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Quality of the Trace Element Analysis: Sample Preparation Steps

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1. Introduction

Current status of elemental analysis performed using atomic spectroscopy techniques is to reach the best results in the shortest time and with minimal contamination and reagent consumption. Various spectroscopic methods such as flame- and graphite furnace atomic absorption spectrometry (F- and GF-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) have been used for many years for determination of elements, since they met needs required in analytical applications. Constant progress in detector technology can still been observed, *e.g.* in terms of lowering quantification limits. Despite these advantages, quality of results does not follow the same tendency and sample preparation is recognized to be a critical point and the most important error source in modern analytical method development. This is especially true for solid samples that have to be brought into solution before measurements. It is dictated by instrumentation requirements dedicated to analysis of liquid samples. Determination of analyte concentrations in solid materials is not an easy task and several factors should be considered in order to minimize uncertainty in sample preparation and to achieve real objectives of analysis. It includes sample type and its matrix composition responsible mainly for the degree of difficulties during sample preparation and analyte determination. Therefore, the good choice of sample treatment and confidence of its application become a key ensuring to obtain reliable results.

2. Analytical sample

Samples to be analyzed can be divided generally into two main groups: **liquids** and **solids** (Hoenig, 2001).

- **Liquid samples** represent those that are already in an aqueous solution (*e.g.,* various waters, beverages, milk, blood, urine) or in other liquid form (*e.g.,* oils, fuels, organic solvents);
- **Solid samples** can be categorized due to their matrix composition as follows: those of organic nature (*e.g.,* plants, animal tissues and organs, excrements, plastics) or those with advantage of inorganic composition (*e.g.,* soils, sediments, dusts, metals).

It is well known that in most cases **sample preparation** step is needed for analysis based on atomic spectrometry techniques and leads to conversion of samples into homogenous forms

like aqueous or acidic solutions. Despite aqueous solutions, which can be directly analyzed without any special pre-treatment, solid samples must be solubilised by an appropriate dissolution method, depending on the sample composition (main matrix, content of trace elements).

3. From sampling to reporting – steps of analytical process

Routine chemical element analysis involves several succeeding steps. It starts with planning a suitable strategy for a given analyte in a particular matrix, followed by representative sampling, sample pre-treatment, preparation procedure and instrumental measurement. It ends with interpretation of obtained data. A schematic diagram of the whole analytical process is drafted in Figure 1.

PRELIMINARY ⟶ Planing of analysis

SAMPLING

SAMPLE PREPARATION ⟶ Pre-treatment

Solubilization

MEASUREMENTS

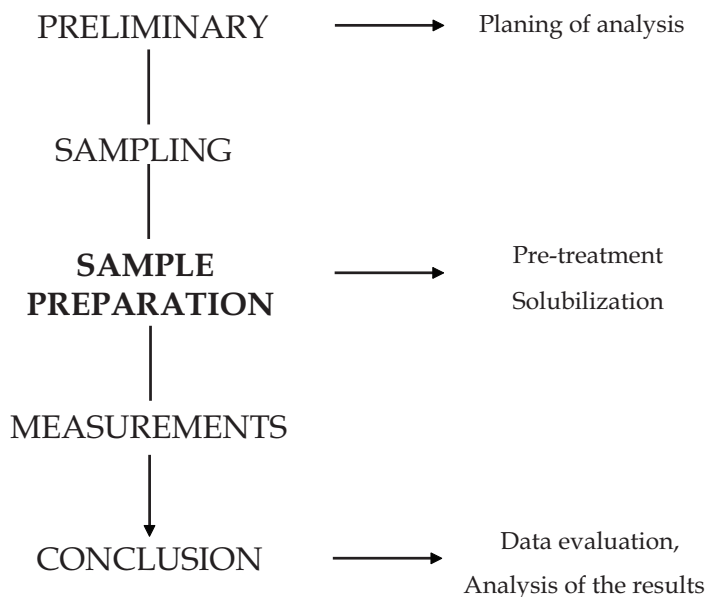CONCLUSION ⟶ Data evaluation,

Analysis of the results

Fig. 1. Steps in analytical process (based on Hoenig, 2001)

An ideal method would allow performing all steps in one single, simple and quick process. In practice, each step in the analytical protocol contains an error, which affects reproducibility and accuracy of results. **Sample preparation** is recognized to be the largest source of errors and one of the most **critical points** of each analysis. Precisely, the **sample matrix** responds mainly for a difficulty of analysis. The sample matrix may impose a relatively pronounced effect during the preparation step or interferences during measurements, thus, eliminating or overcoming the troublesome matrix influence is necessary. Unfortunately, because of a wide number of analytes and a variety of sample types, there is no unique sample preparation technique that would maintain all requirements of analysts. Among strategies of sample preparation, dilution, acid digestion, extraction, slurry sampling or direct solid sample analyses are those that are mostly considered.

4. Quality assurance (QA) and quality control (QC)

Selection of the proper sample preparation method heavily depends on several factors. Availability of a variety of analytical techniques and instrumentation in addition to a great assortment of samples and preparation procedures make that selection of the right analytical approach is critical for method development. The incorrect sample preparation, *i.e.*, due to incomplete digestion or analyte losses, commonly can not be compensated by a versatile analytical technique and/or instrumentation. On the other hand, limitations of the instrumentation should be also taken into account since even for well-prepared sample they can lead to inadequate and untrue results. There is no doubt that the analyst should decide when his method of sample preparation used satisfies quality criteria and when results can be accepted. It is not an easy task and several different concerns can occur. However, at present, normally asked questions can lead to simple answers as follows:

Question: Which method of sample preparation should be used?
Answer: Check it.
Question: When the set of results can be accepted?
Answer: When their quality/accuracy is well demonstrated/verified.
Question: How it can be achieved?
Answers: Quality assurance and quality control concept.

Quality assurance (QA) claims to assure the existence and effectiveness of procedures that attempt to make sure that expected levels of quality will be reached (Rauf & Hanan, 2009). A particular attention should be paid to intermediate steps of an analytical protocol such sample treatment (preparation) that strongly contributes to total uncertainty of measurements. It should be improved, guaranteed and recorded by the analyst. Sample preparation is prone to errors like contamination, degradation or analyte losses and matrix interferences, which may, however, go unobserved by the analyst and affect final results.

Quality control (QC) refers to procedures that lead to control different steps in measurement process (Rauf & Hanan, 2009). It includes specific activities ensuring control of the analytical procedure. Among key points to be included during sample preparation, the most important is to demonstrate adequacy of the investigated method, *i.e.*, (1) accuracy, (2) precision, (3) efficiency and (4) contamination.

- *Accuracy* is the measurement of how close an experimental value is to the true value. It is realized by use of **control samples** with known compositions, which are treated in the same way as routine samples. Control samples allow monitoring the performance of the whole analytical procedure, including all sample preparation steps. Accuracy is based on the absence of systematic errors and the uncertainty of results corresponds to coefficients of variation. Nowadays, to demonstrate accuracy of the method, analysis of (standard, certified) **reference materials** (RMs) is the most commonly used. Another way to confirm accuracy of the method of interest is to compare results with those obtained with well established (**reference**) and independent **procedures**;
- *Precision* (reproducibility) is the degree to which further measurements or calculations show the same or similar results. It is expressed by means of relative standard deviation of measurements (RSD). The smaller RSD value, the higher precision is obtained;
- *Efficiency* in analyte determination may be demonstrated by adequate **recovery** using the **method of standard additions**. Analysis of spiked samples also allows to demonstrate accuracy of the method and recognize possible **interference effects**, which could lead to erroneous results;

- *Contamination* is a common source of error, especially in all types of environmental analysis. It can be reduced by avoiding manual sample handling and by reducing the number of discrete processing steps, however, the best way to asses and control the degree of contamination at any step of sample treatment is to use **blank samples**.

5. Sample preparation procedures

5.1 Liquid samples

In general, aqueous samples can be introduced to analysis directly and without any previous special pre-treatment, *i.e.* total or partial decomposition, as long as measured concentrations using spectrometric methods are reliable and satisfactory while possible interferences are under control.

In most cases only very little sample preparation is required and the easiest way is simple sample dilution. The dilution factor used in this case depends on concentrations of analytes and main matrix components; knowledge about the sample composition could be very helpful. Such an approach certainly reduces the analysis time and sample handling. It leads to low reagent consumption and generation of minimal residue or waste. Such simplification in sample manipulation decreases the risk of contamination and analyte losses. To minimize possible matrix interferences, standard additions and matrix-matched standards are proposed for calibration. Direct determinations from liquid samples (*e.g.*, waters, beverages) with minimal sample treatment such as dilution, degassing or matrix components evaporation provide a viable alternative to digestion as a mean of sample preparation:

El-Hadri et al. (2007) developed a highly sensitive and simple method for direct determination of the total As using HG-AFS in refreshing drink samples (colas, teas and fruit juices). Concentrations of As were directly determined in samples after pre-reduction with KI and acidification with HCl. Cola samples needed a more care, *i.e.*, degasification by magnetic stirring and sonication before analysis. Accuracy of the developed procedure was confirmed by recovery study and by comparison with a well established (reference) dry ashing digestion procedure. Quantitative recoveries (94-101%) were obtained with variation coefficients within 0.1-9%. The detection limit (DL) for As ranged from 0.01 to 0.03 ng mL^{-1}. In addition, no blank correction was required.

Matusiewicz & Mikołajczak (2001) proposed the method of direct determination of the total As, Sb, Se, Sn and Hg in untreated beer and wort samples using HG-ET-AAS. Samples were analyzed with little erased preparation: degassing by filtration for beer and sonication for wort. Calibration was made by standard additions. Accuracy and precision were ensured by using five well-established reference materials (SRMs or CRMs) and microwave (MW)-assisted digestion with HNO_3. Precision was typically better than 5% as RSD. DLs were restricted by variations in blank absorbance readings. Nevertheless, sub-ng mL^{-1} values were obtained. The problem of analytical blanks for ultrasensitive techniques was also discussed. Additionally, in terms of minimizing the risk of sample contamination, several procedures for removing CO_2 from beer were examined, including filtration, shaking, stirring, sitting overnight, storing with acid in open vessels overnight and ultrasonication.

Karadjova et al. (2005) develop a simple and fast procedure of sample preparation for the total As determination by HG-AFS directly in diluted undigested wine samples. Application of an appropriate wine dilution factor allowed minimizing ethanol interferences on HG-AFS measurements. Depressive effects by the small ethanol content (2–3% (V/V)) could be

tolerated in 5–10- fold diluted samples by using solvent-matched calibration standard solutions. The method was validated through recovery studies and comparative analyses by means of HG-AFS and ET-AAS after MW digestion. Recoveries were in the range of 97–99% and precision was varied between 2 and 8% as RSD.

In the work of Tašev and co-workes (2005) simple ethanol evaporation was the only pre-treatment procedure proposed for direct wine samples analysis on the content of inorganic As species (As(III) and As(V)) by HG-AAS. Accuracy of this procedure was proved by recovery study and comparative analysis using ET-AAS. The total As content was determined after microwave digestion. Also here, preliminary evaporation of ethanol was recommended to avoid over-pressure and ensure better conditions for complete mineralization of wine organic matter. DLs of 0.1 mg L^{-1} were achieved for both species. Precision for this procedure (as RSD for ten independent determinations) varied between 8 and 15% for both As species present in the range of 1–30 mg L^{-1}. Accuracy of the aforementioned procedure (in terms of the total As content) was proved by recovery study and comparative analysis using ET-AAS.

Nevertheless, some types of liquid samples necessitate a particular caution before being introduced into detection systems. For example, blood coagulates in contact with some chemical compounds like $PdCl_2$ or $Pd(NO_3)_2$ (often used as modifiers in ET-AAS analyses) and this may partially or totally clog an autosampler capillary. Milk can not either be directly analyzed if HG is used as a sample introduction technique. The treatment with HCl (required for HG measurements) involves protein precipitation and creates a solid phase that can contain or partially retain elements under study. In this case slurry sampling (SS) is recommended.

The direct introduction of non-aqueous samples, however possible, significantly depends on their viscosity. In F-AAS analysis viscosity should be similar to that of water and organic solvents as ethanol or methyl isobutyl ketone fulfill this condition. In ET-AAS any organic solvents can be used due to similarity of analyte responses to those obtained in aqueous solutions. In ICP-OES several types of organic liquids can be introduced but an increase of the RF power is required to maintain a stability of the plasma (Hoenig & de Kersabiec, 1996).

5.2 Solid samples

Compared to liquids, preparation of solid samples is more complex. In general, unless the analytical method involves direct analysis of solid samples, they need to be in solution before analysis. Major concerns in selection of a solid sample preparation method for elemental analysis are requirements of the analytical technique used for detection, the concentration range of analytes and the type of matrix in which analytes exist. Many types of solid samples are converted into aqueous solution and therefore dissolution of sample matrices prior to determination is a vital stage of analysis aimed at releasing analytes into simple chemical forms.

The composition of sample matrices varies from purely inorganic (*e.g.,* ash, rocks, metallurgical samples) and purely organic (*e.g.,* fats) to mixed matrices (*e.g.,* soils, sediments, plant and animal tissues). Dissolution of inorganic matrices leads to clear solutions, where analytes are in their ionic forms. Both, purely organic and mixed matrices are more troublesome and dissolution does not guarantee complete matrix decomposition. Analytes may still be partially incorporated in organic molecules and masked from determination. In

such case undecomposed organic matter may interfere in analysis leading, in consequence, to decrease in quality of final results. Of the methods responded for total decomposition of organic samples and normally used for sample preparation are (1) wet digestion and (2) dry ashing procedures. Alternatively, extraction of analytes from samples without total matrix destruction was proposed.

5.2.1 Dry ashing

Dry oxidation or ashing eliminates or minimizes the effect of organic materials in mineral element determination. It consists of ignition of organic compounds by air at atmospheric pressure and at relatively elevated temperatures (450-550°C) in a muffle furnace. Resulting ash residues are dissolved in an appropriate acid.

Dry ashing presents several useful features: (1) treatment of large sample amounts and dissolution of the resulting ash in a small acid volume resulted in element pre-concentration; (2) complete destruction of the organic matter, which is a prerequisite for some detection techniques (*e.g.*, ICP-OES); (3) simplification of the sample matrix and the final solution condition (clearness, colourless and odourless); (4) application to a variety of samples. Nevertheless, dry ashing presents either some limitations: (1) high temperature provokes volatilization losses of some elements; to avoid losses of volatile As, Cd, Hg, Pb and Se, and improve procedure efficiency, ashing aids (high-purity $Mg(NO_3)_2$ and MgO) are used; (2) on the other hand, the addition of ashing aids significantly increases the content of inorganic salts, which may be a problem in subsequent determinations of trace elements and contribute to contamination that necessitates careful blank control; (3) it does not ensure dissolution of silicate compounds and consequently of all elements associated with them (it can be encountered during plant analysis); after a procedure without elimination of Si (by evaporation with HF), poor recoveries for some elements can be observed, particularly traces; (4) open dry ashing exposes samples to airborne contamination (Hoenig, 2001; Sneddon et al., 2006).

Reliability of dry ashing procedures was demonstrated in some recent papers:

Vassileva et al. (2001) investigated the application of dry ashing for determination of the total As and Se in plant samples. The proposed method was a combination of dry ashing, conventional wet digestion with HNO_3 and HF and (in some cases) addition of a Mg containing solution as the ashing aid. The resulting ash was dissolved in HNO_3. It was established that plants of terrestrial origin may be mineralized using the dry ashing procedure without any As and Se losses. This was confirmed by analyses of several reference terrestrial plant and laboratory control samples in addition to direct analysis of the same plants using SS-ET-AAS. The addition of ashing aids seemed to be dispensable as errors observed were negligible. Unfortunately, more volatile As and Se species were present in plants of aquatic origin (*e.g.*, alges) and a separate wet digestion procedure remained unavoidable.

Grembecka et al. (2007) determined concentrations of 14 elements (Ca, Mg, K, Na, P, Co, Mn, Fe, Cr, Ni, Zn, Cu, Cd, Pb) in market coffee samples after dry mineralization of both dry samples and infusions evaporated to dryness prior to F-AAS measurements. Samples were ashed in electric furnace at 540°C with a gradual increase of temperature and subsequent dissolution of residues in HCl. Reliability of this procedure was checked by analysis of certified reference materials (CRMs). Recoveries of elements analyzed varied between 73.3% and 103% and precision (as RSDs) was within 0.4–19.4%.

Matos-Reyes et al. (2010) presented a method to quantify As, Sb, Se, Te and Bi in vegetables, pulses and cereals using HG-AFS. Samples were dry ashed and ashes dissolved with diluted HCl. Accuracy was assured by analysis of CRMs. A good accordance was always found between determined and certified values. For comparison the t-test (at 99% confidence level) was used but no significant difference between both sets of data was found. In addition, recovery studies on spiked samples before dry ashing was done. Recoveries determined ranged from 90 to 100% and indicated no loss of analytes and no contamination during the whole procedure.

5.2.2 Wet ashing

Wet digestion is used to oxidize the organic part of samples or to extract elements from inorganic matrices by means of concentrated acids or their mixtures. Commonly it is carried out in open vessels (in tubes, in beakers, on a hot plate, in a heating block) or in closed systems at elevated pressure (digestion bombs) using different forms of energy: thermal, ultrasonic and radiant (infrared, ultraviolet and microwave) (Hoenig, 2001; Sneddon et al., 2006).

Compared to dry ashing, wet digestion presents a wide range of varieties, concerning the choice of reagents as well as devices used. However, the sample nature and its composition as well as the composition and concentration of the reactive mixture should be considered before analysis. It includes: strength of the acid, its oxidizing power and boiling point, solubility of resulting salts, safety and purity of the reagent. In general, HNO_3, HCl, H_2SO_4, H_3PO_4, $HClO_4$, HF and H_2O_2 are used for organic samples, alloys, minerals, soils, rocks and silicates. Concentrated HNO_3 is the most favourable oxidant for destruction of the organic matter. Unfortunately, due to relatively low oxidation potential it may lead to incomplete digestion of materials with organic-rich matrices. It easily decomposes carbohydrates, however fats, proteins and amino acids require the addition of stronger H_2SO_4 or $HClO_4$. At present, the mixture of HNO_3, H_2SO_4 and H_2O_2 is a very efficient medium for different wet digestion procedures. Main disadvantages associated with the use of H_2SO_4 are its tendency to form insoluble compounds and its high boiling point. The high boiling point makes difficult to remove its excess after completion of oxidation. While $HClO_4$ is a strong oxidizing agent, it is extremely hazardous. HCl and HF ensure dissolution of inorganic compounds. Aqua regia (HCl with HNO_3 (3:1)) is widely used to dissolve soils, sediments and sludges.

The type of acid used in the sample preparation procedure may strongly affect the measurement step. In all atomic spectrometric techniques, HNO_3 is the most desirable reagent. In general, in spite of sometimes observed signal suppressions in its presence (*e.g.*, in ICP-OES), problems associated with it at concentrations up to 10% are rather occasionally observed as far as the acidity in sample and standard solutions are similar. Also, the mixture of HNO_3 and H_2O_2 used for digestion does not decrease a quality of analytical measurements. The presence of HCl is not troublesome in ICP-OES analysis, however, its use is prohibited in ET-AAS analysis because of a possible formation of volatile and difficult to dissociate analyte chlorides leading to spectral and/or vapour-phase interferences. In consequence, the latter phenomenon reduces absorbance signals of analytes. This problem may be overcome after addition of HNO_3 during the digestion procedure. For some applications, HCl should be avoided in ICP-MS analyses due to isobaric interferences, *e.g.*, during As determinations. Because of high viscosity that may provoke interferences in transport of solutions, utilization of H_2SO_4 is usually avoided despite its great efficiency in destruction of organic matrices. Its presence is particularly undesirable in analytical techniques where the sample introduction is realized by means of aspiration or pneumatic nebulisation of sample solutions (F-AAS, ICP-OES, and ICP-MS).

Main problems associated with wet digestion methods are: (1) much lower temperatures as compared to dry ashing procedures, however minimizing volatilization losses or retentions caused by reactions between analytes and vessel materials, they may lead to incomplete solubilisation of sample constituents and (2) co-precipitation of analytes with precipitates formed by main matrix elements within reactive mixtures. Both, they represent a real danger concerning reliability of analysis and hence, a good choice of a procedure and adequate reagents is critical for QA/QC of results.

5.2.2.1 Conventional wet decomposition

Wet decomposition in open vessel system (Teflon or glass beakers or glass tubes on hot plates) has been performed for many years. It may be very useful for relatively "easy" samples as food or agricultural products and materials, but generally, it is unsuitable for

Sample	Analyte	Reagents	QA/AC	Detection technique	Reference
Composts	Cd, Cr, Cu, Mn, Ni, Pb, Zn	HNO_3	- Reference material - Accuracy (recovery test) - Spiked sample	F-AAS	Hseu, 2004
Fish, mussel	Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn,	HNO_3	- Reference material - Accuracy (recovery test) - Precision (RSD)	ICP-OES	Türkmen & Ciminli, 2007
Xanthan gum	Ca, K, Mg, Na	HNO_3	- Matrix matched calibration - Independent analytical procedure - Precision (RSD)	F-AAS	Abentroth Klaic et al., 2011
Dairy products	Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, Zn	$HCl+H_2O$	- Reference material - Accuracy (recovery test) - Independent analytical procedure - Precision (RSD)	ICP-OES	Kira & Maihara, 2007
Nuts	Al, Ba, Cd, Cr, Cu, Fe, Mg, Mn, Pb, Zn	$HNO_3+H_2SO_4+H_2O_2$	- Reference material - Accuracy (recovery test) - Calibration with standard additions - Precision (RSD)	ICP-OES	Momen et al., 2007
Legumes, nuts	Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn	$HNO_3+V_2O_5$	- Calibration with standard additions for blank and samples - Accuracy (recovery test) - Precision (RSD)	ET-AAS	Cabrera et al., 2003
Plant, fungs	Hg	$HNO_3+H_2SO_4$	- Reference material - Precision (RSD)	CV-AAS	Lodenius & Tulisalo, 1995
Crude oil distillation products	Cu	H_2SO_4	- Reference material - Accuracy (recovery test)	ET-AAS F-AAS ICP-MS	Kowalewska et al., 2005
Herbal medicines	Al, Cr, Fe, V	HNO_3+HClO_4+HF	- Reference material - Accuracy (recovery test)	ET-AAS ICP-OES	Gomez et al., 2007

Table 1. Conventional wet digestion for diverse samples

such samples that require lengthy dissolution times (up to 24 h). Other problems to be considered are: time consumption (hours), contamination from environment, use of large amounts of reagents (especially strong oxidizing agents), pre-concentration of reagent impurities, and evaporative loss of volatile elements. Despite these drawbacks, conventional wet digestion in open vessel system allows achieving rather reliable and accurate results (according to QA/QC standards) and some recent applications are given in Table 1.

5.2.2.2 Microwave-assisted digestion

MW-assisted sample preparation with HNO_3 or its mixtures with HCl or H_2SO_4 (with or without added H_2O_2) is these days predominantly used for decomposition of a variety of inorganic and organic materials. The interaction of microwave radiation with samples and reagents results in fast heating of reaction mixtures and their efficient decomposition. Advantages of this strategy over conventional dry or wet ashing procedures are: broad application, much shorter reaction time needed (minutes), direct heating of samples and reagents, reduced need for aggressive reagents, minimal contamination and lack of loss of volatile elements. The use of small amounts of reagents decreases signals from the blank and increases accuracy of results. Usually, a mixture of HNO_3 and H_2O_2 is used for botanic, biological and food samples, while a mixture of H_2SO_4 and H_2O_2 is mainly used for oily samples. Acid mixtures are recommended for inorganic materials such as metals, alloys, minerals and for extracts from soils and sediments. Two different systems for MW-assisted digestion are used: pressurized closed vessels and open focused vessels. MW-assisted digestion in closed vessels under pressure is the most commonly applied. It offers safety radiation, versatility, energy control and possibility for addition of solutions during digestion. The only limitation is time required for cooling before vessels can be opened (even hours). In case of open focused MW system loss of volatile elements can occur. Results for low-level elements might also be affected by higher amounts of reagents used (increased risk of sample contamination). Both drawbacks can be, however, minimized by using vapour-phase acid digestion, which has been proven to be very effective in minimizing the residual carbon content (Hoenig, 2001; Sneddon et al., 2006).

In comparison to other digestion methods, accurateness and quality of MW digestion procedures for sample treatment can be found in numerous work. Some examples are presented below:

Demirel et al. (2008) compared dry ashing, wet ashing and MW digestion for Se, Fe, Cu, Mn, Zn and Al determination in various food materials (*e.g.*, rice, nuts, mushrooms, meat, milk, wine) using the F-AAS and GF-AAS detection. It was found that MW digestion procedure yielded more accurate results, required shorter time and enabled to achieve the highest recoveries for CRM analysis. Moreover, it allowed quantitative recoveries of volatile elements such as Se. For wet and dry ashings only 60 and 22% recoveries of Se were obtained. Poor recoveries (86%) were either obtained for Al when dry ashing was adopted. RSD values were below 10% and the proposed MW-assisted digestion procedure was free from matrix interferences.

Aydin (2008) tested dry, wet and MW digestion procedures for quantification of Co, Ni, Zn, Cu, Mn, Cd, Pb, Cr, Fe, Na, K, Ca and Mg in wool samples using ICP-OES. Different digestion mixtures, temperatures, dissolution times and proportions of HNO_3 and H_2O_2 were examined. The chosen MW-assisted digestion procedure maintained satisfactory recoveries, detection limits and precision for trace element determination in wool samples. For dry and wet ashings respective RSD values were considerably higher.

Du Laing et al. (2003) examined six destructive methods for determination of heavy metals (Cd, Cu, Pb, Zn, Ni, Cr, Fe and Mn) in red plants with atomic absorption detection. QC for concentration measurements was performed by analyzing adequate CRMs. MW digestion using HNO_3 yielded the best overall recoveries, whereas dry ashing was proved to be totally inappropriate for trace metal analyses of red plants (very poor recoveries). In case of Cr and Ni, the MW digestion procedure was the only one acceptable. It was concluded that red plants presented a difficult matrix and analysis of CRMs is needed for QC.

Szymczycha-Madeja & Mulak (2009) tested four digestion procedures for determination of major and trace elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn) by ICP-OES in a spent catalyst. Two MW-assisted and two conventional hot-plate wet digestion procedures were applied. MW digestion with an HCl, HNO_3 and H_2O_2 mixture was the most effective. Quality of results was evaluated by analysis of CRM (CTA-FFA-1, fine fly ash). The proposed method provided a better solubilization of the matrix and much increased reproducibility. Results were sufficiently precise and accurate (RSD <5%). In contrast, MW digestion with a HNO_3 and HF mixture was found to be not suitable for proper determination of examined elements; errors in analysis of catalyst samples were encountered.

Do Socorro Vale et al. (2009) studied the effect and compared different procedures to treat the gum (deposits found in internal combustion engines) prior to determination of various elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Si and Zn) by ICP-OES. To evaluate the best decomposition methodology, experiments were performed with one gum sample called a "reference sample". Two procedures were tested: (1) dry ashing followed by high temperature dissolution with HF and (2) MW digestion with a HNO_3 and H_2SO_4 mixture The latter procedure was found to be less time-consuming as compared to dry ashing and showed high recovery efficiencies in Cr, Cu, Fe, K, Ni, Pb, Si and Zn determinations.

5.3 Ultrasound-assisted extraction

Wet and dry digestion procedures, however excellent for sample decomposition, entail tedious, time-consuming and laborious steps, in addition to possible loss of analytes and contamination of samples. In consequence, obtained results can be far from true values. Today, ultrasound (US)-assisted procedures are considered as other alternatives for solid sample pre-treatments. They were found to be superior in facilitating and accelerating such sample preparation steps as dissolution, fusion and leaching. Chemical effects of US are attributed to acoustic cavitation, that is, bubble formation and subsequent disruptive action. It leads to generating local high temperature (*ca.* 5000 K) and pressure (*ca.* 10 GPa) gradients and to mechanical action between solid and liquid interfaces, which help in sample preparation. In US-assisted procedures diluted acid media are normally used for leaching element ions from powdered materials, thus, decreasing blank values, reagent and time consumptions and preventing analytes' losses. Smaller sample amounts can be used as well. Extractions are realized in ultrasonic baths or with sonoprobes, which are commonly employed for decomposition of organic compounds. However, a rigorous experimental control is strongly recommended to avoid losses of precision and accuracy. Uncontrolled US extraction procedures can provoke decomposition of analytes and hinder in this way extraction of organic compounds. When inorganic species are considered, ultrasonic irradiation does not present any decomposition risk; excellent results are obtained for diverse matrices (Santos Jr. et al., 2006).

Recently, ultrasonic effects have been exploited for sample preparations in agricultural, biological and environmental applications in order to improve analytical throughput. Nascentes et al. (2001) proposed a fast and accurate method for extraction of Ca, Mg, Mn and Zn from vegetables. Optimized conditions of such procedure were: 1 L of water, 25°C and 2% (v/v) detergent concentration. The best conditions for extraction were: 0.14 mol L^{-1} HNO$_3$, 10 minutes of sonication and a sample particle size <75 μm. Accuracy of this procedure was assessed by analyzing CRMs, as well as comparing results with those achieved with wet digestion. Recoveries determined were from 96 to 102%.

The US-assisted extraction procedure for estimation of major, minor and trace elements in lichen and mussel samples (IAEA lichen 336 and mussel tissue NIST 2976) using ICP-MS and ICP-OES was developed by Balarama Krishna & Arunachalam (2004). Parameters affecting extraction, including extractant concentration, sonication time and ultrasound amplitude, were optimized to get quantitative recoveries of elements. The procedure using a 1% (v/v) HNO$_3$ was fast (15 minutes) and accurate for most of elements. Solubilization of elements was achieved within 4 minutes of sonication at 40% sonication amplitude and a 100 mg sample weight. Overall precision was better than 10%.

In contrast, Maduro et al. (2006) pointed out some limits of US-assisted procedures affecting quality of analytical results. They compared three different ultrasonic-based sample treatment approaches, the automated ultrasonic SS, the ultrasonic assisted acid solid–liquid extraction (ASLE) and the enzymatic probe sonication (EPS) for determination of Cd and Pb by ET-AAS in CRMs of biological samples (spruce needles, plankton, white cabbage, oyster tissue, algae). The sample mass was 10 mg and the liquid volume was 1 mL of diluted HNO$_3$ (1 mol L^{-1}). Accuracy was evaluated by comparing results with those obtained using total acid digestion. The best results were obtained with the SS procedure with which accurate and precise determinations of the Cd and Pb content was possible in case of four from five analyzed CRMs. A good performance (quantiative extraction) of ASLE for Cd was only achieved in case of two from four CRMs, whereas total Pb recovery was only possible in case of three from four CRMs. Quantitative extraction with the EPS procedure was only obtained for Cd in oyster tissue. Neither ASLE nor EPS procedures were able to extract Cd or Pb from spruce needles. The Pb concentration obtained after EPS was found to be highly dependent on sample centrifugation speed and time.

5.4 Slurry sample preparation

The use of conventional wet acid digestion or dry ashing is time consuming and usually requires excessively hard sample treatment strategies. Recently, several methods for direct analysis of complex matrices by atomic spectrometric techniques have been developed and the SS approach as an alternative way of sample preparation is highly recommended (Cava-Montesinos et al., 2004; Bugallo et al., 2007). SS means preparation of a suspension of solid powdered particles of a sample in a liquid phase. Usually, after grinding the solid sample, the slurry is formed in water or in diluted acid (mainly HNO$_3$) in order to partially or totally extract analytes to the aqueous phase. It is possible to change the slurry concentration by simple dilution; hence, SS combines advantages of both liquid and direct solid sampling (Hoenig, 2001).

Main advantages of the SS procedure are: (1) elimination of a tedious and time-consuming step of sample dissolution; (2) avoidance of use of concentrated reagents and dilutions introducing contaminants; (3) safety and simplification of operation; (4) minimization of

analytes' losses (especially volatile) and (5) possibility of use of smaller amounts of samples (1-100 mg in most common analyses). In addition, calibration performed using simple aqueous standards can be used. Nevertheless, several disadvantages affecting accuracy and precision of measurements and such variables as: (1) stabilization of the slurry; (2) its homogeneity; (3) sample particle size and (4) sedimentation must be carefully considered. Slurried samples must be stirred periodically by magnetic stirring or ultrasonic mixing before introduction to a measurement device. This helps to avoid sedimentation of sample particles, which may result in unrepresentative sample weight. Settling of solid particles in liquid-suspended samples can also be overcome by preparation of more stable slurries in a viscous medium or by using thickening agents. Concerning sample representativeness, only very fine particles in the slurry may ensure correct results; the presence of larger particles was found to be the most critical factor in analysis. For that reason, an intensive grinding of samples prior to analysis is of a great importance.

The SS procedure may be helpful in analysis of microsamples (*e.g.*, dust) or samples hardly soluble in common acid (*e.g.,* minerals). This procedure may be useful for the QC purpose of another sample preparation technique.

Recently, a lot of work has been done to maintain minimal sample manipulations with simultaneous assurance of reliability of results and at this field, SS has been proved to be quite suitable for this purpose:

Cava-Montesinos et al. (2004) developed a simple and fast procedure for determination of As, Bi, Sb, Se and Te in milk samples using HG-AFS. Samples were treated with *aqua regia* for 10 minutes in an US water bath and pre-reduced with KBr or with KI/ascorbic acid for total Se and Te or As and Sb determinations. Hydrides were generated from slurries in the presence of Antifoam A using a $NaBH_4$-HCl mixture. Calibration solutions were prepared and measured in the same way as samples. Obtained results were well comparable with those found after MW-assisted digestion. The advantage of the method was that only 1 mL of milk was required for analysis.

Matusiewicz & Ślachciński (2007) developed a SS procedure for simultaneous determination of hydride forming (As, Bi, Ge, Sb, Se, Sn), vapors (Hg) and conventional (Ca, Fe, Mg, Mn, Zn) elements in biological and environmental CRMs and real samples (coal fly ash, lake sediment, sewage) using a dual-mode sample introduction system (MSIS) coupled with MIP-OES detection. The slurry concentration up to 4% (m/v) was prepared in 10% HNO_3 containing 100 µL of decanol by ultrasonic agitation. Calibration was carried out by standard additions. An ultrasonic probe was used to homogenize the slurry. DLs below µg g^{-1} and good recoveries for all elements were obtained. Memory effects were not observed and hence, long washing times between samples were not needed. This sample pretreatment was minimal and involved only the slurry preparation procedure.

Bugallo et al. (2007) proposed a novel MW-assisted slurry tprocedure for Ca, Cu, Fe, Mg and Zn determination in fish tissues by F-AAS. The suspension was optimized for each analyte and it was established that MW irradiation in HNO_3 containing 0.3% glycerol for 15-30 s at 75-285 W permitted efficient recoveries for Ca, Fe, Mg and Zn. Only Fe recoveries were not higher than 46%, however, reduction of matrix interferences was realized by additional short MW-assisted suspension treatment. For Cu, an HCl suspension medium and homogenization with magnetic stirring (5 minutes) was found to be the most appropriate. Results obtained using SS were not significantly different from those achieved with MW-assisted digestion. Accuracy was checked using a CRM.

Da Silva et al. (2008) combined a cryogenic grinding and SS for Cu, Mn and Fe determination in seafood samples by F-AAS. Samples (80 mg) were grounded in a cryogenic mil, diluted with 1 mol L^{-1} HNO$_3$/HCl and sonicated for 30 min. Calibration curves had been prepared using element standards in the same suspension medium. DLs below µg g^{-1} and precision expressed as RSD lower than 4% were obtained. Accuracy of the procedure was confirmed by analysis of a CRM of oyster tissue; reliability by comparing it with ICP-OES after complete wet digestion in a HNO$_3$/H$_2$O$_2$ mixture. The proposed method offered the low contamination risk, simple handling and possibility of standardization using aqueous reference solutions.

5.5 Direct solid sampling

Another good alternative to wet digestion procedures used in elemental analysis is direct solid sampling (DSS). In addition, it is the most widely used technique in metallurgical laboratories. Among different techniques that can be used for DSS in combination with AAS, ICP-OES or ICP-MS there are laser ablation (LA) and electrothermal atomization or vaporization (ETV). Nowadays, direct analysis of solid samples using graphite furnace atomic absorption spectrometry (DSS-GF-AAS) has been shown to be the most attractive and convenient technique (Vale et al., 2006).

Main attributes of this method are: (1) low DLs; (2) minimal sample manipulation; (3) operational simplicity; (3) short time required to obtain results; (4) higher accuracy since errors due to analyte loss or contamination can significantly be reduced and (5) higher sensitivity due to the lack of any sample dilution. In most cases aqueous standards can be used for calibration. Drawbacks are associated with (1) quite short linear working ranges in AAS, which limits analysis to determination of low concentrations and, in consequence, of low sample weights (in many cases solid powdered samples must be diluted with graphite powder and re-homogenized before analysis); (2) natural samples inhomogeneity resulting in precision of results of order of 10% and (3) enhanced interferences as compared to analysis of dissolved samples, where matrix is simplified as a result of mineralization. Both small and large amounts of samples used for analysis can lead to overestimation or underestimation of final results.

Very recently, high-resolution continuum source atomic absorption spectrometers (HR-CS-AAS) for DSS have been proposed. By this, the entire spectral environment of analytical lines at high resolution can be observed and allows to detect, correct and avoid many spectral interferences.

Many researchers consider these exceptional facilities of DSS and according to QC/QA present very consistent results:

Sahuquillo et al. (2003) validated determination of the total and leachable As in sediments by DSS-GF-AAS. Calibration with both liquid standard solutions and CRMs of sediments was made. Under optimised instrumental conditions the DL of As of 0.44 mg kg^{-1} and long-term reproducibility within 10-15% were obtained.

Oleszczuk et al. (2007) showed DSS-ET-AAS to be a powerful tool for determination of Co, Cu and Mn in green coffee. The method was validated by analyzing several botanical CRMs and a number of pre-analyzed samples of green coffee. Measurements with ICP-OES after MW-assisted digestion were used as a reference method. Mn and Co could be determined using aqueous standard solutions for calibration, but calibration with a CRM was necessary to get accurate results for Cu. DLs for Cu and Co were more than one order of magnitude

better than in case of SS-GF-AAS due to absence of sample dilution. Moreover, DSS did not require any sample preparation besides grinding of coffee beans.

Detcheva & Grobecker (2006) determined Hg, Cd, Mn, Pb and Sn in seafood by DSS-GF-AAS with Zeeman-effect background correction and an automatic solid sampler (except for Hg). A calibration range was extended using a three-field dynamic mode. Very high concentrations of elements could be determined without need for dilution of solid samples. Calibration with CRMs of organic matrices was applied. Under optimized conditions no matrix effects were observed and obtained results were in a good agreement with certified values.

Ribeiro et al. (2005) investigated determination of Co in biological samples (*e.g.,* fish) by comparison DSS-GF-AAS and tetramethylammonium hydroxide (TMAH) sample dissolution followed by conventional GF-AAS with HR-CS-GF-AAS. It was found that analysis of samples is much easier when using HR-CS-GF-AAS, however, the best DL of 5 ng g^{-1} was obtained with both DSS and HR-CS-GF-AAS.

6. Conclusion

Measurements of elements in various materials are the only way to get the knowledge about their composition. A variety of instrumental techniques including atomic, emission or mass spectrometries gives a possibility to perform reliable and accurate trace and ultra-trace determinations. It was expected that more and more sensitive detectors would guarantee and assure accuracy of analytical results. In fact, the key to the success of the whole analysis is selection of the sample preparation method. Appropriate sample preparation allows obtaining required and reliable information about element concentration of samples. There are several aspects to be considered when selecting a given sample preparation procedure like: kind and amount of samples, sample matrices, quantities of elements, need of total or partial digestion, instrumental methods for element determinations as well as traceability and uncertainty of measurements. All operations undertaken during sample preparation should be kept under control to properly represent the original status of analyzed samples. The analyst should decide when his method satisfies quality criteria and when obtained results can be accepted at expected probability. The concept of QA and QC is the best way to achieve this goal.

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Wide Spectra of Quality Control

Edited by Dr. Isin Akyar

Quality control is a standard which certainly has become a style of living. With the improvement of technology every day, we meet new and complicated devices and methods in different fields. Quality control explains the directed use of testing to measure the achievement of a specific standard. It is the process, procedures and authority used to accept or reject all components, drug product containers, closures, in-process materials, packaging material, labeling and drug products, and the authority to review production records to assure that no errors have occurred.The quality which is supposed to be achieved is not a concept which can be controlled by easy, numerical or other means, but it is the control over the intrinsic quality of a test facility and its studies. The aim of this book is to share useful and practical knowledge about quality control in several fields with the people who want to improve their knowledge.

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