate the principle [156, 194]. First, pressure digestion followed by UV photolysis. Thus, it has been shown that analysis of olive leaves for heavy metals by voltammetric methods leads to distorted results after "pressure digestion" alone. Reliable data can be obtained only by supplementing the digestion with UV irradiation to ensure adequate decomposition of the matrix [194]. Second, a novel microwave-assisted high-temperature UV digestion procedure was developed for the accelerated decomposition of interfering dissolved organic carbon prior to trace element determination in liquid samples. This new technique significantly improved the performance of the process of UV decomposition (oxidation) and is especially useful for ultratrace analysis due to its extremely low risk of contamination [156, 230].

In order to investigate the completeness of dissolution of inorganic materials, the recovery (or incomplete recovery) and accuracy of major, minor, and trace element determinations are usually applied. If silicates are present, which is usually the major inorganic component of many matrices (i.e., soils, sediments, sludges, ceramics, and other similar samples), the use of HF to achieve complete dissolution is mandatory [231, 232].

1.5.1.5 Comparison of wet decomposition techniques

A careful comparison of several digestion techniques is the only way of assuring accurate results, particularly when little experience is available with respect to the digestion of a specific matrix, or existing reports are contradictory. The analyst must choose the sample preparation technique carefully to ensure that the system is optimal for the analyses at hand. However, there is still no universal sample preparation system. With respect to requirements specific to contamination or losses through volatilization or retention, convection-heated or microwave-assisted wet digestion, quartz-lined high-pressure wet digestion, UV digestion, and vapor-phase acid digestion seem to be the best choice. However, all of these techniques require considerable investment for apparatus. Digestion of samples in an open vessel presents a serious risk of significant analyte loss despite the use of a reflux condenser. As far as economic aspects are concerned (low procurement, short digestion time, high sample throughput), microwave-assisted wet digestion and especially microwave-assisted pressurized

online digestion appear to rank high. According to completion of the digestion, complete degradation of many samples is achieved only through high-pressure, high-temperature Teflon- or quartz-lined pressure vessel digestion, or by combination of a closed wet digestion system with UV irradiation.

Table 1.5 summarizes the advantages and disadvantages of the wet digestion techniques discussed in Section "Wet decomposition" with respect to losses of analytes, blank levels, contamination problems, sample size, digestion time, degree of digestion, and economic aspects.

1.5.1.6 Decomposition systems

Presently, the instrumentation market offers many devices to make wet decomposition more efficient and easier to manage by means of possible automation, but this is achieved principally with microwave energy.

Wet decompositions in open vessels are undertaken with or without refluxing. Because it is very critical to adhere very closely to the optimized time and temperature digestion parameters, mechanization of the digestion not only leads to higher sample throughput with less human intervention but also to the avoidance of errors. The simplest form of mechanization can be implemented through a time (programmable timer) and temperature (via an autotransformer) controlled heating block. There are many models of heating blocks on the market. A greater degree of mechanization would also incorporate control of reagent reflux during digestion.

These procedures operate batchwise. Continuous sample handling has some advantages over discontinuous handling; the former generally better matches analytical needs. The automated wet digestion device (VAO, Anton Paar, Austria) is such a continuously operating digestion system, and an ideal instrument for laboratories requiring high throughput of similar samples with which all methods of wet chemical decompositions can be performed [233]. With the help of a microprocessor, all important digestion parameters are controlled. Automation controls the time-temperature/pressure program for sample digestion, so that different sample materials can be processed under optimum conditions. The loading or charging of the high-pressure asher with sample material is achieved manually. A fully automated version of this high-pressure asher is not available. Berghof pressure digestion systems [234] serve for sample preparation of inorganic and organic matrices at high temperature (max. 200–250 °C) and high pressure (max. 100 and 200 bar) in pure, isostatically pressed PTFE or quartz vessels.

As noted already, three basic types of microwave-assisted digestion systems have evolved: atmospheric pressure, elevated pressure (closed vessel), and flow-through, working in the two common modes: multimode cavity and focused-type (waveguide). Reviews of commercially available microwave-assisted digestion systems and vessels (summary of the vessels, ovens, and oven systems) are given in Refs. [103, 235] together with specifications and features for elevated pressure, atmospheric pressure, and flow-through units. The simplicity and efficacy of microwave digestion easily

Table 1.5: Advantages and disadvantages of wet decomposition methods.

Decomposition technique	Possible ways of losses	Source of blank	Sample size (g)		Maximum		Decomposition time	Degree of decomposition	Economic aspects
			Organic	Inorganic	Temperature (°C)	Pressure (bar)			
Open systems									
Conventional heating	Volatilization	Acids, vessels, air	<5	<10	<400		Several hours	Incomplete	Inexpensive, needs supervision
Microwave heating	Volatilization	Acids, vessels, air	<5	<10	<400		<1 h	Incomplete	Inexpensive, needs supervision
UV decomposition	None		Liquid		<90		Several hours	High	Inexpensive, needs supervision
Ultrasound-assisted decomposition	Volatilization	Acids, vessels, air					Several minutes	Incomplete	Inexpensive, needs supervision
Closed systems									
Conventional heating	Retention	Acids (low)	<0.5	<3	<320	<150	Several hours	High	Needs no supervision
Microwave heating	Retention	Acids (low)	<0.5	<3	<300	<200	<1 h	High	Expensive, needs no supervision
Flow systems									
Conventional heating	Incomplete decomposition	Acids (low)	<0.1 (slurry)	<0.1 (slurry)	<320	>300	Several minutes	High	Expensive, needs no supervision
UV online decomposition	Incomplete decomposition	None	Liquid		<90		Several minutes	High	Inexpensive, needs no supervision
Microwave heating	Incomplete decomposition	Acids (low)	<0.1 (slurry)	<0.3 (slurry)	<250	<40	Several minutes	High	Expensive, needs no supervision
Vapor-phase acid decomposition									
Conventional heating	None	None	<0.1	<0.1	<200	<20	<1 h	High	Needs no supervision
Microwave heating	None	None	<0.1	<0.1	<200	<20	<20 min	High	Needs no supervision

lends itself to automation and robotics. Systems have been developed that are capable of weighing samples, adding acids, capping and uncapping vessels, accomplishing microwave-assisted digestion, diluting digestates, transferring vessels, and even cleaning and reusing the vessels. Once such a system is operational, the only thing the analyst has to do is supply and place the representative sample(s) in locations recognized by the system and then initiate the controlling program.

1.5.1.7 Safety of acid decomposition

The reagents, instruments, and operations employed in the digestion of materials are potentially hazardous, even when used as directed. The operator must always be properly protected with a laboratory coat, gloves, and safety glasses or, better still, face protection. Some concentrated fuming acids (HF, HNO_3, HCl) are to be handled only in a well-ventilated hood. Oxidizing acids (HNO_3, $HClO_4$) are more hazardous than nonoxidizing acids (HCl, H_3PO_4, HF), being more prone to explosion, especially in the presence of reducing agents, such as organic matter. Perchloric acid is oxidizing only when it is concentrated and hot; it must never be brought into contact with organic matter unless diluted with nitric acid.

Acid digestion must be conducted in a fume cupboard with efficient scrubbers installed. The evaporation of perchloric acid is to be performed only in an appropriate stainless steel, stoneware, or PP hood, with washing facilities to eliminate any perchlorate deposit.

Great care should be taken when using "pressure digestion" methods. Pressure digestion vessels (bombs) contain the acid fumes and are useful for rapid, one-step digestions without losses. But, again, there are restrictions; in some reactions (especially spontaneous), potentially explosive gases are produced that exceed the safety limits of the vessels. For instance, nitric acid and especially the spontaneous HNO_3 and H_2O_2 decomposition of organic matter in a closed vessel may result in explosion due to unintended pressure build-up within the vessel. These systems produce high-pressure spikes, which can be avoided by decreasing the sample weight or by applying a gradual temperature increase.

Microwave-assisted sample digestion has its own safety requirements. As a result of the direct energy absorption and rapid heating, microwave techniques introduce unique safety considerations that are not encountered in other methods. Differences in conditions between traditional laboratory practices and microwave-implemented methods should be examined before microwave energy is applied to heat reagents or samples. An excellent summary of this aspects is extensively reviewed in Refs. [82, 83, 236].

1.5.1.8 Combustion

a) Combustion in open systems

Dry ashing. The term **dry ashing** is intended to encompass all processes based on gaseous or solid ashing reagents. Such a distinction relative to wet decomposition

processes is not absolutely essential, but it does offer certain practical advantages. Strictly speaking, dry ashing refers to the oxidation (combustion) of a substance in air at a temperature of several hundred degrees Celsius, often in a muffle furnace or similar apparatus.

For samples that contain much organic matter, which are being analyzed for non-volatile metals, dry ashing is a relatively simple method of removing the organic matter that can be used for relatively large samples (2–10 g) and requires little of the analyst's time. Classical dry ashing relies on the pyrolysis and combustion of the organic sample in a muffle furnace or laboratory flame, with the oxygen in air at 400–600 °C to remove the organic constituents. The organic is converted into CO_2 and H_2O [237]. The resulting inorganic "ash" residue is generally soluble in dilute acid. Crucibles used for ashing are usually made of silica, quartz, porcelain, platinum, zirconium, or Pyrex glass.

Dry ashing is rarely applied anymore and has largely been replaced by wet decomposition (ashing) because it has several disadvantages, such as losses due to volatilization, very low ashing of some materials, difficult dissolution of ashed materials, and contamination.

Advantages of this method are that no reagents are used and little operator attention is required.

Recently, analytical instruments have been developed to dry ash samples based on thermal and microwave heating: dry mode mineralizer (TESSEK, APION A), microwave ashing furnace (MILESTONE MLS 1200 PYRO), and microwave ashing system (CEM, MAS 7000).

Low-temperature ashing. For the determination of volatile elements, such as Se, As, Sb, Cd, Zn, and Tl, in organic materials, a very gentle treatment is required. For this, a low-temperature (<200 °C) ashing with excited oxygen at a pressure of 1–5 Torr is very suitable [238].

The oxygen plasma can be produced either by a radio-frequency power supply or by microwave energy (up to 300 W at 13.5 MHz); created reactive oxygen species (free oxygen radicals and excited oxygen) reacts effectively with the organic sample surface (up to 2 g), thus forming an organic ash residue. The ash and the elements adsorbed onto the cooling finger are then solubilized by refluxing with acid. An advantages of this method is that the elements are obtained in a comparatively high concentration. This method can be used for sample preparation of all kinds of combustible solids such as wood, paper, coal, food, or polymers.

One commercial system based on this technique is available: the Cool Plasma Asher CPA-4 (Anton Paar)

Cool plasma ashing (Wickbold). The Wickbold combustion technique is very suitable for processing liquid combustible samples, which are hardly decomposed by other techniques such as petroleum products [239]. In the Wickbold combustion system, an oxygen-hydrogen flame is used to sample decomposition at high temperatures

(2,000 °C). Liquid samples are directly introduced to flame while for solid samples a preliminary pyrolysis step in a precombustion unit is necessary. After the combustion, the resulting products are condensed in a quartz surface and absorbed in a suitable solution.

A Wickbold combustion apparatus V5 (Heraeous) is commercially available.

b) Combustion in closed systems

Oxygen flask combustion (Schöniger). Combustion in an oxygen flask, or commonly called Schöniger technique, offers advantages when readily volatilized elements such as halogens, Se, S, P, B, Hg, As, and Sb, are to be determined. The combustion is performed with oxygen in a sealed container and the reaction products are absorbed in a suitable solvent before the reaction vessel is opened.

A simple apparatus for performing such oxidation has been suggested by Schöniger [240]. It consists of a flask (500–1,000 mL capacity) fitted with a ground glass stopper. Attached to the stopper is a platinum gauze basket that holds from 2 to 200 mg of sample. If the sample is a solid, it is wrapped in a piece of low ash-content filter paper. Liquid samples can be weighed into gelatin capsules that are also wrapped in a filter paper. A small volume of an absorbing solution is placed in the flask. During the combustion, the flask is inverted to prevent the escape of the volatile oxidation products. Subsequently, the vessel is opened and the resultant solution containing the analytes is removed and diluted for analysis. The necessary time for the decomposition using the oxygen flask is typically less than 10 min; in addition, materials and equipment are relatively inexpensive. However, the procedure needs a continuous attention of the analyst during the combustion and is commonly applied for processing only one sample each time.

The apparatus of Schöniger system is a commercially available, flask-type combustion apparatus HERAEUS MIKRO K.

Oxygen bomb combustion. Combustion bomb is the classical technique successfully applied for several matrices and analytes [241].

In this technique, the samples, as pellets, are introduced in an ignition cup with two platinum wires that are connected to two electrodes. About 10 mL of absorbing solution is added at the bottom of vessel that is made in stainless steel or covered with platinum. After closing, the system is pressurized with oxygen at 20–30 bar. Then, the ignition is performed by electric current and after the combustion the gaseous are absorbed. After cooling, the system is opened and the absorbing solution is removed. In the combustion bomb, a relatively high sample mass (>0.5 g) can be burnt with high decomposition efficiency and the procedure takes place in less than one hour.

Commercially available apparatus such as oxygen combustion bomb PAAR and pressure decomposition device SIEMENS BIOKLAV can be employed for sample preparation applications.

Combustion in a dynamic system (Trace-O-Mat). The dynamic system (also called Trace-O-Mat) was developed by Knapp et al. [242] in the early 1980s and allows the sample combustion with a minimum contamination, which enables not only combustion in a closed system but also further treatment. The Trace-O-Mat combustion unit VAE-II is commercially available.

The sample is burnt in a stream of pure oxygen in a system made entirely of quartz. An essential feature is the cooling system above the combustion chamber having a volume of only 75 mL, which is filled with liquid nitrogen and condenses all volatile traces together with the combustion products CO_2 and H_2O. After combustion, the nitrogen is evaporated and the residual ash and the condensed volatile elements are dissolved by refluxing in 1–2 mL of high-purity HCl or HNO_3 and are then collected in the reagent vessel placed below. Solid samples are pressed into pellets. For liquid organic samples, a special sample holder is available. Maximum sample amounts of 0.7–0.8 g and a minimum of 1 mL of acid result in solution with high element concentrations.

1.5.1.9 Fusion decomposition

Fusion (especially alkaline fusion) is a powerful technique especially both for organic matrices and those with a high silica and alumina content having relatively high trace element contents. In general, a salt fusion is performed by mixing a sample with salts, melting the mixture with heat, cooling it, and, finally, dissolving the solidified melt. The fusion-flux properties range from acidic to basic, according to the Lewis acid–base definition, in which an acid can accept and a base can donate an electron pair. The flux properties may also be termed as oxidizing or reducing.

While acid attack was a classical means of dissolving silicate samples, the use of lithium metaborate fusion was a new departure, originating in the work of Ingamells [243], who showed that a clear aqueous solution could be easily and quickly prepared from silicates. Fluxes will decompose most substances at the high temperature required for their use (500–1,000 °C) and the high concentration of reagent brought into contact with the sample. The sample in the form of a very fine powder is mixed with perhaps a tenfold excess of the flux in a graphite of platinum (sometimes nickel or zirconium) crucible. The crucible is then placed in a muffle furnace at 500–1,000 °C for a few minutes to several hours to give a “melt.” After cooling, the melt is dissolved.

Different fluxes can be used. Basic fluxes employed for the attack of acidic materials include carbonates, hydroxides, peroxides, and borates. As acidic flux, pyrosulfates can be used. If an oxidizing flux is required, sodium peroxide can be used. As an alternative, small quantities of the alkali nitrates or chlorates can be mixed with sodium carbonate. Basic and acidic fluxes are respectively dissolved in an acid or basic medium.

The addition of fluxes increases the risk of raising the blank value, owing to the amount of flux required for a successful fusion. In addition, the final aqueous solution obtained from the fusion will have a high salt concentration, which may cause

difficulties in the subsequent steps of the analysis. The high temperatures required for a fusion increase the danger of volatilization losses.

These disadvantages make fusion a less-than-ideal technique for extreme trace element determination. However, for the determination of major, minor, and even some trace elements in such matrices as fly ash, silicates, slags, and dust good results can be obtained.

1.6 Conclusions and future trends

Trace element research imposes a stringent discipline on its practitioners. Provided, of course, that one has modern equipment, mistakes today in analyzing trace elements are generally not so often caused by equipment. They occur, on the contrary, during preparation of the test material, especially when the sources of sampling, contamination, and converting solid or liquid samples to solutions are not recognized and done away with. The analyses must be performed under rigorously controlled conditions to protect the samples from artifacts due to the containers, the reagents, or the ambient air.

If we want to improve our understanding of the role of trace elements in nature, we will have to learn to work more precisely. Along with this, we must not put restraints on our work in microanalysis through contamination in our own laboratories. This requires a change in thinking and a change in the way we have worked up to now. We should take as an example modern surgeons who operate as germ-free as the present level of technology permits in sterile oxygen tents with helmets and breath removal suction – and we should in our own way with the help of modern methods try to carry out our analysis with as few impairing factors as possible.

The chief methods used for the decomposition of organic and inorganic samples have been evaluated. A brief summary of applications of these techniques to various sample matrices is presented in Table 1.6. The variety of approaches currently available for the decomposition of solid and liquid samples allows the most suitable method to be selected for each application, depending on both the matrix and type of analyte, and the subsequent steps to be developed in order to complete the analytical process. In spite of that, it is fair to point out that sample decomposition must not be looked at as an isolated step, but one that needs to be integrated into the entire analytical process.

Attention has been focused on decomposition at elevated temperature and pressure. High-pressure decomposition with its large decomposition temperature range is the most universal decomposition system at present. This is the technique of choice from the vast majority of both inorganic and organic materials. New ways to further increase the efficiency of sample preparation should continue with the development of hyphenated decomposition technique. A novel, microwave-assisted, high-temperature UV digestion for accelerated decomposition of dissolved organic

Table 1.6: Summary of applications of total wet decomposition procedures to the analysis of materials (determination of elements).

Material/matrix/sample	Required acid(s)[a]	Decomposition technique (mode)[b]
Water(s)	H_2O_2, HNO_3	UV irradiation
Environmental samples		
Coal	HNO_3, HCl, HF	Open or closed system
Coal fly ash	*Aqua regia*[c] + HF[d]	Open or closed system
Dust	*Aqua regia* + HF	Open or closed system
Catalysts	*Aqua regia*	Open systems
Waste materials		
Sewage sludge	HNO_3, HCl	Open or closed or flow systems
Waste water	HNO_3	Flow systems
Botanical systems		
Botanicals	$HNO_3 + H_2O_2$ + HF	Open or closed system
Plants	$HNO_3 + H_2O_2$ + HF	Open or closed system
Clinical	HNO_3	Open or closed system
Marine	HNO_3	Open or closed system
Forensic	HNO_3	Open or closed system
Food(s)	HNO_3	Open or closed system
Beverages	HNO_3, H_2O_2	Open or closed or flow systems
Silicates		
Soils	*Aqua regia* + HF	Open and/or closed systems
Sediments	*Aqua regia* + HF	Open and/or closed systems
Glasses	HF	Open systems
Geological samples		
Rocks	*Aqua regia* + HF[e]	Open or closed systems
Ores	*Aqua regia* + HF	Open or closed systems
Minerals	HF + H_2SO_4, HCl	Open systems
Petroleum products		
Fuels	HNO_3+ HCl	Open or closed systems
Oils	HNO_3+ HCl	Open or closed systems
Drugs and pharmaceuticals	HCl, HNO_3	Open systems
Metals		
Ferrous	HNO_3+ (HF lub HNO_3	Open systems
Nonferrous	lub H_2SO_4)	Open systems
Alloys	HCl lub HNO_3lub HF	Open systems
Steels	woda królewska+ HF	Open systems
	HCl + HNO_3, $HClO_4$[f]	
Chemicals	HCl, HNO_3, HF, H_2SO_4	Open or closed systems
Polymers	HCl, HNO_3, HF, H_2SO_4	Open or closed systems
Refractory compounds[g]		
Ceramika	HNO_3, HCl, HF, H_2SO_4, H_2O_2	Open or closed systems
Kompozyty	HNO_3, HCl, HF, H_2SO_4, H_2O_2	Open or closed systems
Nuclear materials	HNO_3 or HCl, H_3PO_4, $HClO_4$	Open or closed systems

[a]Concentrated acids are usually employed; H_2O_2 is 30 %; in most cases alternative decompositions are possible depending on requirements of analyst.
[b]Conventional or microwave.
[c]Unstable.
[d]Use only Teflon vessels, the addition of HF is required to obtain quantitative recoveries for Cr.
[e]Addition of H_3BO_3 to neutralizm of HF by forming tetrafluoro-boric acid.
[f]Danger of explosion.
[g]Certain refractory materials are not decomposed; these must be solubilized by fusion.

compounds or slurries was developed [156]. This new technique is ideal for extreme trace analysis due to the low blank values and low acid concentration. In addition, this digestion method can be used for the determination of nonmetals by ion chromatography. Alternatively, within the limits of the Teflon-lined digestion vessels, improvement in the decomposition efficiency can be achieved by adding optimum concentrations of strong oxidizing agents, such as ozone or oxygen, which appear to be efficient decomposition agents for the treatment of biological material. Again, this has the advantage that the agent does not contribute to the analysis blank. It should be mentioned that vapor-phase acid digestion offers an alternative solution to these problems: reduced concentration of acid in the digestate and the possibility of using a technical grade acid without any deterioration of the analytical blank. Another example where significant improvement in decomposition and dissolution was obtained is the use of a reactor that combines microwave and ultrasound energy [103]. It is expected that these two methods could open a new research field **combined digestion techniques**.

It can be said with certainty that the majority of all digestions will be performed in the future by means of microwave assistance. Progress has been made over the past several years in reducing systematic errors and improving detection limits with microwave digestion, as well as its automation. A noticeable trend toward pressurized closed-vessel systems permitting high-temperature decomposition compatible with trace analysis has occurred. While some researchers advocate high-pressure (>100 bar) digestion at 250–300 °C to destroy interferences in refractory compounds, manufacturers are working to device sample vessels that can withstand these conditions.

There has been a growing trend in recent years toward the development of fully automated online analysis techniques. Microwave-assisted high-pressure flow digestion system with PTFE or PFA tubes for digestion temperatures up to 250 °C opens up new possibilities for fully automated sample preparation [103]. On the other hand, the development of new high-temperature/high-pressure flow digestion systems that incorporate resistively heated capillaries for the continuous digestion of various samples, coupled with atomic spectrometric instruments, has arisen [159–161]. It is predicted that flow systems will become dominant for liquid samples and slurries and extend the analytical capabilities of instrumental methods by combining sample preparation with simultaneous analysis using only micrograms of sample and microliters of reagents. The final goal of these studies should be the adaptation of standard batch digestion methods to online systems combining flow-through digestion directly to analyzers.

It is evident that wet decomposition methods will remain a fertile area for development. New digestion techniques need to be designed that address the limitations for the instrumentation and maximize its potential. Development trends for conventional and microwave instruments will focus on sample throughput, enhanced vessel performance specifications, the use of new materials, further refinement of *in situ* vessel

control (direct temperature and pressure, incident and reflected microwave power), and computer-controlled sample digesters with automated capability.

Finally, the development of automated methods for wet decomposition of solid samples without human participation can only be achieved with the use of a robotic station [244]. Nevertheless, a number of auxiliary energies and commercially available modules can facilitate and/or accelerate one of the most time-consuming steps of the analytical process, that is, to obtain the analyte(s) from a solid sample in the form of a solution.

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Chapter-1

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