Flame and Graphite Furnace Atomic Absorption Spectrometry in Environmental Analysis

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Atomic absorption spectrometry (AAS) is one of the most often used techniques for the quantitative determination of elements in environmental materials at trace and ultratrace levels. AAS is an optical atomic spectrometric technique based on the measurement of the specific absorption originating from free nonionized atoms in the gas phase. To transfer the analyte to free atoms, different types of atomizer are in use, the flame and the graphite furnace types being the most often used. Typical detection limits of flame atomic absorption spectrometry (FAAS) are of the order of 1–100 μg L^{-1}, making it a perfect tool for the determination of minor and trace elements, at least for contaminated samples. Graphite furnace atomic absorption spectrometry (GFAAS), offering detection limits which are about a factor of 20–200 lower than for FAAS, is the standard method for many trace elements, especially for background values, and for unpolluted samples, such as fresh water and biological materials. AAS in its conventional configuration is a single-element technique, which has to be used in a sequential mode when more than one element has to be determined. However, there are commercial instruments available that can be used for the determination of 6–8 elements simultaneously.

1 INTRODUCTION

AAS is one of the most often used techniques for the quantitative determination of elements (up to 60–70 analytes) in environmental materials at trace and ultratrace levels down to nanograms (ng, 10^{-9} g) and picograms (pg, 10^{-12} g). It is a very well established, reliable and cost-effective analytical tool in thousands of laboratories throughout the world. Its high degree of maturity is reflected in the declining interest of researchers in fundamental research devoted to AAS on one side, while on the other maintaining intensive application of this technique in various areas of analytical chemistry, which is traceable through about 1000 publications per year.

AAS is an optical atomic spectrometric technique based on the measurement of the specific absorption originating from free nonionized atoms in the gas phase. To transfer the analyte to free atoms and provide the hostile environment for these atoms at least for a short moment, different types of atomizer are in use. A scheme of the principle components of an AAS instrument is given in Figure 1.

In FAAS, flames with different fuel–oxidant combinations are used for atomization, whereas in electrothermal atomic absorption spectrometry (ETAAS) different types of electrothermal atomizers are used, such as the graphite tube furnace in GFAAS or the quartz tube atomizer (QTA) in hydride generation atomic absorption spectrometry (HGAAS). These atomizers are meant to provide just the necessary energy via a chain of reactions to transfer the sample into atoms. Most of these atoms are in their electronic ground state with energy, E_0, and are able to absorb energy ($\Delta E = E_1 - E_0 = h\nu = hc/\lambda$) from a radiation source (lamp), where E_1 is the energy of the (first) excited state, h is Planck's constant, c is the velocity of light and ν and λ are the frequency and the wavelength of the atomic spectral line, respectively. The probing beam from the radiation source passes through the observation volume of the atomizer, wherein the radiation is absorbed by the cloud of atoms, which are

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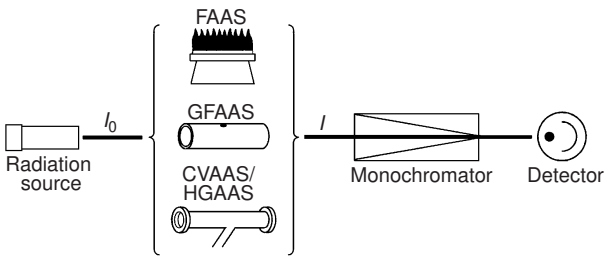

Figure 1 Schematic view of atomic absorption (AA) spectrometric techniques. CVAAS, cold vapor atomic absorption spectrometry.

excited to one of their permitted upper energy levels (E_1, E_2, etc.). According to Beer's law, the radiation absorbed is proportional to the number of absorbers in the absorption volume. The ratio of the incident radiant power, I_0, and the power transmitted through the absorption volume, I, is then determined by the detection system of the spectrometer and processed to yield the analyte signal, absorbance, A [Equations 1 and 2]:

$$A = \log_{10} \frac{I_0}{I} = -\log_{10} T \qquad (1)$$

$$A = abc \qquad \text{(Beer's law)} \qquad (2)$$

where T is the transmittance, a is the absorptivity, b is the thickness of the absorption volume and c is the concentration of the absorbing analyte atoms. The relationship between the concentration of the analyte in the sample, c_{sample} and the concentration of the analyte in the absorption volume, c, is normally established via a calibration graph [Equation 3]:

$$c_{\text{sample}} = f(A) \qquad (3)$$

The very high selectivity of AAS originates from the simplicity of the absorption spectra, where only a limited number of lines limits the chance of cases of spectral interference, and the use of line sources that emit just the radiation specific to the analyte, such as the hollow-cathode lamp (HCL) or the electrodeless discharge lamp (EDL). Multielement HCLs are available, but should be used with care, because of the reduction in selectivity due to the possibility of spectral interferences.

The role of the spectrometer in this configuration is limited to the separation of the analytical line from other lines emitted by the radiation source and from emission originating from other sources than the lamp, e.g. the atomizer itself and from emitting species inside the absorption volume. For this reason, the radiation of the lamp is modulated electronically or mechanically with a certain frequency of 50–300 Hz and the detection system is synchronized with this modulation. In order to distinguish the specific AA from other nonspecific absorption due to, for example, molecular absorption or scattering, the AA spectrometer in general uses a background correction system. Commercial instruments are equipped with at least one of the following systems: (a) deuterium background corrector, (b) halogen lamp background corrector, (c) Smith–Hieftje background corrector or (d) Zeeman-effect background corrector, the last one being the most accurate and powerful technique.[1]

2 ATOMIC ABSORPTION TECHNIQUES AND THEIR CAPABILITIES FOR ENVIRONMENTAL ANALYSIS

2.1 Flame Atomic Absorption Spectrometry

Flames with different fuel–oxidant combinations are used for atomization in FAAS, the air–acetylene and the nitrous oxide–acetylene flames being the most popular. The air–acetylene flame generates a flame temperature of about 2525 K, is transparent over a wide spectral range and only starts to absorb radiation below 230 nm. Also, the emission of the air–acetylene flame is very low, so ideal conditions are given for most elements. Normally, this flame is operated stoichiometrically or slightly oxidizing, but it can be operated also in a reducing mode. However, in the reducing mode the lower partial pressure of oxygen is responsible for a reduced flame temperature, enhancing the risk of interference problems. Interference through ionization occurs only in a few cases, for example, for alkali metals, and can be easily avoided by the addition of an easily ionizable element as an ionization buffer, such as sodium, potassium or cesium. There are about 30 elements that in effect cannot be determined with the air–acetylene flame since they form refractory oxides, such as aluminum and silicon. Such elements require a hotter flame in order to break the element–oxygen bond, such as the nitrous oxide–acetylene flame; this flame is operated with a slight excess of fuel, providing reducing conditions and a flame temperature of about 2975 K. Both flames can be safely operated, and modern instruments contain sensors and interlocks for fully automated operation.

Samples are introduced into flames normally in the liquid form by a pneumatic nebulizer and mixed in a spray chamber with the flame gases before these reach the head of the (premixed) burner, where they are ignited. The burner has a single slot of appropriate length providing a certain depth for the absorption volume (comparable to a cuvette length), that is essential for the sensitivity of the method. Absorption of light coming from a primary light source is directed through this absorption volume and is measured at an observation height in the flame

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Table 1 Comparison of relative instrumental detection limits ($\mu g\,L^{-1}$) for FAAS and GFAAS (after Welz and Sperling[2])

Element	FAAS	GFAAS	Element	FAAS	GFAAS	Element	FAAS	GFAAS
Ag	1.5	0.02	Ho	60		Ru	100	1.5
Al	45	0.1	In	30		Sb	45	0.15
As	150	0.2	Ir	900	3	Sc	30	
Au	9	0.15	K	3	0.008	Se	100	0.25
B	1000	20	La	3000		Si	90	1
Ba	15	0.35	Li	0.8	0.06	Sm	3000	
Be	1.5	0.01	Lu	1000		Sn	150	0.2
Bi	30	0.25	Mg	0.15	0.004	Sr	3	0.025
Ca	1.5	0.01	Mn	1.5	0.01	Ta	1500	
Cd	0.8	0.003	Mo	45	0.03	Tb	900	
Co	9	0.15	Na	0.3	0.02	Te	30	0.4
Cr	3	0.01	Nb	1500		Ti	75	0.35
Cs	15		Nd	1500		Tl	15	0.25
Cu	1.5	0.1	Ni	6	0.3	Tm	15	
Dy	50		Os	120		U	15 000	
Er	60		P	75 000	130	V	60	0.06
Eu	30		Pb	15	0.1	W	1500	
Fe	5	0.1	Pd	30	0.8	Y	75	
Ga	75		Pr	7500		Yb	8	
Gd	1800		Pt	60	2	Zn	1.5	0.1
Ge	300		Rb	3	0.04	Zr	450	
Hf	300		Re	750				
Hg	300	1.0	Rh	6				

some millimeters above the burner exit, where the atom concentration is at its maximum. Operational parameters to control flame atomization are very few (e.g. the flame stoichiometry, the nebulizer uptake and the observation height). Typical detection limits of FAAS are of the order of $1–100\,\mu g\,L^{-1}$ (see Table 1) and are similar to those obtained by radially viewed inductively coupled plasma optical emission spectrometry (ICPOES). The precision of measurements can be better than 0.3% using optimum conditions.

FAAS has found wide application in environmental analysis and is often still used as standard method. However, owing to its lack in sensitivity, its application is limited to the determination of the main and minor elements and some trace elements, especially for contaminated samples (sewage sludges, wastewater, sediments, etc.).

2.2 Graphite Furnace Atomic Absorption Spectrometry

GFAAS offers detection limits which are about a factor of 20–200 lower than for FAAS (see Table 1). This significant improvement is the result of the improved residence time of the atoms in the absorption volume, which is mainly dictated by diffusional losses from the tube. In principle, the much longer residence time should also lead to greater freedom from interferences, provided that atomization takes place under isothermal conditions. To come as close as possible to the ideal state of isothermal atomization, different efforts have been made, of which platform atomization is the most prominent. Platform atomization together with the use of a powerful Zeeman effect background correction (ZBC) system, fast signal evaluation and the application of matrix (chemical) modification, forms the basis of the stabilized temperature platform furnace (STPF) concept.[3] A step even further in this direction is the transversely heated graphite atomizer (THGA), which heats uniformly over the whole tube length avoiding any cold spots,[4] which are observed in longitudinally heated furnaces, owing to the necessity for cooling the tube ends for reasons of reproducible electrical contact.[5]

The disadvantage of GFAAS compared with FAAS is the lower sample throughput. In a graphite furnace system the measurement cycle starts with the injection of liquid samples (digest, extract, suspension, standard solution) of about $5–50\,\mu L$ into the graphite tube or into the cavity of a platform. Thereafter a temperature program is initiated, including drying, pyrolysis (thermal pretreatment for the decomposition of organic matrix or the volatilization of other matrix components), atomization (with temperatures up to 2800 °C), and an additional cleaning step to remove remaining matrix components from the furnace. The whole cycle takes typically about 50–100 s (i.e. about 10 times a regular FAAS measurement) and must be optimized for a particular analyte–matrix combination. During the steps of this cycle the furnace is flushed with an inert purge gas stream (argon is recommended) in order to protect hot graphite

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parts against oxidation and to remove volatile reaction products. Other alternative gases such as air, oxygen and hydrogen can be added during the first steps, in order to facilitate thermal pretreatment. GFAAS is called a mature technique, not only with respect to instrumentation, but also with respect to methodology. Using STPF conditions together with integrated absorbance for signal evaluation, it can be shown that the characteristic mass (i.e. the mass of element in picograms that produces an integrated signal equivalent to 0.0004 A s) for various elements in different matrices differs by only around ±15% between different instruments,[6] offering a way towards standardless analysis (sometimes even called 'absolute analysis'). At least such possibilities can be used for semiquantitative analysis for screening purposes and for system diagnosis. With respect to environmental analysis, GFAAS is the standard method for many trace elements, especially for background values, and for unpolluted samples, such as fresh water and biological materials.

2.3 Other Atomic Absorption Spectrometry Techniques

Since neither FAAS nor GFAAS offers a particular detection power for mercury and hydride-forming metalloids such as antimony, arsenic, selenium, and tin, special vapor generation techniques to measure these elements after volatilization in the gas phase were developed and are commercially available. Mercury is commonly reduced, after digestion of solid samples or directly in liquids, to elemental mercury by the addition of stannous chloride or sodium tetrahydroborate and analyzed at ambient or slightly increased temperature by the cold vapor technique with detection limits at or below the micrograms per liter level. In a similar manner, the hydride-forming elements are measured by the hydride generation technique, in which the analyte is volatilized by reduction with sodium tetrahydroborate and analyzed by atomization in a heated QTA or after in situ trapping in the graphite furnace. These different vapor generation techniques often provide detection limits improved by a factor of about 10 in comparison with GFAAS of liquid samples. Disadvantages of vapor generation techniques are the additional sources of interference during the process of vapor generation and atomization, which for the case of QTAs takes place at temperatures limited to about 1000 °C. In order to reduce the problems with vapor generation, special attention has to be paid to sample preparation, for which the requirements are the most stringent in comparison with other AAS techniques. An extensive discussion of the hydride generation technique can be found in a monograph by Dedina and Tsalev[7] and a detailed discussion of both vapor generation techniques can be found in a monograph devoted to AAS by Welz and Sperling.[2]

The call for automation of the vapor generation techniques was one of the driving forces behind the development of using flow injection (FI) as a sample managing system for AAS.[8] The basic principle of using FI for the transport of sample solution for AAS is shown in Figure 2.

Nowadays the coupling of FI has been realized with all AAS techniques, including the GFAAS technique, with great benefits for AAS in many respects. FI can be used just for sample introduction in FAAS, improving the tolerance for high-salt matrices, but also can be used for sample dilution, calibration, separation, preconcentration and speciation in combination with all AAS techniques. The main advantages of FI for AAS can be summarized as its high potential for automation and its high repeatability and reproducibility of all the process. Further, FI provides a closed system, which reduces external contamination to very low levels and is operated under thermodynamically nonequilibrated conditions, which allow for high sampling rates. The ease of automation comes from the generally simple system, which normally consists of one or two independent multichannel peristaltic pumps, a multichannel injection valve, a manifold made from polymeric tubing, flow conjunctions, mixers, reactors, separators and columns, with all the active parts under computer control. Commercial systems are available and integration of FI into the AAS software has been realized.[9] Environmental analysis can greatly benefit from the coupling of FI with AAS in all cases where the automation reduces costly manpower or the sensitivity or selectivity of AAS alone is not sufficient for the analytical task. Examples of such applications will be briefly discussed in section 4.

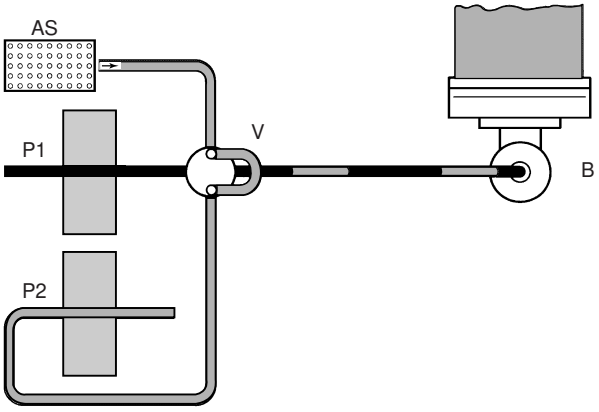

Figure 2 Simplest principle using FI for the transport of measurement solution for FAAS. P1 = pump for carrier solution; P2 = pump for measurement solution; AS = autosampler; V = injection valve; B = AAS burner. (Reproduced by kind permission of Perkin-Elmer.)

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3 METHOD DEVELOPMENT AND VALIDATION

3.1 The Analytical Task

Environmental chemical analysis very often is the basis of other environmental studies, such as risk assessments, or court actions, such as the withdrawal of allowances, involving decisions which have an enormous economic impact. In order for analytical results to provide the information necessary to support such decisions, confidence in the quality of the analysis must be sufficiently high. Those parameters that will influence the decisions, the data quality objectives (DQO) should be defined, in order to fit the analysis for the purpose. Two basic parameters should be considered when discussing analytical results: *accuracy* (closeness of the agreement between the result of a measurement and a true value of the measurable quantity of an analyte) and *uncertainty* (expressed as the confidence of variation or the confidence interval) due to random errors and random variations in the procedure.[10] While accuracy is of primary importance, an unacceptably high uncertainty renders the result useless. Apart from the requirements on the quality of the results, the whole analytical procedure must be designed to answer the questions of the analytical task in an economical way (i.e. it should be fit for purpose). Errors can occur in every step of an analysis and negatively influence its accuracy to a degree corresponding to their share of the entire method. In order to reduce such errors, it is of major importance that all steps of an analytical method are documented and that special attention is paid to steps that are particularly critical. Table 2 presents a general scheme of the analytical process for trace metal analysis, where the actual analytical procedure covers steps III–XI. When comparing the estimation of possible errors in each step, it becomes obvious that the most often discussed step, 'instrumental determination', is normally the most accurate and precise step of the analytical procedure, while the most critical step, the sampling, often is not even under the control of the analyst. It cannot be overemphasized that the analyst should have all the steps of a method under control since only then can possible problems be recognized, evaluated and, if necessary, remedied.

Table 2 General scheme of a trace element analysis

Step	Topic	Associated problems	Influence on final results[a]
I	Defining the analytical task	Defining the scientific problem: general association (degree of difficulty), extent (number of samples, frequency of sampling), urgency	++++++
II	Planning	Orientation of task on the potential of the laboratory (instrumentation, methods and staff; organizational structure and time schedule)	+++++
III	Sampling	Representativeness of the sample with respect to the objective of sampling; contamination during sampling, subsampling or homogenization	+++++
IV	Sample preservation	Contamination; losses; disturbance of speciation	++++
V	Sample storage	Stability of the constituents for short-, medium- or long-term storage (specimen banking)	++++
VI	Sample digestion or decomposition	Analyte losses due to volatilization or insufficient digestion; contamination from reagents and containers	++++
VII	Trace–matrix separation	Efficiency of separation; completeness of preconcentration; contamination from reagents and containers	++++
VIII	Instrumental determination	Suitability and performance of the selected procedure for the given analytical task; conditions of the instruments used	+/++
IX	Calibration	Selection of a suitable calibration technique; quality of the calibration samples and calibration solutions employed; adequate weighting of the blank values	++/+++
X	Data evaluation	Selection of all relevant values and statistics; sample identifiers	++
XI	QC	Adequate statistical control of all analytical steps; selection of appropriate QC samples; interlaboratory comparison	++
XII	Analytical report	Adequate assessment of the analytical results and QC	++
XIII	Interpretation	Adequate assessment of the analytical results with respect to the environmental task (ecochemical, ecological, geological, oceanographical, ecotoxicological, toxicological, occupational, epidemiological, etc.)	++++++

[a] + = 2–20%, ++ = 20–50%, +++ = 50–100%, ++++ = 100–300%, +++++ = 300–1000%, ++++++ = production of 'data cemetery'.
QC, quality control.

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A number of rules for the conductance and documentation of an analysis, meant to facilitate achievement of such a goal, are generally summarized under the term good laboratory practice (GLP). Further, it is of equal importance to use methods which are fit for the purpose and are well known to the analyst. If such methods are available and validated, their performance has to be controlled throughout the whole duration of the analysis. The installation of a suitable QC program is often a part of the contract or, as many other aspects of environmental analysis, is part of national and international regulations. General guidelines for the installation of such programs are available.[11] In case of lack of validated methods, effective method development must take place, which has the role of detecting possible sources of errors and eliminating or reducing them to an acceptable level. Normally such method development starts by modifying existing methods rather than starting from scratch.

3.2 Sampling and Sample Pretreatment

3.2.1 Sampling

The analytical procedure starts with the removal of a portion from the material to be examined; this is the laboratory sample that subsequently will be analyzed.[12] During the sampling procedure, care must be taken to ensure that the laboratory sample is representative of the material from which the sample was taken or of the situation which is to be examined. Incorrect sampling renders even the most accurate analysis ad absurdum, a fact often underestimated, since the largest errors take place during sampling and cannot subsequently be corrected. In general, a differentiation can be made between two procedures for representative sampling: (a) random sampling and (b) systematic sampling. Random sampling means the random collection of individual specimens from a total parent population frequently aiming at the determination of an average value (e.g. collection of birch leaves from a birch forest to determine average calcium content at time x). Systematic sampling, on the other hand, mainly refers to problems of changeable values as a function of space and time (e.g. the collection of spruce needles of a certain age or from various levels of a spruce tree to determine the exposure to air pollutants), thereby coupling a specific systematic study to a random sample. Regardless, the following three fundamental sampling rules are valid for both types of sampling:

1. The sample taken from the system should have exactly the same chemical composition as the original material.
2. The probability of being taken as a sample from a total population or total mass of material must be equally great for each individual samples.
3. The greater the variability between individual samples and the greater the number of individuals or the greater the mass of material to be evaluated, the greater are the efforts required for sampling.

Generally, different sources of error prevent the first two fundamental rules from being fulfilled, such as problems with the sampling strategy (place, time, duration and method of sampling), the selection of the apparatus (contamination from the materials used, sorption losses), the execution (sampling, subdividing, homogenization, filtering, preservation) and delivery (transport, identification, protocol). The particular problems depend very much on the type of material or situation to be investigated, and therefore will be discussed later (see section 4).

3.2.2 Sample Preservation

If an analysis is to have any meaning, care must be taken to ensure that the laboratory sample is unadulterated during transportation to and storage at the laboratory while awaiting further sample pretreatment. The preservation of a sample in all of its complexity is impossible and therefore can only be replaced by a 'freeze' of selected properties of the sample, such as pH and pE values, as well as the contents of main and trace constituents, matching the needs of the given task. Microbiological activity must be suppressed just as much as analyte concentration changes caused by adsorption losses or contamination. Subdivision of the sample into a number of portions may be necessary if a number of constituents must be determined that require different stabilization. If a number of analytes are in a dynamic equilibrium (e.g. redox equilibrium), such as in speciation analysis, preservation is exceedingly difficult, if not one of the most difficult steps of the whole procedure.[13–15]

3.2.3 Sample Pretreatment

Since the risk of systematic errors increases with the extent of sample pretreatment, the number of steps and the mass of reagents used during such treatment should be kept to a minimum. Similarly, direct methods are preferred to methods which require extensive preparation such as separation and preconcentration. However, solid samples can generally only be directly analyzed relatively free of problems by GFAAS, so that a digestion is usually required prior to determination. Sample decomposition is prone to three different types of error sources: (a) incomplete dissolution, (b) loss of analytes by volatilization and (c) contamination by the reagents

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(acids, etc.). Fusion and dry ashing are the most seriously affected with respect to volatilization losses owing to the higher temperatures employed, but acid digestions are not without problems. All digestion procedures performed in open systems are prone to external contamination, which can be best avoided by operation in closed vessels under pressure.

The risk of errors also increases with decreasing analyte concentration. For those cases in which a low analyte concentration requires separation and preconcentration, all steps should be either carried out under clean working conditions (clean room or clean bench) or performed in a closed system, such as provided by FI manifolds.

3.3 Atomic Absorption Analysis and Methods

It has been pointed out already that normally the determination step is the most accurate and precise step of the whole analytical procedure. However, such a general statement can be valid only if the determination step is following a well-developed method, using an appropriate technique and instrumentation that is well calibrated and maintained in good condition. Each of the AAS techniques (e.g. FAAS, GFAAS, HGAAS) has an optimum working range with respect to concentrations, analytes and matrices and should not be used outside this range. AAS is a relative technique in which quantitative determinations are performed by comparison with calibration samples (calibration solutions). Since changes in the instrument parameters, the condition of the instrument, and the conditions of measurement are reflected in the calibration and are thus eliminated (except drift), it is still possible to obtain quantitative results even when the sensitivity is far from optimum. Despite this possibility, working in this manner cannot be recommended since then substantial control of the condition of the instrument is lost. Apart from the fact that the performance characteristics of an analysis are degraded under these conditions, judgment of the analytical data is questionable since significant changes in the sensitivity or noise are indications of malfunctions of the instrument or errors in the method, which may lead to measurement errors.

3.3.1 Instrument Fault Recognition

The absence of instrumental faults is a prerequisite for a meaningful analysis. For this reason a protocol of the performance characteristics of every analysis should be carefully maintained, and any larger deviations from specified values or values in earlier protocols should be a reason to search for the cause.

Frequent causes of a lack of sensitivity in AAS are in general as follows:

1. dilution errors when making up the calibration solutions;
2. wrong or faulty lamp; too high a lamp current;
3. analyte losses in the stock or calibration solutions due to insufficient stabilization or unsuitable containers;
4. incorrect wavelength or too large a slit width;
5. matrix effects due to the use of either the wrong buffer or modifier, or the absence of either.

The following causes can be additionally present in FAAS:

6. wrong flame type or nonoptimized flame stoichiometry;
7. nonoptimized horizontal or vertical burner position;
8. clogged sampling capillary, nebulizer, or burner slot; incorrect aspiration rate;
9. unsuitable inserts in the spray chamber; misaligned impact bead.

Frequent causes of reduced sensitivity in GFAAS (enhanced characteristic mass) are as follows:

10. erroneous sample dispensing;
11. preatomization analyte losses; these can be due to a pyrolysis temperature that is too high or to either an unsuitable or missing modifier;
12. unsuitable (excessive) atomization temperature;
13. erroneous blank value or baseline correction;
14. too high a gas flow rate during atomization or the use of an unsuitable purge gas;
15. too low a heating rate; this can be caused by an unsuitable power supply or poor electrical contact of the graphite tube;
16. too low a magnetic field strength for ZBC (e.g. insufficient voltage at the electromagnet).

Much more seldom than decreased sensitivity is enhanced sensitivity (reduced characteristic mass). This can be traced almost without exception, especially in trace analysis, to accidental introduction of the analyte. If this occurs a systematic search should be made to determine the cause. All analytical results generated under such conditions, and also all corresponding publications, should be regarded with considerable scepticism.

Insufficient precision or excessive noise generally has one of the following causes:

1. low lamp energy; poor quality lamp;
2. wrong lamp current or poor lamp alignment;
3. wrong wavelength or too narrow a slit width;
4. contaminated optical components (windows, lenses, mirrors, etc.);
5. emission noise;

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6. poor alignment of the line source and the continuum source for background correction;
7. inhomogeneous sample solution or slurry, the presence of suspended matter in the measurement solution, nugget effect for solids analysis.

For FAAS the following specific causes in addition to those above may be considered:

8. partially clogged nebulizer or burner; defective nebulizer;
9. contaminated spray chamber or inserts (large droplets on the surface are an indication of wetting problems);
10. irregular drain flow from the spray chamber;
11. irregular gas flow (e.g. too low a gas pressure);
12. unsteady flame caused by drafts, strong ventilation system, change of solvent, etc.;
13. an excessively short integration time or insufficient damping.

Specific causes of insufficient precision or excessive noise in GFAAS include the following:

14. irreproducible dispensing of the test sample solution;
15. spattering of the solution caused by either too rapid or incomplete drying;
16. irregular spreading of the measurement solution over the atomization surface (wetting problem);
17. aged graphite tube or contacts;
18. an excessive integration time or incorrect integration window;
19. baseline offset correction (BOC) too short or erroneous.

Finally, drift is often caused by one of the following problems:

1. changes in the radiant intensity of the lamp (or lamps) or of the line profile during the warming-up phase or in the event of a defect; changes in the ratio of the radiant intensities of the line source and the continuum source for background correction;
2. evaporation of the solvent from the measurement solution;
3. for FAAS, warming or cooling of the burner or the formation of encrustations on the burner slot;
4. for FAAS, changes in the rate of aspiration or in the efficiency of nebulization due to physical changes in the sample capillary or the nebulizer;
5. for GFAAS, aging of the graphite tube or the accumulation of residues (e.g. carbon from biological materials).

This list of frequent causes of marked deviations in the most important performance characteristics can only serve as a starting point for troubleshooting. Nevertheless, deviations of this sort are nearly always an indication of a malfunction or an operational error and must therefore be taken seriously. The important performance characteristics such as sensitivity (or characteristic mass or concentration) and the signal-to-noise ratio (S/N) should always be documented with the analytical results so that malfunctions or operational errors can be traced or eliminated. In modern instruments, functions such as monitoring the condition of the instrument and maintaining a protocol are performed automatically with the corresponding algorithms being implemented in the instrument software.

A convenient procedure for monitoring further instrumental functions in GFAAS, in addition to the sensitivity and S/N, has been described by Slavin et al.[16] Using a certified reference material (CRM) (Trace Elements in Water, NIST 1643b), the characteristic masses and the Zeeman factors for chromium, copper and silver are determined without a chemical modifier and under easily reproducible conditions; additionally the lamp energy is recorded. Copper exhibits the greatest loss in sensitivity at the 324.8-nm line when ZBC is applied and is very sensitive to changes in the magnetic field strength. This element can thus serve as an indicator for an insufficiently strong magnetic field. Chromium is a difficult to volatilize element and requires a relatively high heating rate; at the 257.9-nm line its determination is sensitive to emission interferences, which can indicate a poorly aligned graphite tube atomizer. Silver, on the other hand, is not noticeably influenced by the magnetic field strength, the heating rate or the alignment of the graphite tube. If the sensitivity of all three elements is influenced to the same degree, this is an indication of dispensing problems or that the actual temperature deviates markedly from the rated value. If this test is performed at regular intervals, it serves as a powerful tool to document the state of the instrument.

3.3.2 Instrument Optimization

Various strategies have been applied for optimizing the instrument parameters of AAS techniques, such as methods of experimental design,[17] simplex optimization[18] or complete response-surface mapping.[18] The use of such chemometric methods for optimization is useful, since running simple series of experiments changing one parameter at a time may lead to nonoptimum conditions. The situation is further complicated, since different performance characteristics can exhibit varying optima, so that compromise conditions may represent the practical optimum. For example, often it is the case that the conditions for optimum sensitivity are not the same as the

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conditions for the best possible tolerance to constituents of the matrix. The required task must therefore be defined before optimization can be undertaken. Frequently, the task is to optimize analytical performance characteristics such as detection capability, precision, working range or tolerance to matrix constituents, but occasionally considerations of economics, such as high sample throughput, minimal manual effort, low sample or reagent consumption or low costs, are more important.

In FAAS we can observe that a burner position or a nebulizer which is optimized for maximum sensitivity can exhibit very low tolerance to matrix constituents. In the case that high sensitivity is not the primary objective, the nebulizer/burner should be optimized for high tolerance against matrix constituents. This is normally done by adjusting the nebulizer and its impact bead (if used) for generating mostly very fine droplets rather than for maximum aerosol density. Also, the observation height for the best sensitivity and the lowest interference effects might be different.

In GFAAS, the stabilizing effect of a modifier (e.g. palladium) can lead to a lower rate of atomization, so that broader signals are obtained than if a modifier were not used. Such signal broadening may lead to a deterioration of the S/N and therefore to a poorer limit of detection (LOD). On the other hand, the linear working range can be extended upward since the limiting absorbance is only reached at higher analyte masses, and the tolerance against concomitants is significantly improved owing to more effective separation during the pyrolysis step and the higher effective atomization temperature.

For samples that do not require the best detection limits achievable by GFAAS, the sample throughput can be enhanced and the analysis costs reduced.[19] This is possible by the reduction of the furnace cycle time. A set of strategies can be combined to achieve fast furnace programs: (a) reduction of the sample volume to the minimum for the required sensitivity allows for (b) shortening of the drying step and (c) if the sample matrix is not complex, for the omission of the pyrolysis step. The drying step can be further shortened if started already during sample dispensing (hot injection). For maximum throughput, the addition of modifiers can be either omitted totally or done in advance directly into the sample cups rather than the graphite tube.

A different strategy leads to improved detection power. Since the measurement signal of GFAAS is proportional to the analyte mass and not to the concentration, the detection capability can be improved by dispensing larger volumes of the measurement solution. When the upper limit for a single dispensing is reached, which is dependent on the particular design about 40–100 µL, multiple injections each followed by a drying step can be used with modern autosamplers to enhance the total sample mass further. The additional time required for these steps can be reduced by injecting into a preheated graphite tube.

The greatest improvement in sample throughput can be achieved by using simultaneous multielement analysis. However, multielement methods require particular attention to be paid to the optimization of the FAAS[20] or GFAAS[21] operational parameters. The conditions normally chosen for pyrolysis and atomization of various analytes in graphite furnaces differ significantly. This behavior appears to stand in the way of attaining acceptable compromise conditions. However, the selection of compromise conditions is relatively simple, since the most volatile analyte dictates the maximum pyrolysis temperature and the least volatile analyte dictates the minimum atomization temperature. Nevertheless, the use of a transversely heated atomizer with an integrated platform is decisive, since it allows one to apply STPF conditions for both volatile and nonvolatile elements. Losses in sensitivity and selectivity under such compromise conditions are much smaller than assumed when a modern instrument concept is applied. For example, the loss in sensitivity because of an increase in the atomization temperature above the optimum due to increasing diffusional losses[22] is partially compensated for by an increase in the absorption coefficient with increasing temperature. Furthermore, the signal narrows with increasing temperature, improving the LOD since shorter integration times lead to an improvement in the S/N.[22] All in all, only small losses in the detection capability by a factor of 2–3 are expected for multielement determinations, which can be tolerated in many cases.

3.3.3 Recognizing and Overcoming Interferences

As a result of a lack of selectivity, the presence of concomitants in the test sample can cause interferences in the determination of the analyte. An interference can influence both the mean value of the analytical results and the attainable precision. A false mean value may lead to measurement errors if it is not eliminated or if it is not taken into consideration in the evaluation report. Measures for the elimination can be instrumental, such as appropriate background correction, or the choice of a suitable calibration technique, such as the analyte addition method, or the use of chemical additives. According to the International Union of Pure and Applied Chemistry (IUPAC), two types of interference can be distinguished, spectral and nonspectral interferences. Spectral interferences are due to the incomplete isolation of the radiation absorbed by the analyte from other absorption or radiation sources. Nonspectral interferences directly affect the number of free analyte atoms in the absorption volume and can be further classified according to the place or time of their occurrence.

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3.3.3.1 Spectral Interferences Since AA spectra are much simpler than those of optical emission spectrometry (OES), spectral interferences are encountered far less frequently than in OES. The following cases can be distinguished:

1. direct overlap of the analytical line with an absorption line of another element;
2. absorption of the radiation of the analytical line by gaseous molecules;
3. absorption by concomitants of other radiation from the radiation source (or sources) that is not separated by the monochromator;
4. radiation scattering caused by particles in the absorption volume;
5. thermal emission of concomitants in the bandwidth of the monochromator.

While the thermal emission of concomitants is generally corrected for in AAS by modulating the primary radiation source, the light still reaches the detector. In the case that the amount of light from this interfering source is significant with respect to the modulated light from the primary source, increased noise is detected, lowering the attainable precision.

Only a limited number of direct overlaps occur in AAS, and of the 38 cases reported[2] only 10 are related to primary analytical lines. In most cases the interfering element must be present in a large excess to cause false measurement, which has not been reported in environmental analysis.

Spectral interferences of type 1 and 3 can be observed more often and also have been reported for environmental analysis. When a continuum source is used for background correction, any concomitant that exhibits an analytical line within the bandwidth of the monochromator can absorb radiation from the continuum source to a degree corresponding to its concentration. This supposed background absorption is then falsely subtracted from the AA, leading to overcompensation and thus to a measurement error. In order to absorb significant amounts of the radiation from the deuterium source, the interferent must be present in high concentrations. Normally this type of interference can be observed in the determination of trace elements in metallurgical samples such as alloys. However, a few cases have also been reported for environmental samples, where the matrix element iron interferes with the determination of Pb 217.0 nm and Cd 228.8 nm[23] and Se 196.0 nm and Sb 217.6 nm[24] and aluminum interferes with the determination of As 193.7 nm[24,25] and Sb 217.6 nm.[24] Molecular absorption also can lead to interference, either directly by overlapping with the analytical line (type 2) or by absorbing radiation from the background correction channel (type 3). Particularly cumbersome are the interferences from P–O for the determination of arsenic, selenium and tellurium and from S–O for the determination of selenium.

Generally, problems arising from background absorption (interference type 3/4) are more frequent with GFAAS than with FAAS.[26] In flames, background absorption is rarely significant at wavelengths higher than about 240 nm, rarely exceeding 0.05 absorbance. In furnace analysis, background absorption can be significant at wavelengths up to 500 nm, exceeding signal levels of 2 absorbance units. Type 4 spectral interferences (light scattering) is caused by the condensation of the sample matrix (or the modifier!), by forming a smoke or mist. This event occurs when a huge amount of volatilized matrix reaches cooler regions in the absorption volume, caused by temperature gradients inside the atomizer.

The prerequisite to counter such interferences is to recognize them. Spectral interferences can be detected by changing to another alternative analytical line, by changing the slit width of the monochromator and by measuring a matrix blank solution that is identical to the test solution but does not contain the analyte. In GFAAS, careful inspection of the time-resolved absorption signal may give indications of spectral interferences, for example, when the analyte signal falls below the baseline or when the analyte signals shows minima coinciding with maxima in the background channel. To counter such interference problems, there are some complementary measures available to the analyst:

1. selection of the appropriate background correction;
2. optimization of the temperature programming;
3. use of chemical modifiers.

Interferences of type 2 and 3 can in general be compensated by ZBC with the exception of molecules showing a Zeeman effect.[27] Such behavior has been reported for the molecular species N–O in the determination of Zn 213.9 nm[28] and Se 196.0 nm[29] and P–O in the determination of Ag 328.1 nm, Cd 326.1 nm, Fe 248.3 nm, Hg 253.6 nm and Pd 244.8 nm.[30,31] For such cases the optimization of the method is the only measure to avoid these interferences. The goal of method optimization is either to avoid the interferent species (do not use phosphate modifier, phosphoric acid, in digestions or extractions) or to separate the analyte and the interferent species by optimizing the thermal programming of the atomizer and the use of appropriate modifiers.

3.3.3.2 Nonspectral Interferences Nonspectral interferences are those which have an influence on the number of analyte atoms in the absorption volume. In the case where the mechanism of the interference is known, the interferent can be classified by naming the place where it

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is acting or the process in which it is involved, for example, condensed-phase interferences concern all processes with the liquid and solid sample until it vaporizes, while vapor-phase interferences occur thereafter. For example, a condensed-phase interference might occur in FAAS when the presence of a particular matrix influences the transport of analytes from the solution to the absorption volume. This would cause a transport interference by influencing the nebulizer uptake rate, its nebulization efficiency (due to changing viscosity and/or surface tension) or the transport of the aerosol from the spray chamber to the flame. Volatilization interferences can be observed in both FAAS and GFAAS. In FAAS this type of interference occurs when the analyte forms a specific compound together with the interferent, which shows a different thermal stability (most often higher stability) in the flame or is occluded in a matrix particle of a difficult to melt or volatilize substance. In GFAAS, the most common form is premature loss of the analyte during thermal pretreatment by forming a volatile species with the analyte. Vapor-phase interferences can occur in all AAS techniques when the fraction of analyte that is dissociated, ionized or excited in the vapor-phase is changed owing to the presence of an interferent.

The presence of such nonspectral interferences can be diagnosed by comparing the slope of the calibration graph for a standard solution with that obtained from the complex sample solution. Nonspectral interferences can generally be eliminated by matching the test sample solutions and the calibration solutions as closely as possible. A practical way of doing this is to modify the sample composition by adding a spectrochemical buffer to all solutions (in the case of FAAS, called ionization buffers or releasers depending on the type of interference to be overcome) or a modifier (in the case of GFAAS), counteracting the interference effect. Another practical way of matching samples and standards is the application of the standard addition technique, where the calibration graph is directly obtained from the sample by spiking it with known quantities of the analyte.

3.3.4 Method Development and Validation

A suitable analytical method must have been developed and adequately characterized before analysis can take place, that is, measures must be taken to ensure that major problems such as interferences or instrument malfunctions are recognized and eliminated, and that the method generates reasonably accurate results. In particular the following tasks have to be performed during methods development and validation:

1. check for contamination;
2. determination of the precision within a series and between series;
3. determination of the LOD and limit of quantification (LOQ);
4. determination of the linear working range;
5. check for possible interferences;
6. comparison of the analytical results with those from alternative methods;
7. comparative analyses with other experienced laboratories;
8. analysis of CRMs closely matching the composition of the target sample.

Since a contract laboratory can only select methods that have been adequately characterized, in principle it cannot accept chance analytical tasks.

3.3.5 Measurement, Calibration, Evaluation

The material obtained after suitable treatment or preparation of the laboratory sample is the test sample (or, if only analytical chemistry is involved, the analytical sample). A test (or analytical) portion is removed from this for analysis. If the sample is a solid material, it may be analyzed directly by solid sampling GFAAS. In most cases it is transferred into a test sample solution, by performing a digestion, extraction or dissolution. The test sample solution can be used directly or after further treatment steps, such as dilution, addition of buffers or modifiers, and so on, for the measurement. After having sorted out all the possible error sources during method development and instrument maintenance, only a few errors sources remain that may influence the final measurement. The measurement solution actually used for the measurement by AAS must be stable for the duration of the analysis. This is especially important if an autosampler with numerous sample cups is used, since the measurement solutions can stand for several hours before being analyzed. While solvent extracts with volatile solvents or complexes with unstable metal chelates are particularly critical, even aqueous solutions become more concentrated with time; this effect becomes greater the smaller is the volume of the sample container. The evaporation rate from 2-mL standard GFAAS autosampler cups at normal room temperature is about $35\,\mu L\,h^{-1}$ and can be reduced to about $10\,\mu L\,h^{-1}$ when the autosampler is covered, and additional containers filled with water for humidification are placed below the cover.[16]

Another significant source of errors for the instrumental determination is the calibration.[32] Errors occur mainly during the preparation of calibration solutions by dilution of stock solutions. The dilution error increases with both the number of dilutions and the ratio of the dilution step.[33] In order to reduce such errors, only calibrated volumetric devices of quality class A should be used or, better, the dilutions should be performed gravimetrically;

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dilution factors of 1 : 100 per dilution step should not be exceeded. Another error source in calibration is the purity and stability of the stock solution, which especially for speciation analysis cannot always be guaranteed. Also problematic is the handling of any blank solutions, which often are misused as the zeroing solution for evaluation of the signal baseline of the instrument, but for which the pure solvent should be used.[34] Blank solutions must be analyzed in the same manner as other sample solutions, and the result for the analyte concentration of samples should be corrected accordingly. Further, calibration can be significantly in error if the wrong calibration function is used. This is especially the case when a linear calibration is assumed in situations where the calibration function is nonlinear.

3.4 Quality Assurance

The accuracy of a determination depends not only on the selection of a suitable procedure, but also on the stability of the performance characteristics of that procedure. In principle, two different strategies are applied to verify that both goals are met. QC is the mechanism of verifying the absence of errors, while quality assessment is the mechanism of verifying that the system is operating within known and acceptable limits.[35] Quality assurance (QA) for environmental analysis was a growing feature of the 1990s, as illustrated by the number of QA guidelines and systems which are currently being implemented. The increasing interest is also reflected in the launch of the journal *Accreditation and Quality Assurance* in 1996.

3.4.1 Internal Laboratory Operations

The quality of laboratory operations, in the most general sense, is measured by the dedication of higher management to emphasizing quality in a delicate balance with the ever-present demands of productivity. QC always requires a high level of effort and must therefore be accommodated to the DQO (i.e. the higher the requirements on the accuracy of a method, the greater is the effort required for QC). Nevertheless, higher costs for QC can be justified when costs in other areas are reduced, such as those caused by repeated measurements or by false results.

The first requirement for implementing a QA program is the organization of events in the laboratory following certain rules that are generally summarized as GLP and good analytical practice (GAP). GLP provides guidance in the organization of laboratory events and for the conditions under which laboratory investigations are planned, conducted and assessed. By maintaining a protocol and issuing a report of the investigation, the aim of GLP is to make procedures in the laboratory so transparent that they can be verified by third parties (e.g. regulatory authorities, clients). The scope of these rules are laid down in the chemical legislation in force in most industrial nations. The installation of such rules is most often part of the contract between the client and the laboratory. A detailed discussion on this topic is beyond the scope of this article and the interested reader is therefore referred to introductory monographs.[36] Maintaining all the rules of GLP is both expensive and requires a considerable increase in personnel. Some typical violations of GLP rules are as follows:

1. balances remaining uncalibrated;
2. failure in recertifying mechanical pipets;
3. use of pH buffers of unknown age or origin;
4. use of unsuitable purity standards;
5. application of software beyond its purpose.

On the other hand, GLP alone cannot guarantee the trueness and quality of analytical data. The final responsibility for QA still remains with the analyst. QC and quality assessment programs must be implemented and the rules of GAP must be followed in a laboratory to reach the DQO. The rules of GAP include the following:

1. performing the analysis with an adequate number of adequately trained staff;
2. the use of validated methods;
3. analytical instruments that are calibrated and maintained in good condition;
4. the use of CRMs for calibration;
5. an effective internal QA program.

As far as possible, effective QC should be incorporated directly into the analytical program. Analytical results cannot first be generated and then deliberations subsequently made about their quality. Typically, the more complex the sample, the greater the effort the laboratory should make with respect to QC. Depending on the DQO, the QC program must be designed either to maximize the probability of error recognition or to minimize the probability of a false warning. By trapping and excluding error sources such as drift, the QC program can lead to an improvement in the method performance.

In order to be effective, at least the following procedures should be part of the internal quality assessment:

1. characterization and optimization of the precision and accuracy of the calibration function;[37]
2. characterization of the blank values;
3. characterization of the instrumental repeatability (precision on replicates);
4. characterization of the method repeatability (precision on duplicate samples);

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5. characterization of the method performance by analyzing a control sample of known analyte content (recovery);
6. characterization of the accuracy of the method by analyzing a CRM (recovery).

To assure that the method is under statistical control, the results of such performance checks are documented in the form of control charts. Control charts serve multiple functions,[38,39] including:

1. recognition of drift or malfunctions;
2. to uncover errors in sampling or sample preparation;
3. to decide, whether the analysis is fit for purpose;
4. to support the analyst with respect to his/her clients by assuring his/her results.

3.4.2 External Quality Control

Outside evaluation of the laboratory provides an opportunity for the laboratory to view quality from another perspective. The GAP rules include the following external QC:

1. regular participation in interlaboratory ('round-robin') trials;
2. quality assessment by an independent QA unit;
3. accreditation or other certification of the laboratory by regulatory authorities.

Regular interlaboratory trials are organized by several national and international quality programs, sending performance evaluation samples to the participants before an audit or as part of ongoing performance checks. An on-site audit by a third party group can be very effective in reviewing the installed quality programs.

4 ENVIRONMENTAL REGULATIONS AND METHODS

Environmental studies cover a broad range of disciplines, for example, analytical chemistry, geology and biology, and include several aims such as monitoring (routine analysis), research (studies of environmental pathways) and modeling. In many cases chemical analyses are the basis of these studies. Environmental analysis traditionally is divided into the analysis of water, soils and the atmosphere. Such 'classical' division cannot be strictly followed here in view of the multitude of different environmental samples originating from the different compartments of the 'environment' and the mutual interactions that can be expected between them (see Figure 3).

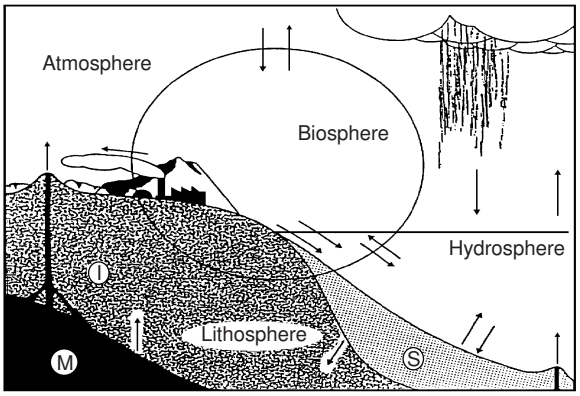

Figure 3 Schematic representation of our environment and the interactions that can be expected. S = sediments; I = soils and rocks; M = magma. (Reproduced by permission from Mitra.[105])

Nearly all types of sample materials can become the target of environmental analysis, at least when the material is disposed of as waste. In order to assign the most widely varying materials into suitable categories, three categories were chosen. The categories are based on the analytical methods used for their analysis, rather than the environmental compartment from which they are taken; the categories are (a) water samples, (b) solid materials of mainly mineral phases and (c) biological materials.

A particular characteristic of environmental analysis is that most aspects of the analysis, (i.e. the frequency of the analyses, the strategy and methods of sampling, the pretreatment and instrumental determination, the QC of analytical results and the data presentation) are governed to a large extent in the finest detail by laws, regulations and guidelines. An overview of prescribed analytical methods and of international and German standards was given by Hein and Kunze.[40] Since the analyst must procure and follow the original method exactly, in order to be compliant with these rules, details of such methods will not be presented here. Instead, information will be given that will point to the most important work.

Introductory information on environmental analysis is available in the form of monographs[40–45] and review articles.[46–52] Publications on the determination of individual elements in environmental samples are also available, for instance, for aluminum,[53–55] arsenic,[56–61] cadmium,[62–65] chromium,[66–71] cobalt,[72] copper,[73] lead,[74–78] manganese,[79] mercury,[80–85] molybdenum,[86] nickel,[72,87,88] platinum,[89,90] selenium,[91–95] tellurium,[92] thallium,[96,97] tin,[98,99] vanadium[100] and zinc.[101] Regular reviews of environmental analytical chemistry appear annually in the *Journal of Analytical Atomic Spectrometry*[102] and every second year in *Analytical Chemistry*.[103] The application of AAS in

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environmental analysis has been recently reviewed by Sturgeon.[104]

4.1 Water Analysis

Although the compound H_2O is clearly defined for the chemist, the matrix 'water' offers an unbelievable multitude of forms for the analyst, reflected in the number of methods for its analysis. Water samples can be classified by legislators, analysts or users by the degree of its anthropogenic contamination (natural waters, processed water, polluted water, wastewater), by its salinity (fresh water, briny water, seawater), by its environmental compartment (atmospheric precipitation, surface water, groundwater, glacial ice) or by its intended use (drinking water, cooling water, bathing water, process water). Correspondingly, the palette ranges from highly pure waters to waters containing extremely high contents of impurities, with respect to both the analyte concentration and the matrix content. The parameters analyte concentration, total salt concentration and organic content are decisive for the procedure and the selection of the analytical technique.

Even though most natural waters contain over 99.9% of H_2O, accurate determination of elements in this simple matrix is frequently not as straight forward as would first appear. Most unpolluted natural waters contain less than $10\,\mu g\,L^{-1}$ of the commonly determined toxic metals and it is easy to obtain significantly biased results when measuring such low concentrations. The problem is obvious from the history of published concentrations of trace elements in seawater, which had decreased by around an order of magnitude within a decade. This is primarily due to (a) the improvements in the control of contamination during sampling, storage and analysis, and (b) the improved separation techniques and advances in the development of the instrumentation.[106] Therefore, the majority of data on the determination of the base concentrations of metals in seawater published before 1986 is practically worthless.[107] The same is probably true for other non-polluted waters and rainwater. Toxic metal levels in sewage and effluents are normally significantly higher than those of natural waters. However, interlaboratory comparison studies have demonstrated that inaccurate results at these higher concentrations can still occur unless meticulous attention to detail is observed in this case particularly to the control of interferences.

For an overview on water analysis, special monographs[108–112] and review articles[113] on this topic or more specific publications on seawater analysis[114–117] should be consulted. Review articles on the determination of trace elements in water are available for aluminum,[118–120] antimony,[121,122] iron[123] and mercury.[124] The journals *Water Research* and *Vom Wasser* (in German) deal exclusively with this subject.

4.1.1 Water Analysis and Legislation

As mentioned previously, environmental analysis is regulated to a large extent by national and international laws and regulations. Since water is a prerequisite for life, it is of primary concern. The different types of water meant to be consumed or used by humans or being discharged into the environment are extensively regulated and controlled. It is beyond the scope of this article to discuss such regulations in detail. However, some limits for a range of elements in treated (potable) water are given in Table 3 in order to discuss the applicability of AAS for the control of water quality.

In order to monitor for these elements at concentrations close to the limits set by regulations and to determine compliance, the LOD of the analytical technique should ideally be at least 10 times lower than the actual limit. By comparing the achievable LODs of different AAS techniques with these control limits, it is clear that FAAS can only be used to monitor directly seven of the 16 elements listed in Table 3.

4.1.2 Sampling and Sample Conservation

Appropriate sampling and subsampling techniques are a crucial prerequisite of the generation of meaningful

Table 3 Some international standards for treated potable waters (all concentrations in $\mu g\,L^{-1}$)[a]

Element	USA limit	EEC guideline value	EEC limit	WHO guideline value	German limit	Preferred method
Ag	50		10		10	FAAS, ETAAS
Al		50	200		200	ETAAS
As	50		50	50	40	ETAAS, HGAAS
Ba	1000	100			–	FAAS
Cd	10		5	5	5	ETAAS
Cr	50		50	50	50	ETAAS
Cu	1000	100[b] 3000[c]			–	FAAS
Fe	300	50	200		200	FAAS
Hg	2		1	1	1	CVAAS
Mn	50	20	50		50	FAAS
Na		20	150			FAAS
Ni		50			50	ETAAS
Pb	50		50	50	40	ETAAS
Sb			10			ETAAS, HGAAS
Se	10		10	10		ETAAS, HGAAS
Zn	5000	100[b] 5000[c]				FAAS

[a] EEC, European Economic Community; WHO, World Health Organization.
[b] At the water treatment plant.
[c] After 12 h in the pipe.

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environmental data. The technique of sampling has to be selected in accordance with the requirements determined by the type of water that is to be sampled, such as piped water (drinking and industrial waters), springs and wells, groundwater (bore holes, seepage waters), flowing surface waters (canals, creeks, rivers, streams), still surface waters (ponds, lakes, barrages), marine waters and precipitation. The majority of still and flowing waters exhibit substantial variations in their element concentrations over time and in their spatial distribution. It is therefore relatively difficult to take a 'representative' sample. The required task must therefore clearly be established before sampling is undertaken. The simplest case is to take random samples, for example, at an outflow location at a given time. However, sampling of this type is only meaningful when the place and time of sampling are clearly defined, based on prior detailed information, and refer to a special situation. Much better information can be obtained for one or several analytes by determining the change in concentration with time, either continuously or at regular time intervals. For example, such sampling could be meaningful for the inflows and outflows of a sewage treatment plant. The degree of information can be further enhanced by a network of sampling points (e.g. along the length of a river or over the depth profile of a lake), and changes at each sampling point over the short term (days) or over the long term (months, years) are monitored. Multivariate statistical procedures can aid in the interpretation of such complex data.[125] Sampling strategies are described in numerous national and international standards,[40] some of which are given in Table 4, and also in a number of review articles.[106,113,126]

The collection of wet precipitation (rain, snow, cloud aerosols, etc.) is especially challenging,[127] particularly when the wet precipitate must be kept separate from the dry precipitate. For this purpose, rainwater collectors have been designed using a device that covers the collector during dry periods and opens only at the onset of rain[128–131] or by changing the exposed collection funnel by moving the cover at that moment.[132] Materials for such precipitation collectors have to be selected with care, since substantial errors can occur owing to adsorption on the walls of the collection funnel and sample container.[133] Collection time is also important, especially if an appropriate preservative has not been added.[134]

Also problematic is the collection of seawater samples from different depths or from the water surface, which contains high concentrations of surface-active compounds (biofilm). The ship itself and all the equipment used for sampling (winches, wires, bottom weights, samplers and messengers) are potential sources of contamination either due to their material or by their action (mixing different layers). These problems are discussed in more detail in review papers on seawater sampling.[106,135]

The sample pretreatment following the sampling of water samples depends on whether the total concentration or the concentration of dissolved analyte should be determined. In the first case, the water sample may have to be digested depending on its properties and the selected analytical technique. In the second case, the water sample is filtered after sampling, usually through a membrane filter of pore size 0.45 μm. Even such a simple task might not be without problems. Dissolved analytes might be lost during filtration owing to adsorption on the filter material or apparatus,[136] or the sample might become contaminated during filtration.[137] Various parts of colloidal forms of the analytes might pass through the filter, depending on the state of the filter with respect to loading with solid material.[138–140] For these reasons, those variations introduced during sampling of water are

Table 4 National and international standards for water sampling

Topic	International	USA	UK	Germany
Sampling strategy	ISO 5667-1/1991		BS 6068-6.2	DIN EN 25 667-1
Sampling techniques	ISO 5667-2/1991			DIN EN 25 667-2
Terminology	ISO 6107-1-9/1989		BS 6068-1.2	
Frequency of sampling		EPA 0004.3		DIN 38 402-6
QA for water sampling	ISO 5667-14/1998			
Marine water	ISO 5667-9/1992		BS 6068-6.9	DIN 38 402-16
Wastewater	ISO 5667-10/1992	EPA 0006.8	BS 6069-6.10	DIN 38 402-11
Precipitation	ISO 5667-8/1993		BS 6068-6.8	DIN 38 402-17
River and stream water	ISO 5667-6/1990		BS 6068-6.6	DIN 38 402-15
Drinking water	ISO 5667-5/1991		BS 5667-6.5	DIN 38 402-14
Lakes, barrages	ISO 5667-4/1987		BS 6068-6.4	DIN 38 402-12
Aquifiers	ISO 5667-11/1993	EPA 600/2-81-160 EPA 625/R-93-003a		DIN 38 402-13
Mineral and medical springs				DIN 38 402-18
Swimming pools and baths				DIN 38 402-19
Tidal waters				DIN 38 402-20
Cooling water, boiler water	ISO 5667-7/1993			DIN 38 402-22

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often significantly higher than the instrumental variation of the measurement.[141] Immediately following filtration, or sampling if the sample is not filtered, the sample must be stabilized, usually through the addition of 10 mL of nitric acid per liter of water sample. The requirements for preservation are different for the different water samples (e.g. high salinity acts in a stabilizing manner), and also depend very much on the elements to be determined. In general, the pH value must be <1.5 in order to minimize the risk of analyte concentration changes due to precipitation or wall reactions. Different procedures may be required if individual element species are to be determined (see section 4.1.5). If the sample has been filtered, it may be of interest to examine the residue separately, following a method often very similar to those used for the analysis of sludges or sediments (see section 4.2).

Preconcentration at the site of sampling has been proposed as a strategy for sample preservation;[142] the claimed advantages are (a) large volumes of sample do not need to be transported, (b) concentrated samples are more stable and (c) the risk of contamination during transport and storage is reduced. The disadvantages are that preconcentration is a selective procedure, including only (a) selected elements, (b) mostly ionic species and often (c) only one oxidation state of the analyte, unless a comprehensive sample preparation procedure is performed at the sampling site. If interferences occur during preconcentration, it is very difficult to recognize them subsequently, since the original sample is no longer available. This strategy has not received wide acceptance and has only been used for special cases such as the determination of gold[143] and the determination of species of chromium[144] and mercury.[145]

Samples should be analyzed soon after sampling, especially when species determination is desired. Stabilized samples should be kept in appropriate containers, whereby the most suitable material depends on the target analytes and the concentration levels [details can be found in an overview published by Sturgeon and Berman[126]]. The best materials for the storage of samples with very low concentrations of analytes are fluoropolymers with a very smooth surface,[146] such as perfluoroalkoxy (PFA) [polyfluoroethylene (Teflon®PFA)][147–149] or polished polytetrafluoroethylene (PTFE) (Teflon®)[150] with the exception of mercury, for which glass is the best material.

4.1.3 Methods for Flame Atomic Absorption Spectrometry

According to most official methods for water analysis by FAAS, a digestion can be omitted if the analyte can be completely detected without such pretreatment. Normally, this is the case for filtered and stabilized water samples and often even for unfiltered water samples, provided that they do not contain large amounts of suspended matter that could block the sample introduction system or cannot be fully atomized in the flame. However, the direct analysis of water samples by FAAS is limited by its lack in sensitivity. Apart from the main elements sodium, potassium, calcium and magnesium, and under given conditions strontium, none of the trace elements can be determined in unpolluted surface waters, rainwater and seawater directly by FAAS. If the task is to monitor given limiting values, such as in the drinking water regulations or other corresponding international guidelines (see Table 3), then it is also possible in some cases to control for barium, copper, iron, manganese and zinc, and under given conditions for cobalt and chromium. For the analysis of some wastewaters, seepage waters or more strongly polluted surface waters in general, it is also often possible to determine elements such as cadmium, lithium, nickel and lead satisfactorily by FAAS. However, for such types of sample, a digestion is often indispensable.

By far the most often used digestion procedure for the determination of heavy metals in polluted waters by FAAS is digestion in nitric acid–hydrogen peroxide. Nitric acid and hydrogen peroxide are added to the water sample in a beaker and the volume is reduced to a wet residue, if required under repeated addition of hydrogen peroxide. The residue is taken up in nitric acid and water and the digestate is analyzed by FAAS.

In order to avoid potential interferences, to which especially the analysis of strongly polluted waters might be exposed, the following points should be particularly observed:

1. Background correction should be used for all determinations at wavelengths < 350 nm.
2. The nitrous oxide–acetylene flame should be used for the determination of chromium and is also strongly recommended for the determination of iron and manganese in water samples with complex matrices (e.g. wastewater), even if the sensitivity with this flame is poorer than that with the air–acetylene flame.
3. The addition of at least $2\,g\,L^{-1}$ La as the chloride is required if calcium and magnesium are determined with the air–acetylene flame.
4. The addition of $1\,g\,L^{-1}$ Cs as an ionization buffer is recommended for all determinations with the nitrous oxide–acetylene flame and also for the determination of sodium and potassium with the air–acetylene flame.
5. The operating conditions should be optimized for minimum interferences rather than for maximum sensitivity, particularly for strongly polluted waters.

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If the sensitivity is then inadequate, a more sensitive AAS technique should be chosen (e.g. GFAAS).

Before GFAAS was introduced as a more sensitive technique in AAS, preconcentration by solvent extraction in combination with FAAS was used for the determination of trace elements in fresh waters. In this case complete digestion of the sample is essential. Nowadays, such methods are seldomly used routinely even though large numbers of these have been and continue to be published. The arguments against such methods are numerous (e.g. lack of sample throughput, involvement of too much manual work, contamination problems and the presence of interferences are only some examples). As a general rule, direct determination by other more sensitive techniques is generally preferred. A possible exception is on-line preconcentration,[151] for example, by sorption on packed microcolumns,[152–156] and this aspect is discussed in more detail together with GFAAS. Table 5 lists methods for the analysis of water samples by FAAS.

4.1.4 Methods for Graphite Furnace Atomic Absorption Spectrometry

With a sensitivity of about 2–3 orders of magnitude higher than that for FAAS, GFAAS offers the best prerequirements for the direct determination of a large number of trace elements in water. Also, digestion is not required for the majority of water samples, since in situ pretreatment such as oxygen ashing can be made part of the GFAAS heating procedure. Even water samples with a high content of suspended particles, which call for a homogenization directly prior to dispensing, can be directly analyzed with the aid of a slurry sampler.[170] The quantities of reagents and external

Table 5 Methods for the analysis of water samples by FAAS

Element	International	USA	Germany	Other methods and applications (see refs.)
Ag		EPA 272.1 EPA 7760A	DIN 38 406-18	
Ba		EPA 208.1 EPA 7080A		157–159
Ca	ISO 7980-1986	EPA 215.1 EPA 7140		157, 158, 160–165
Cd	ISO 8288-1986 ISO 5961-1995	EPA 213.1 EPA 3170		159, 166
Co	ISO 8288-1986	EPA 219.1 EPA 7200	DIN 38 406-24	160
Cr	ISO 9174-1990	EPA 218.1 EPA 7190		159, 160, 166, 167
Cu	ISO 8288-1986	EPA 220.1 EPA 7210	DIN 38 406-7	158–160, 166, 167
Fe		EPA 236.1 EPA 7380		158, 160, 167, 168
K	ISO 9964-2/1993	EPA 258.1 EPA 7610	DIN 38 406-13	158, 160, 162–165
Li		EPA 7430		160, 169
Mg	ISO 7980-1986	EPA 242.1 EPA 7450	DIN 38 406-3	157, 158, 160, 162–165
Mn		EPA 243.1 EPA 7460		158–160, 167, 168
Na	ISO 9964-1/1993	EPA 273.1	DIN 38 406-14	158, 160, 162–165
Ni	ISO 8288-1986	EPA 249.1 EPA 7520	DIN 38 406-11	159, 166
Pb	ISO 8288-1986	EPA 239.1 EPA 7420	DIN 38 406-6	166
Sr		EPA 7780		157, 160
Zn	ISO 8288-1986	EPA 7950	DIN 38 406-8	158–160, 166, 167

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pretreatment steps can be thus reduced to a minimum for GFAAS, which is a prerequirement for accurate results in the extreme trace range. This reduction of sample pretreatment compensates for the often-cited disadvantage of GFAAS that the measurement time is relatively long and the sample throughput is low, which can be largely overcome by the use of state-of-the-art instrumentation, providing fully automated sequential or even simultaneous multielement analysis.

Another often cited disadvantage of GFAAS is its susceptibility to interferences. The relevance of such interferences, especially those reported in the early history of the development of the GFAAS methodology, has been greatly reduced with the introduction of the STPF concept by Manning and Slavin in 1983.[171] These and later authors showed that numerous trace elements in surface waters could be determined free of interferences against matrix-free calibration solutions by applying the STPF concept, including platform atomization, the use of matrix modification and ZBC.[172–174] Nowadays, many standard methods are based on a direct determination, such as EPA 200.9 for the determination of Ag, Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn and Tl and EPA 7010 for the determination of Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Tl, V and Zn. Similar methods exist in Europe for Ag (DIN 38 406-E18), Cd (ISO 5961-1995, DIN 38 406-E19), Co (DIN 38 406-E24), Cr (ISO 9174-1990, DIN 38 406-E10), Ni (DIN 38 406-E11), Pb (DIN 38 406-E6), Se (DIN 38 405-E23), Tl (DIN 38 406-E21) and Zn (DIN 38 405-E8), and STPF conditions are recommended, even if they are not directly prescribed. Publications of direct determinations of trace elements in natural water samples are very numerous, and only selected papers are given in Table 6.

The probability of interferences increases with the complexity of the sample matrix and the requirements for low detection limits. Strongly polluted water samples usually contain a higher analyte content and therefore allow for substantial dilution, which greatly reduces interference effects during analysis by GFAAS. Mineral and therapeutic waters can nevertheless cause considerable analytical problems on occasion if they have a high matrix content, e.g. of sulfur compounds,[183,206] or when the analyte concentration is very low. Samples of such complexity require very careful method development, method optimization, validation and QC.

If the sensitivity of GFAAS is inadequate for the direct determination of trace elements in very pure water, the sensitivity can be markedly increased by using multiple injections[207–209] or by carefully reducing the sample volume by evaporation.[210–213] Nevertheless, while such procedures can easily be used for waters with low concentrations of inorganic or organic concomitants, more problems are expected when applied for wastewater, high-salt mineral water or seawater, so that the application for such samples is limited to cases where the analyte can be easily separated from the large amounts of matrix by thermal pretreatment.[214–218] Often, separation and preconcentration steps cannot be avoided for such complex samples.

The trace element concentrations in unpolluted seawater are in the lower micrograms to nanograms per liter range. From a comparison of the best published LOD for GFAAS with the trace element concentrations of two unpolluted seawater samples of different origins, one could conclude that it should be possible to determine a number of trace elements directly by GFAAS (see Table 7). However, an additional difficulty with seawater samples is the total salt concentration of $35\,g\,L^{-1}$ on average, which can lead to spectral and nonspectral interferences.

State-of-the-art systems providing high-performance ZBC together with STPF conditions are able to overcome these problems in some cases, as is demonstrated by selected publications on the direct determination of trace elements in seawater compiled in Table 8.

However, scrupulous optimization of the instrumentation and methods is necessary in order to reduce interferences to an acceptable level and to achieve the necessary S/N level. For this purpose the following points should be taken into consideration:

1. The STPF concept must be applied consistently to minimize spectral and nonspectral interferences. A THGA with integrated platform provides the best results.
2. As much of the chloride matrix as possible must be removed prior to atomization. The addition of ammonium nitrate or nitric acid as a modifier aids in vaporizing the chloride as NH_4Cl or HCl.
3. The thermal stability of volatile elements should be enhanced by the addition of modifiers (e.g. Pd) and/or the addition of hydrogen to the purge gas during the pyrolysis.
4. Since high background attenuation is to be expected, even when the matrix is largely removed, the application of ZBC is recommended.
5. A polarizer is not required for the longitudinal configuration of the magnet for ZBC. This configuration thus provides a better S/N than other configurations.

Even then, only a limited number of elements can be determined directly in seawater. For the others, as with the analysis of fresh water, preconcentration is indispensable. Great care is required to avoid errors at such a low concentration range $< 1\,\mu g\,L^{-1}$[113,126] owing

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Table 6 Selected publications on the direct determination of trace elements in natural waters by GFAAS

Analyte	Test sample	Remarks[a]	Ref.
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn	Spring water	STPF conditions	175
Ag, Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Zn	Surface water, drinking water		173
Ag, Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn	High-altitude Alpine snow	Clean room conditions	176
Ag, Cd, Pb, Sb	Drinking water	STPF conditions, THGA, simultaneous determination	177
Al	Mineral water	Mg modifier	178
		PD–Mg modifier	179
Al, As, Cd, Pb	Mineral water		180
Al, As, Be, Cd, Co, Cr, Mn, Ni, Pb, Se, V	Surface water	STPF conditions	3
Al, As, Be, Cd, Cr, Pb, Sb, Se, Tl	Drinking water, mineral water	STPF conditions	158
Al, Cu, Fe, Mn, Pb, Zn	Cloud aerosol, Alpine precipitation		163
As	Drinking water	STPF conditions	181
As, Cd, Ge, Sb, Se	Thermal waters rich in Fe	Platform, Mo modifier, ZBC	182
As, Se	Mineral waters rich in sulfates	STPF conditions, ZBC	183
B	Surface water	Ca–Mg modifier	184
	Surface water, wastewater	Ni modifier, Zr-coated tube	185
Ba	Drinking water	ZBC	186
Be	Drinking water		187
	Natural water		188
Bi	Wastewater	Pd modifier	189
Cd, Cr, Cu, Ni, Zn	Rainwater	Influence through seawater aerosols	190
Cd, Cr, Pb	Wastewater	STPF conditions, ZBC	174
Cd, Cu, Fe, Mn, Pb, Zn	Rainwater	Comparison with PIXE	191
Cd, Cu, Pb	Rainwater	Comparison with ASV	192
Cd, Cu, Pb, Zn	Precipitation	Comparison with ICPOES	193
Cd, Fe, Mn, Pb	Surface water	Platform, HNO_3 modifier	194
Cd, Pb	Surface water	Platform, La modifier	195
Cr	Surface water	V–Mo modifier	196
Cu, Pb	Drinking water	STPF conditions, fast program	197
Mo	Surface water	Ca modifier	198
	Surface water	Pd^0 modifier, ZBC	199
Sb	Wastewater	Comparison with HGAAS	200
	Drinking water		201
Se	Surface water	STPF conditions, Pd^0 modifier	202
Si	Drinking water	Co modifier, Ti–C-coated tube	203
Sn	Tap water	STPF conditions, Mg or Pd–Mg modifier	204
V	Water	Ascorbic acid modifier	205

[a] PIXE, particle-induced X-ray emission; ASV, anodic stripping voltammetry.

to contamination or analyte losses, and the following guidelines should be considered:

1. The number of necessary steps in the procedure, the number of containers, funnels, etc. and the mass of added reagents should be kept to a minimum.
2. All containers should be used exclusively for trace analysis and must be cleaned thoroughly prior to use, preferably by fuming out with nitric acid[240–242] or in the case of very clean PFA by leaching with dilute aqueous solutions of H_2O_2, ammonia and triethanolamine, which reveals comparable cleaning effects for this material.[243]
3. All reagents must be of the highest purity. If necessary, they must be further purified, e.g. by subboiling distillation.
4. All procedures should be performed in a clean room, clean work-bench or at least in a dust-free environment in a closed system, to minimize contamination from the laboratory atmosphere.

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Table 7 Trace element concentrations ($\mu g\,L^{-1}$) in unpolluted seawater reference materials compared with the published LODs for GFAAS.[219] (Reproduced with permission from B. Welz, M. Sperling, 'Atomic Absorption Spectrometry', Wiley-VCH, Weinheim, 1999)

Element	NASS-1[a]	ICES-5[b]	LOD
As	1.65	1.4	0.2
Cd	0.029	0.020	0.003
Co	0.004	0.004	0.15
Cr	0.184	0.08	0.01
Cu	0.099	0.123	0.1
Fe	0.192	0.376	0.1
Mn	0.022	0.240	0.01
Mo	11.5	–	0.03
Ni	0.257	0.202	0.3
Pb	0.039	0.049	0.1
Zn	0.159	0.392	0.1

[a] National Research Council Canada.[220]
[b] International Council for the Exploration of the Sea.[106]

5. Polymer containers, funnels, etc. become aged with usage, developing active sites on the surface,[149] being able to exchange ions,[244] and therefore must be exchanged regularly for new ones.
6. On-line procedures in closed systems[151] are superior to all manual batch procedures owing to the significantly lower risk of contamination and to their much better repeatability and reproducibility.

For preconcentration, different techniques, such as liquid–liquid extraction,[245,246] coprecipitation,[247] ion exchange and solid sorbent extraction[48] electrodeposition,[249] might be considered, but some specialities have to be taken into account with respect to their combination with AAS techniques.[250] For the combination of solvent extraction techniques with GFAAS, the following facts should be considered:

1. Although organic solvents have the advantage of enhancing the sensitivity in FAAS, they tend to be a disadvantage in GFAAS since they often wet graphite and can spread uncontrollably.[251]
2. Organic solvents containing halogens are a potential source of gas-phase interferences.[252,253]
3. Organic solvents tend to evaporate from the sample cups, and some of the complexes extracted are unstable, calling for a back extraction into aqueous media.

The most often used methods for solvent extraction of trace metals from seawater are based on the use of dithiocarbamates as chelating agents.[254] A standard procedure is based on the use of equal amounts of ammonium pyrrolidine dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) at pH 4–5, which is adjusted with an acetate buffer.[255–257] Freon TF (1,1,2-trichloro-1,2,2-trifluoroethane) is chosen as an organic solvent because of its low toxicity, its

Table 8 Selected publications on the direct determination of trace elements in seawater by GFAAS

Element	Modifier	Background correction	Refs.
Ag	Pd–ascorbic acid	Deuterium	221
As	Pd	Deuterium	222
As, Cd, Pb	Pd	Deuterium	223
Ba	V–Si	ZBC	224
Cd	NaOH	ZBC	225
	$(NH_4)_2HPO_4$–HNO_3	ZBC	218
Cd, Mn, Pb	Pd–ammonium oxalate	ZBC	226
	Pd–$NH_4H_2PO_4$–$Mg(NO_3)_2$	Deuterium	227
Cr	W	Deuterium	228, 215
Cr, Cu, Mn	HNO_3 or oxalic acid	ZBC	229
Cr, Mn, Mo	Pd–$NH_2OH{\cdot}H_2O$ for Cr, $Mg(NO_3)_2$ for Mn, Pd for Mo	ZBC	230
Cu	HNO_3	ZBC	231, 232
	NH_4NO_3	ZBC/deuterium	233
Cu, Mn	Pd, Pd–Mg	ZBC, THGA	234
Mn	NaOH	ZBC	235
Mo, V	Ascorbic acid	Deuterium	236
Ni	Pd	ZBC, THGA	217
Pb	Pd–Mg or oxalic acid	ZBC, THGA	237
Sn	Pd	Deuterium	238
Zn	NH_4VO_3	ZBC	239
	HNO_3 or ascorbic acid	ZBC	28

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very low solubility in water (0.017% m/m at 21 °C), its quick separation from the aqueous phase and its low metal blank even at technical-grade quality.[256] Alternatively, the metal chelates may also be extracted into chloroform.[255,258] In order to overcome stability problems of the extract, the analytes are transferred back into acidic aqueous solution. This can be performed by either back extraction into dilute nitric acid[259] or by smooth evaporation of the solvent and acidic redissolution of the metals. Very high preconcentration factors of up to 6000 have been reported by such a combination of extraction and back extraction.[260]

Coprecipitation as a method for preconcentration has also often been combined with GFAAS determination, having its own advantages and disadvantages:

1. Carriers for coprecipitation are a potential source of contamination, since they are added in excess.
2. Coprecipitation carriers that can be easily vaporized or decomposed during the pyrolysis step are particularly suitable; these include elements such as indium, mercury, selenium[261] and tellurium[262] and organic reagents.[263–266]
3. Coprecipitation carriers, that act as modifiers, such as magnesium,[267,268] nickel[269] and palladium,[270] can also be advantageous.
4. The use of hydroxy precipitates[267,271–275] is preferred to that of sulfides,[276] which tend to create interference effects.
5. An interesting aspect of preconcentration by coprecipitation in combination with GFAAS is the direct analysis of the precipitate as the solid or a slurry.[263,277,278]

The use of ion exchangers and solid sorbents for preconcentration has found particular attention recently:

1. Column-based methods are particularly suitable for automation and even on-line methods are possible.
2. The sorbent can be used repeatedly, and often the amount of added reagent is reduced compared with other preconcentration methods.
3. Closed systems in general are easier to control for contamination. However, some ion-exchange resins and solid sorbent materials produce persistent and irreproducible blanks, owing to contamination of the polymeric material during its production.[279]
4. Organically bound metals might be lost during preconcentration, especially when using ion-exchange or solid-sorbent extraction, calling for a digestion procedure prior to preconcentration [e.g. ultraviolet (UV) photolysis].

Since ion exchangers seldom have the desired selectivity for the trace analytes, other solid-sorbent techniques have been developed, based on the use of more selective functional groups. At least two different approaches can be differentiated:

1. A chelating compound is added to the sample or preloaded on to the column. The column is often a hydrophobic (reversed-phase) material, which retains the chelating agent or the metal–chelate complex by sorption. Often used sorbents for this approach are silica C-18,[280,281] activated carbon[282] and macroporous resins such as Amberlite XAD-4.[283]
2. A functional group is permanently bound to the base material by a coupling reaction during the synthesis of the sorbent. Typical sorbents of this type are Chelex-100,[283] Muromac A-1[283,284] and 8-hydroxyquinoline bound to controlled-pore glass (CPG) or silica.[285]

A standard method using macroporous iminodiacetate chelating resin is available [EPA Method 200.13[286]] and can be used for the preconcentration of Cd, Co, Cu, Pb and Ni. Further details on solid-sorbent extraction techniques can be found in some review articles.[248,283]

On-line procedures especially for sorbent extraction with GFAAS detection, mostly based on FI, have been increasingly applied, using the same or similar sorbents as for off-line techniques. These on-line procedures offer a number of advantages:

1. The analysis time may be substantially reduced, since an equilibrium state is not needed.
2. There is a much lower risk of contamination since preconcentration and elution are performed in a closed flow system. Only inert materials and small surface areas are used, and the reagents can be purified on-line.
3. Since reactions such as acidification, complexing and sorption take place on-line and can follow each other in rapid sequence in a reproducible way, it is also possible to work with unstable complexes or intermediate products.
4. All processes can be easily automated.

On-line preconcentration procedures have made possible the determination of trace elements in the lower nanograms per liter range in seawater on a more or less routine basis. Commercial instrumentation including the necessary software, allowing for the coupling between FI and GFAAS, is available.[287] Proposed methods are based on the use of the reversed-phase sorption of chelate complexes with

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dithiocarbamates[288–290] or dithiophosphates,[291] immobilized 8-hydroxyquinoline[292] or Muromac A-1.[293] An overview of such techniques was given by Fang and Tao[284] and progress has been reviewed by Fang.[294]

4.1.5 Methods for Speciation Analysis

Speciation analysis is an area which has found increasing interest in the 1990s. Element species can be distinguished by their oxidation state (redox species), by their molecular form (organometallic compound), by coordination (complex), by the phase in which the analyte exists (dissolved, colloidal, suspended) or by its solubility (leachability, bioavailability). In this broad sense, the analysis of filtered water samples is in principle already a form of speciation analysis. This physical separation can be refined to a fractionation of particulate and colloidal species via multistage filtration and ultrafiltration[295] and can be automated by means of FI-type manifolds[296] or field-flow fractionation. Methods used for such a type of speciation for water samples have been reviewed by De Mora and Harrison.[297] Considerably more detailed deliberations on the term 'species in aquatic systems' can be found in the monographs by Batley,[298] Krull,[299] Ure and Davidson[300] and Tessier and Turner.[301] In this section, however, the focus is on chemical species such as redox species and organometallic compounds. Very few direct methods exists for the determination of such species. More often, separation techniques have to be combined with suitable detection techniques. As far as speciation analysis is concerned, the FAAS technique lacks sensitivity, whereas the more sensitive ETAAS is not particularly suitable for detection in gas chromatography (GC), high-performance liquid chromatography (HPLC), and other chromatographic techniques most often used for the separation of trace element species. Therefore, AAS techniques can be ranked in the following decreasing order of their potential for speciation: HGAAS > CVAAS $\gg$ ETAAS > FAAS.

Since vapor generation techniques (HGAAS and CVAAS) are not the topic of this article, only speciation by ETAAS and FAAS techniques will be discussed briefly. Both techniques have been used in the past as detection methods for chromatographic separation techniques, as discussed by Ebdon and Hill,[302] but have been overtaken by more powerful detection techniques such as inductively coupled plasma mass spectrometry (ICPMS). Although FAAS and GFAAS are not very suitable to be coupled directly with chromatographic separation techniques, their combination with nonchromatographic separation methods is more straightforward, as we have discussed already for the case of preconcentration. Techniques such as solvent extraction or solid-sorbent extraction used for preconcentration can also be used for speciation purposes, for example, when the separation process is selective for one oxidation state of the analyte. Such combined methods, using GFAAS for speciation analysis, have been reviewed by Das and Chakraborty.[303] Often such nonchromatographic separation methods can be automated by using FI manifolds. When used for separation, FI provides only limited separation power, which mostly is exploited for binary separation of the type retained/not retained, for example, for preconcentration. While such a technique is not very well suited to separate a great number of analytes, it seems well fitted for screening purposes requiring high sample throughput. Further, for cases where the separation of species can be reduced to two, FI can be successfully used for speciation analysis. This is actually true for many cases of speciation of oxidation states of metal ions and metalloid ions, where the chemistry of these elements normally allows only for the presence of two different oxidation states in the presence of each other, at least under normal environmental conditions. Methods have been developed for the determination of As(III)–As(V),[304] Cr(III)–Cr(VI),[305–309] Fe(II)–Fe(III),[310] Sb(III)–Sb(V),[311] Se(IV)–Se(VI)[312] and V(IV)–V(VI).[313] The approach of binary separation can also be used for those cases where interest in the degree of speciation can be reduced to a binary differentiation. For example, such limited separation is useful for the differentiation of inorganic and organic species, labile and stable complexes, bound and free element species or the particulate and dissolved part of the analyte. This approach can also be applied for cases when other characteristics of the species can be grouped into two different categories, such as toxic/nontoxic. In this area of binary speciation, methods have been developed for the determination of free and complexed Cu[314] and of free and complexed Al.[315]

4.2 Soils, Sediments, Sludges, Coal, Dust and Other Solid Materials

A variety of widely differing solid materials will be discussed here together, simply because they have some common steps in their analytical procedure while differing in others. Solid materials such as arable soils, contaminated soils, sediments from rivers, lakes and seas, atmospheric dust and waste materials such as sewage sludge, ashes and other solid wastes are collected as samples from different compartments of the environment in order to gain information about the status of that compartment or to learn about the fluxes between them. The emphasis of environmental analysis is on the anthropogenic part of these fluxes and on the impact of such fluxes on the biosphere.

With respect to soils, in addition to the native content, various amounts of metals and metalloids are supplied

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to the soil by dry and wet atmospheric deposition, by agronomic practices via fertilizers, sewage sludges or irrigation water, and so on and by waste discharges or waste disposal. For certain metals the anthropogenic proportion constitutes only a fraction of the natural amount, for others it can be the exclusive source. These metals and metalloids enter the food chain mainly via plant uptake.

Human activities are connected with the 'production' of waste materials including municipal solid wastes, industrial by-products, sewage sludge, dredged material, wastes from mining and smelting operations, filter residues from wastewater treatment and atmospheric emission control, ashes and slags from burning of coal and oil and from waste incinerators. All these wastes pose most challenging problems (e.g. when disposed of on land), creating a potential source for contamination of the soil and the groundwater.

The materials on the lake, stream and ocean floor, known as bottom sediments, are both a sink and a source of contaminants. Sediment-associated contaminants can be transported by resuspension of sediment particles, may accumulate in the food chain or may affect the health of biota and water quality in aquatic ecosystems. Knowledge of the character of the sediments and the fluxes involved is necessary for an understanding of environmental cycles but also in the development of techniques for remediation of aquatic ecosystems or the disposal of the sediments in the dredging of harbors and waterways.

With respect to atmospheric emission, monitoring frequently starts at the raw material stage. For example, emission monitoring of coal-fired power stations, coke works, incineration plants or cement furnaces starts with the analysis of the coal or waste materials to be burned. For the mass balance for such thermal reactors the different streams must be analyzed. While the mass carried with the scrubbed gases is important for the actual emission, the dusts collected in cyclones and electrostatic separators, ashes and other combustion residues such as slags must also be analyzed to characterize the complete system.

Air pollutants can occur in gaseous, fluid (dissolved or suspended) or solid form. Air must therefore be considered as an inhomogeneous, multiphase aerosol, whose composition is subjected to considerable spatial and temporal variations.[316] With respect to metals and metalloids, the gas phase is only of limited interest, since only mercury and a small number of volatile species occur as gases or vapors, especially close to hot emission sources.[317] The liquid phase (rain, snow, etc.), also termed wet deposition, belongs analytically to the area of water, which has been discussed in section 4.1. The analysis of air, with the restrictions mentioned already, is thus largely limited to the analysis of airborne dusts. Looked at globally, the bulk of airborne particles (approximately 90%) are derived from a number of natural sources (terrestrial, marine, volcanic, biogenic),[318] whereby salt from the oceans makes the largest contribution with about $10^9\,t\,a^{-1}$. Looking more specifically into metal emission, the view changes drastically, with a clear dominance of anthropogenic sources of the most important trace elements such as As, Cd, Cu, Cr, Pb and Zn on the global scale.[319] The anthropogenic sources of particle emissions (combustion, industrial, automobile) are by no means evenly distributed, but are related to the typical conurbations in which human activity is the most pronounced. Owing to the relatively high population and industrial density, such sources are concentrated in the northern hemisphere, but because of long-range transport globally these sources have an impact on a large proportion of the population in the form of pollution.[320]

4.2.1 Sampling of Solid Environmental Materials

Obviously, the procedures for sampling, sample homogenization and preparation of such widely differing materials are correspondingly manifold, and cannot be discussed in great detail here. Before one even starts to discuss analytical details, the exact purpose of the analysis should be clarified, since the type of information needed is decisive for the selection of the method. Three general procedures can be distinguished for these samples, determination of (a) the total concentration of an element, (b) the extractable portion and (c) individual species, especially organometallic compounds; the boundaries between these procedures are naturally flexible. The decision about which method to select is driven by the emphasis given to topics such as risk assessment, evaluation of bioavailability or toxicity, pollution control, baseline mapping and transport phenomena. The interested reader is referred to introductory monographs and review articles on the analysis of soils,[321–324] sediments,[325,326] sludges and other waste products,[327,328] and airborne particulates,[329] and on speciation analysis in soils and sediments[330–332] and to general treatises on environmental analytical chemistry, discussing such questions in more detail. The selection of the determination technique (FAAS, GFAAS, etc.) is simple in comparison. It is largely determined by the concentration of the analyte and also by the nature of the matrix.

4.2.1.1 Sampling of Soil, Sediments, Sludges and Solid Waste Materials The problem for sampling soils,[333–337] sediments,[338–341] sludges[328,335] and other waste materials[328,342,343] is the removal of a few grams that should be representative of the situation being investigated from a material that is present to the extent of tons or cubic meters. Meaningful sampling of such

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heterogeneous media requires an understanding of the spatial and temporal variations, which is a prerequisite for answering the basic questions of how many samples are needed and where they should be taken. In the case of soils and sediments the planning of sampling has to start with a site investigation making use of available (e.g. historical) information, which could help to build hypotheses and conceptual models. A site characterization follows, consisting of two major steps, namely site observation and subsequent site mapping. Such site characterization is a multimedia, multidimensional, multidisciplinary effort, that requires vigorous communication among all of the principal parties involved and often includes preliminary sampling. Unfortunately, no checklists are capable of addressing all of the important issues and factors that influence the sampling and analysis of such materials. However, field guides and handbooks are available for soils[334] and sediments[344] that are helpful in defining the task. From all this information a sampling strategy is built, leading to a sampling network design. Depending on the required information, the sampling strategy must consider the local inhomogeneities in the horizontal plane of the sampling site, the dependence of the element distribution on the depth of sampling and possible seasonal variations.[167,345,346] A number of statistical procedures have been elaborated to facilitate representative sampling or to estimate the analytical uncertainty due to sampling errors, for example, in order to characterize contaminated areas.[347–352] Usually a large number of individual samples of the material being investigated are taken from different places (e.g. 25 samples from an agricultural field not bigger than 5 ha) and then combined into a composite sample. The advantages of composite sampling are that it reduces the cost of analysis and provides an estimate of the mean concentration. Its disadvantages are a loss of information about variation and the time required for such pretreatment. In order to avoid sampling errors[353] due to the heterogeneity of the material and the effect of particle size on element distribution,[354,355] one has to follow certain rules dictated by the particulate sampling theory, such as that developed by Gy.[356] In order to create an analytical subsample, the composite sample has to be homogenized and reduced in size. Different techniques for such homogenization exist, such as cone and quartering, sectorial splitting, riffling, milling and sieving. Sample preservation then depends on the analysis. In the case of total element determination the material is often dried and for other cases the samples are simply cooled to 4 °C or frozen (usually at −20 °C). The problems of sampling and sample preservation naturally become even more complex when element species are to be determined.[357,358] In any case, the uncertainty introduced by sampling of such heterogeneous materials supersedes all other following contributions,[339,359,360] and therefore needs careful evaluation in order to create meaningful data. It should be mentioned once again that this area is regulated by national and international rules, for example, for the sampling of soil (ISO-TC 190/SC2), sediments (DIN 38 414-11/1987) and sludges (DIN 38 414-1/1986).

4.2.1.2 Sampling Dusts Collecting the sample is the most critical step in the analysis of dust, as it is for other samples in environmental analytical chemistry. For the analyst, air is a practically infinitely expanded aerosol on which random investigations must be performed according to defined spatial and temporal regulations. The number and size of the random samples, as well as the place, time and sequence of sampling, are decisive for a representative statement on the relationship between quantity of material, space and time. A number of authors have treated the subject of sampling dusts very thoroughly in review articles and book contributions. This has been done either in general[361] or in selected areas such as the free atmosphere[316] or at the workplace.[362–364]

For the investigation of trace substances in the free atmosphere, the temporal and spatial distribution of sample collection in an area to be investigated must be matched to the meteorological conditions, such as wind direction, wind speed, air temperature and humidity. The length of an investigation program, the measurement frequency and the density of monitoring stations have to be carefully selected. Frequently, the concentration of constituents determined by a measurement program is influenced by the geographical location of the monitoring station. This is typical in areas where dust is whirled up strongly or close to the coast where the constituents of the sea spray become clearly noticeable. The extent to which meteorological conditions can influence sampling can be seen when the wind velocity is high, causing turbulence at the sampling port or even causing an under pressure so that the collected sample material can be transported back to the outside.

Dust cannot be sufficiently characterized by only its general composition, but physical and chemical forms (species) have to be differentiated;[365,366] the morphological composition of dust can be very heterogeneous depending on the origin of the particles[364,367] and the various forms can have markedly varying physiological activity. Smooth globular grains have a much smaller surface area, and are thus less reactive than needle-shaped, fine crystalline particles. Apart from the morphology, the size of particles, ranging between 0.001 and 150 μm, also has a decisive influence on the physiological activity. Particles smaller than 10 μm can enter the lungs of humans or animals, while larger particles can be filtered out. Dust samples often show a particle size distribution with characteristic maxima at two or three different particle sizes (bimodal, trimodal size distribution) depending on

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sources and history. A further criterion is the solubility, which decides whether an element can directly enter the nutritional chain, or whether it is initially sedimented.

For sampling aerosols, two different approaches are available: procedures that use suction and those that do not. For the latter, various collectors for dust precipitates are available, which again are often regulated by national standards. In general, such devices do collect preferentially larger particles since these fall out more easily than smaller particles.

For sampling under suction, measurement and maintenance of a constant volume stream by the air pump are essential components of sampling. The sampling method most widely used is the high-volume sampler, which has been standardized in many countries, and operates at sampling rates between 40 and 100 $m^3 h^{-1}$. For sampling gaseous constituents, wash bottles with a suitable absorber solution or tubes being coated with a specific agent, so-called denuders, are frequently used. To separate dust from the air, flat membrane filters made of cellulose materials are most suitable owing to their low and constant element blank values. In high-volume samplers large filters can be used, which later can be cut to several aliquots that can be used for (a) various types of analysis, (b) replicates, (c) sharing samples with other groups or (d) storing them as 'backup' samples. Fiberglass filters do allow a larger volume of air to be taken through, but are less useful for trace analysis of airborne dust because of their high and often markedly varying element blank values.[368] Preseparating inlet systems are available for such samplers, which exclude particles larger than 10 μm, for example, in a cyclone. Cascade impactors most often are used for size separating sampling, which are available with 4–9 stages having size ranges between 0.02 and 20 μm.[361,369,370]

Sampling for emission measurements is usually performed directly in the stack or chimney, for example, of a power station or a waste incineration plant. The difficulties to be expected in taking a sample representative of the total mass flow under isokinetic conditions can be seen from the example of a stack gas stream of several 100 000 $m^3 h^{-1}$ at a temperature of up to 300 °C and with a varying dust content from milligrams to grams per cubic meter. For trace analysis, the problems of the level and scatter of the blank value and also contamination during sampling can additionally be detrimental to the results of the examination. This is more so the case for emission measurements since cellulose filters cannot be used, owing to the high temperatures at the sampling point, and quartz wool must preferentially be used.

For the measurement of dust at the workplace two different strategies exist, using either stationary or personal dust measuring instruments. Stationary measuring instruments are similar to those used for measuring in the free air and have the advantage that the air throughput is relatively high at about 20 $m^3 h^{-1}$, permitting a sampling period of only a few hours. The relatively small personal measuring instruments, on the other hand, have an air throughput of only about 120 $L h^{-1}$ (corresponding approximately to the volume of air breathed), so that sampling is required for the entire length of a working day to collect sufficient material for the subsequent chemical analysis.[362,364,371] Membrane filters made of cellulose materials are used preferentially for dust measurements at the workplace.

In addition to the collectors mentioned so far, which are largely standardized, there is a wide range of collectors designed for special applications, such as the investigation of automobile exhaust gases[372] or soot from Diesel engines,[373] or those that are specific for the subsequent analytical technique. Among these in particular are those developed for GFAAS procedures in which a probe[374] made of porous graphite is used as a filter and inserted directly into the atomizer, or the inner wall of the graphite tube itself is used for collection of aerosols either by impaction or by electrostatic deposition.[375,376] Owing to the high sensitivity of such in situ sampling techniques, very short collection times are possible so that the measurement can be performed virtually in real time. The disadvantages are that only one element can be determined per sample collection, except in simultaneous spectrometers, and that no sample is available for further evaluation. In general, procedures of this nature must therefore be seen as complementary to the standardized collection procedures and not as alternatives. A list of methods approved by United States Environmental Protection Agency (USEPA) was given by Kao,[377] but those for metals are few, however.

4.2.2 Determining the Total Concentration of Analytes

4.2.2.1 Total Dissolution For the determination of the total analyte concentration in a test sample, very harsh decomposition procedures are required, which are aimed at the total dissolution of the sample. Soil and dust samples exhibit considerable variations in mineralogical and chemical composition, including very resistant materials, making the task of total dissolution a difficult one. The total dissolution procedures available for such samples are either fusion methods using sodium carbonate[378–380] or lithium metaborate,[379–383] or acid digestions in the presence of hydrofluoric acid and frequently also perchloric acid.[380,384–386] Although such harsh procedures are time-consuming and the use of such dangerous acids demands special safety measures, they cannot ascertain the total dissolution of a number of minerals, such as cassiterite, chromite, zircon, rutile, monazite and corundum.[387–389] Apart from incomplete

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dissolution, formation of volatile fluorides is another possibility for analyte loss for a number of elements such as antimony, arsenic, boron, germanium and silicon (which should be removed in this way).

Since fusion methods lead to high total salt concentration with a corresponding risk of contamination and interferences in GFAAS due to the high background signal, wet digestion methods are more popular in connection with AAS. However, often the difficult matrix cannot be dissolved by a single-stage dissolution, but calls for a combined multistage digestion using oxidizing acids (nitric acid, perchloric acid, sulfuric acid, hydrogen peroxide) and hydrofluoric acid.[386,390] If necessary, dry ashing can be performed in advance[391,392] and if insoluble, fluoride-containing residues are produced during digestion, they can be taken back into solution by the addition of boric acid.[390] A comparison study concluded that the combination of an acid decomposition with final fusion of insoluble residues is the best method for the hard to extract elements Cr, Y and Zr.[378]

Membrane filters normally used nowadays in dust collectors dissolve in nitric acid and also in organic solvents such as benzene.[371] On the other hand, quartz wool used as a filter medium for emission measurements usually requires digestion in nitric acid or hydrofluoric acid under the addition of hydrogen peroxide.[393]

For the digestion of coal and coal ash often a pressure digestion with hydrofluoric acid–nitric acid[394,395] is used, preferentially with the addition of a strong oxidant such as perchloric acid or ammonium peroxodisulfate.[392,394] Less common is a digestion with perchloric acid (72%) alone, which requires a good deal of attention.[396] The combustion of coal in an oxygen bomb[397] or oxygen combustion[398] and fusion with lithium metaborate[399] have also been described. In a review article, Mills and Belcher[400] discussed in detail the problems of sample pretreatment and digestion for the analysis of coal and ash.

4.2.2.2 Partial Dissolution In general, total dissolution is a difficult task for many samples and, once achieved, leads to high salt concentrations. The latter may pose problems with nebulization in FAAS or create strong background attenuation in GFAAS. The high matrix concentrations require regular blank controls to be performed, and frequently the calibration solutions must be matched to the matrix contents. Owing to such problems, it is very common to avoid 'total dissolution' in environmental analysis. Instead, an extraction with a strong mineral acid such as boiling aqua regia under reflux is preferred.[401–406] This is justified on the assumption that heavy metals insoluble in aqua regia will probably not be relevant for environmental chemistry, at least not in the short term. With the exception of a few cases, a valid approach seems to be that the aqua regia-resistant compounds will not be taken up by plants and cannot be dissolved by water or bacteria.[405]

4.2.2.3 The Microwave Oven Option Microwave-assisted digestions (MWDs) have found rapid acceptance in the environmental analysis of solid samples.[407–409] The major advantages of MWDs are reported to be the substantially shorter digestion times,[410,411] the lower risks of contamination, the reduced reagent requirements[412] and the lower risk of losses.[413] Different acids and acid mixtures have been investigated, mostly using nitric acid or mixtures of hydrochloric acid and nitric acid[414–416] or aqua regia,[417–419] but also including hydrofluoric acid[415,420–423] and perchloric acid.[424] While the careful selection of the acid mixture and the operational parameters was a prerequisite for a successful digestion until recently,[425] the development of systems with automatic pressure and/or temperature control[426–428] have significantly reduced such requirements. Owing to the high effectiveness of MWDs it has also been possible to incorporate them on-line in a flow system with FAAS[429–431] or GFAAS[432] detection.

For the actual determination by AAS, we should always remember the general rule that the best results can be expected when the optimum concentration range is used. This means that FAAS is only suitable for the determination of higher analyte contents, and not for trace analysis. Owing to the frequently complex and refractory matrix, particularly when the digestion is complete, the hottest possible flame should be used in general and the measurement should be performed as high above the burner slot as possible. In other words, the measurement should be optimized for minimum interferences and not for maximum sensitivity. Aqua regia extracts can be analyzed by FAAS relatively free of interferences, since the element concentrations normally to be expected in soil, sediment and dust samples are so high for numerous analytes that the sensitivity of FAAS is fully adequate. Some selected publications of such applications are given in Table 9.

The alternative way of avoiding interferences is higher dilution followed by GFAAS determination. The concentrations of elements in soils, sediments and sludges which are considered to be tolerable depend strongly on regional regulations, but in general they are between 1 and 300 $mg\,kg^{-1}$ for agricultural soils and about a factor of 10 higher for sludges.[455] Owing to the dilution introduced by the acid extraction, such soil concentrations produce solution concentrations between 10 and 3000 $\mu g\,L^{-1}$. Even one tenth of the tolerable concentration is still above the detection limit of GFAAS for most elements. The partial dissolution and the high dilution factor ensure that the matrix concentrations in the sample solution are often

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Table 9 Selected publications on the determination of metals and metalloids in soils, sediments, sludges, dust and solid waste by FAAS

Analyte	Test sample	Remarks[a]	Refs.
Ag	Soils		433
Al, Ca, Fe, K, Mg, Na, Si	Coal, fly ash	$Li_2B_4O_7$ fusion	434
Ba, Be, Cr, Cu, Li, Mn, Ni, Pb, Sr, V, Zn	Coal, coke, fly ash	Australian Standard Method AS-1038	435
Be, Ca, Cd, Co, Cu, K, Li, Mg, Mn, Ni	Coal	Pressure digestion, HNO_3–HF–H_3BO_3	436
Ca	Soils	Addition of lanthanum	437
Cd, Co, Li, Pb	Coal, ash	Dry ashing/pressure digestion, HNO_3–HF–$HClO_4$	392
Cd, Cu, Fe, Mn, Pb, Zn	Sewage sludge	Microwave-assisted extraction	438
Cd, Cu, Pb	Soils, sediments	FI on-line sorbent extraction with DDTC/silica C-18	439
Cd, Cu, Pb, Zn	Sediments (lake)	Extraction overnight with HCl–HNO_3	440
Cd, Pb	Soils	Background interference by iron	23
Cd, Pb, Hg, As	Soils, waste	FI on-line dilution	441
Co	Sewage sludge	German standard method DIN 38 406-E24	442
Cr	Soils, sediments	Interferences, optimization of flame conditions	443–445
Cr	Sediments	Digestion problems	446
Cu	Sewage sludge	German standard method DIN 38 406-E7	447
Cu, Cr, Ni, Pb, Zn	Sewage sludge	Dry ashing at 450 °C	448
Cu, Mn, Pb	Sewage sludge	FI microwave-assisted on-line digestion	429, 449, 450
Cu, Zn	Soils	Microwave-assisted pressure digestion	411
K	Sewage sludge	German standard method DIN 38 406-E13	451
Mn	Soils, silicate materials	Digestion, HF–$HClO_4$	452
Na, K, Ca, Mg	Soils	FI on-line dilution	453
Ni	Sewage sludge	German standard method DIN 38 406-E11	454

[a] DDTC, diethyldithiocarbamate.

very low, so that the matrix remaining in solution might be considered relatively simple. Because of this, method development can often be focused towards fast analysis and high sample throughput.[466,467] Nevertheless, STPF conditions and ZBC frequently have to be used.[423,456–465] In any case, the absence of interferences should be checked, for example, by recovery studies using reference materials. In the meantime, reference materials have been produced for which, in addition to the certified total concentration, information is also provided on the fraction that can be leached by aqua regia, for example, soil samples NIST SRM-2709[468] and SRM-2711,[469] Bureau Communautaire de Référence (BCR) CRM 141R,[470] 142R[471] and 143R[472] and sewage sludge samples BCR CRM 144R,[473] 145R[474] and 146R.[475]

4.2.2.4 Direct Analysis of Solid Samples and Slurries

As has already been mentioned, the graphite furnace can be used as a thermochemical reactor, performing in situ digestion. Procedures have been developed that allow for the determination of the total concentration of an element, either by direct solids analysis[476,477] or by slurry sampling.[478,479] In addition to the benefit of not having to perform a digestion (especially when the digestion is really problematic, e.g. for coal), the major reasons for the application of these techniques are the much lower sample requirement and the increased sensitivity. The application of the STPF concept and ZBC are quasi prerequisites for accurate analyses,[476,480,481] because the matrix often has a substantial influence on the appearance time and the signal profile.[482] A number of authors have attempted to simplify the introduction of the solid dust samples by punching small disks from the filter and analyzing directly.[481,483] The precision of this procedure is nevertheless poorer than when the filter is homogenized in a mill.[484]

In contrast to direct solids analysis, the analysis of slurries is more flexible, and precision and trueness are better for the analysis of slurries in comparison with solids,[485,486] especially when they are homogenized by an ultrasonic probe directly mounted to the autosampler of the GFAAS instrument.[487–491] Further improvements, such as a reduction of the background attenuation, can be obtained by in situ ashing with air or oxygen[492,493] or the addition of hydrogen to the purge gas.[494] Aqueous calibration solutions can often be employed in combination with matrix modification. Special attention has to be paid to particle size and density effects, which might call for particle size reduction, which could then reduce the benefit of reduced sample preparation owing

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to the absence of a predigestion. For the same reason, the atomization of slurry samples by FAAS, which has been performed with sample introduction by FI,[450,495,496] has not attracted great attention owing to the restriction to very fine particles or analytes that can be easily extracted into the aqueous phase during the preparation of the suspension.

4.2.3 *Selective Extraction of Individual Constituents and Bonding Forms*

The determination of the total concentrations of analytes cannot give the right answer to many environmental questions, such as evaluation of the exposure of plants and animals to pollutants, evaluation of the fertility of agricultural soil or risk assessment for a waste dump site. Rather than the total concentrations of elements, the part which is bioavailable to plants and animals, the part which is leachable and mobile and thus can move away from the site and reach the aquifier and so on is of interest for such studies. For this type of element speciation, leaching procedures using a variety of differing reagents, either in a single step or in a sequential extraction scheme, have been used successfully for decades. The choice of extractant will depend not only on the element in question but also on the soil type, the crop or animal species, the weather and the technique for determination. The list of extractants which have been used is correspondingly long and sequential extraction schemes using a set of extractants are also numerous, varying between three and nine steps for differentiation. Descriptions and comparisons of such procedures can be found in review articles which have been published recently for soils and sediments by Rauret,[497] Jones[498] and Ure et al.[499] and for waste materials by Van der Sloot.[500] The method developed by Tessier et al.[501] has been applied to all the materials discussed here and is designed to differentiate between five fractions:

1. *Exchangeable fraction*. Trace metals adsorbed at the surface of particles, which can be desorbed by simply changing the ionic composition.
2. *Carbonate fraction*. Trace metals associated with carbonates, which are susceptible to pH changes.
3. *Fraction bound to Fe/Mn oxides*. Iron and manganese oxides are present as nodules, concretions, cement between particles or as a coating on particles. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions.
4. *Fraction bound to organic matter*. Trace metals bound to organic matter, such as organisms, detritus, coatings on mineral particles, etc. through complexation, peptization or bioaccumulation. These metals can be released by degradation of the organic matter under oxidizing conditions.
5. *Residual fraction*. The residual solid, having resisted the removal of the previous fractions, contains trace metals in the crystal lattice structure. It is believed that normal environmental conditions do not release these metals.

In sequential extraction, the bioavailability of metals is meant to decrease with each step of the scheme, but it is generally recognized that most extraction schemes are less than perfect. Few extractants can be relied on to release elements solely from a particular phase[502–504] and redistribution between phases can occur during the sequential procedure.[505,506] Also, the results will depend on the thermal pretreatment of samples.[507] Also, such operational defined methods do not help any fundamental understanding of the chemistry involved but offer only empirical guidance.[508]

Despite these limitations, they are often specific enough to provide the information necessary for making diagnostic or managerial decisions. However, the different extractants and the numerous extraction schemes used significantly hinder the comparability of results between different studies. In order to overcome such problems, harmonized procedures have been developed, such as those under the auspices of the BCR,[509–511] for the single extraction with ethylenediaminetetraacetic acid (EDTA) or acetic acid and a sequential extraction scheme using three steps, which is given in Table 10. The use of microwave heating for speeding up the extraction procedure[512] can also lead to improved reproducibility. In addition, reference materials are now available for which not only the total element content but also extractable portions are certified.[513–516]

For the determination of the element by AAS, it is of no great consequence whether the sample material is a soil, a sediment, a sludge or a waste material. Since

Table 10 BCR sequential extraction scheme

Extraction	Extractant	(Nominal) phase extracted
Step 1	0.11 mol L^{-1} acetic acid	Exchangeable
Step 2	0.1 mol L^{-1} $NH_2OH{\cdot}HCl$, pH 2	Reducible, Fe/Mn oxide
Step 3	8.8 mol L^{-1} H_2O_2, then 1 mol L^{-1} CH_3COONH_4, pH 2	Oxidizable – organic and sulfide

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only relatively small element concentrations are extracted during the leaching, especially with weak extractants, FAAS is only sufficiently sensitive for a few elements, such as Al, Ca, Co, Cu, Fe, K, Li, Mg, Mn, Na, Sr, Zn.[517–522] This situation might be different for airborne particulates, for which the extractable concentration of some more metals (e.g. Cd, Cr, Ni, Pb) might be sufficient for their determination by FAAS.[365,523–525] However, in many cases for elements such as Ag, As, Cd, Cr, Mo, Ni, Pb, Se, Sb, Sn, Te, Tl, V, it is usually necessary to apply GFAAS[519,520,526–531] or other more sensitive techniques. Owing to the considerably lower total salt concentration, the matrix influences are far less pronounced than with a complete digestion, at least for those extractants that do not add significantly to the total salt concentration.

4.2.4 Speciation Analysis in Soils, Sediments, Sludges, Dust and Other Solid Samples

The determination of redox species and organometallic compounds in solid materials, such as soils, sediments and sludges, is preceded by an extraction procedure, and in this respect is similar to the determination of bioavailable species. The determination of the individual species from the extract is hardly different from the analysis of water. In rare cases where FAAS is sensitive enough for speciation analysis, the separation procedure for the species is coupled with preconcentration, for example, for the determination of Cr(VI).[532–534] The use of GFAAS for speciation analysis has been reviewed by Das and Chakraborty.[303] As has already been pointed out, GFAAS is not a very suitable technique to be coupled with chromatographic separation since all attempts to run GFAAS in a continuous mode were unsuccessful,[535] and coupling between these two techniques[536] has to be done via either a fraction collector or a flow-through subsampling interface.[537] These interfaces require careful synchronization[538] and optimization of the flow rates and sampling intervals,[539] which significantly reduces its applicability. Other techniques, which can be operated continuously, such as vapor generation techniques (CVAAS, HGAAS) or plasma techniques, such as ICPMS, are much better suited.

For those cases where GFAAS has been used for speciation analysis of soils, sediments, sludges and dust samples, mostly nonchromatographic separation procedures have been used. These include the extraction of Cr(VI) in a weakly alkaline medium,[67,540–542] the extraction of tributyltin oxide with *n*-hexane–dichloromethane[543,544] or isooctane[545] and its back extraction with nitric acid.[543,544] The selective extraction of chelates has been applied for the species determination of As(III),[546] Sb(III)[547] and Cr(VI).[548]

The determination of Cr(VI) in welding fumes is one of the most important industrial hygiene examinations owing to the toxicity of this species.[362,549] The influence of the collecting procedure, the welding fumes themselves, the storage period and the analytical procedure have been investigated in detail.[550] While the Cr(VI) content of fiberglass filters did not appear to change over several weeks of storage, Rohling and Neidhart[551] found that during collection Cr(VI) is reduced by SO_2, which can lead to severe losses of Cr(VI), depending on the length of the collection period. Girard and Hubert[552] showed that the Cr(VI) can be quantitatively recovered from the filter medium by extraction with acetic acid–sodium acetate. Brescianini et al.[553] eliminated the interferences caused by large quantities of calcium, iron and sodium during the determination of chromium by GFAAS by separating the analyte on an ion exchanger.

Moreover, ion exchangers, chelating resins and other solid sorbents have been utilized in batch or column procedures to distinguish between different arsenic species such as As(III) and As(V),[554] Cr(III) and Cr(VI)[555] and organotin compounds.[556]

4.3 Biological Materials

Biological materials are investigated not only for environmental analysis, but also for reasons of biological, biochemical or biomedical analysis, toxicological, pharmaceutical, nutritional and clinical analysis, food analysis or biogeochemical analysis; the information sources available about sampling and analysis of such materials are correspondingly spread over a wide range of disciplines. For the purpose of environmental analysis, it is seldom the biological material itself which is the primary target of interest (as in toxicological or biomedical analysis), but its function as an indicator for the environmental compartment from which it was taken. In this function, biological materials are collected from different compartments of the environment. For the same reasons, other inorganic materials are collected, to gain information about the conditions of that particular compartment with respect to being part of a hostile biosphere or to learn about the exchange and fluxes of materials (pollutants) between different compartments or different parts of a compartment. With respect to biological materials, the primary concern is the entrance of pollutants into the food chain and the concentration of such pollutants by bioaccumulation. For plants and vegetable products, sources of pollutants are the soil on which they are grown, fertilizers, crop protection agents, insecticides and pesticides used and atmospheric precipitation, especially due to the proximity of roads or industrial installations. Animals (and humans) are influenced by the environmental conditions either directly (e.g. aquatic environment) or indirectly by

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taking up pollutants (e.g. with their nutrition or drinking water) from that environment.

Those biological objects and systems which respond very sensitively to anthropogenic influences on the environment can be used as bioindicators for the detection of the presence of pollutants and biomonitoring can be used as a more quantitative method for the determination of the pollutants present. For example, low-level plants such as lichens and mosses accumulate large amounts of heavy metals, because their unprotected surfaces provide ion-exchange facilities which allow the effective adsorption of metals. The complexes then formed between the metals and the negatively charged organic groups are fairly stable. The accumulation of heavy metals on such plants is the basis for their use as bioindicators of atmospheric pollution. The problem with biological materials as samples for environmental analysis is biological variation, which hampers the assessment of baseline concentrations and the interpretation of analytical results.

The analysis of biological materials by AAS has a long history. While the reasons for analyzing biological materials are numerous, the different objectives are secondary for the selection of methods and techniques applied to the determination of elements in these materials by AAS. Review articles have been published by Slavin on the use of FAAS[557] and GFAAS[558] for the analysis of biological materials in general, by Hanlon[559] on plant analysis, by Rains[560] on the subject of foodstuffs analysis, by Pritchard and Lee[561] on agricultural samples and by Hoenig and Guns[48] on environmental and biological samples. Apart from review articles on single elements already mentioned (see section 4), numerous other minerals and trace elements are treated in the monographs *Quantitative Trace Analysis of Biological Materials* edited by McKenzie and Smythe,[562] *Trace Minerals in Foods* edited by Smith,[563] *Trace Element Analysis of Biological Specimens* edited by Herber[564] and *AAS in Occupational and Environmental Health Practice* written by Tsalev.[565] Markert gives an overview of plant analysis[566] and the use of bioindicators[567] and Kiceniuk and Ray treat the analysis of contaminants in edible aquatic resources.[568] Annual reviews on the determination of elements in biological materials appear in the *Journal of Analytical Atomic Spectrometry*.[569]

4.3.1 Sampling and Sample Pretreatment of Biological Materials

Again, an analyst should not waste time in investigating a laboratory sample whose history is not known in complete detail and is not documented. Sampling is of decisive significance for the accuracy of the analyses of biological materials. Some problems are common with the sampling of other sample materials, for example, selection of appropriate locations, techniques and designs, errors due to the limited numbers of samples and contamination due to the tools used. However, the main problems are the high biological variability and biotic and abiotic influences on the availability of the sample material and on the reproducibility of its analysis. For example, such influences are as follows:

1. the exposure of the biological species and its behavior with respect to accumulation;
2. the time of sampling with respect to the season and to the phenological state of development of the biological species;
3. fluctuations or trends in the abundance or composition depending on age, gender or physiological state or morphological and genetic variability;
4. fluctuations between sampling locations with respect to edaphic or microclimate factors and exposure to emission;
5. errors due to a selective sampling procedure, favoring individuals or groups, having special characteristics.

For the sampling of plant materials, this means that one has to decide which parts of the plant to sample (roots, leaves, needles, etc.), their location with respect to the soil (distance from the ground) and their exposure (free-standing plant, plant from a forest ecosystem).[570] Furthermore, the time of exposure depends on the age of that particular sample, which must be known (e.g. to create comparable results when sampling tree needles of different ages).[571] Depending on the questions to be answered by the investigation, one has to decide whether external contamination of the plant material by soil and precipitation has to be removed before analysis or not.[572,573] If it has to be removed, the cleaning procedure must be designed to remove only the external contamination, and to avoid leaching the plant components.[574] If external contaminants should not be removed, the sampling procedure has to assure the retention of those components.

When sampling biological materials of animal origin, a practical method of capture, not prone to contamination, and in accordance with ethical rules, is a prerequisite for using that species for environmental analysis. Depending on the type of sample (body fluid, soft tissue, hard tissue) and whether it can be collected without killing the animal (e.g. bird feathers, egg shells, body fluids), one has to account for changes in element distributions due to stress or postmortem changes (autolysis, etc.).[575] Contamination risks are especially high when internal organs have to be taken by dissection or when blood samples have to be analyzed.

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These and other sampling and presampling factors cannot be discussed in detail here. Comprehensive information on this subject has been published by Jones and Case,[576] Keith[577] and Markert.[578] In the laboratory, the sample must be homogenized, conserved and typically stored.[579] Naturally, all precautions to prevent contamination from tools, containers, the laboratory atmosphere and losses due to volatilization or adsorption must be scrupulously observed. For the homogenization of plant and animal tissue samples, cutting and mixing tools that have stainless-steel parts are often used. Contamination can be expected from such tools, especially for Fe, Cr and Ni.[580]

4.3.2 Digestion Procedures

Plants and biological tissues are usually decomposed for the determination of total element concentrations by AAS techniques, although they can be determined also by direct techniques using solid-sample introduction or slurry sampling. The main reason for using routine decomposition techniques is concerns about the homogeneity of sample masses as small as a few micrograms. In addition, the samples often have to be prepared as powders and such pretreatment may take as long as a fast decomposition technique.

For the decomposition of various biological materials, a wide selection of methods have been developed, including dry ashing, wet digestion, pressure digestion and MWD. The selection of an appropriate digestion procedure depends on the analyte, the sample matrix and the method of determination. In general, atomic spectrometric techniques do have a much higher tolerance against residual carbon after the digestion than other instrumental techniques such as electrochemical methods, since residual matrix components can be destroyed during atomization. The amount of residual carbon which can be tolerated by different AAS techniques decreases in the order FAAS > GFAAS $\gg$ HGAAS/CVAAS. Digestion solutions, which are clear and free from particles in general, fulfill the requirements for FAAS.

In the 1960s and 1970s, dry ashing was widely used, since relatively large sample aliquots can be ashed (up to 20 g) and taken up in a minimum volume of acids. In this way, many trace elements could be determined by FAAS, which was the only technique available at that time. Dry ashing can be performed directly or with the addition of ashing aids such as magnesium nitrate or small amounts of nitric acid and sulfuric acid, usually at 450–550 °C. Accurate temperature control, often not available with simple muffle furnaces, is a prerequisite for complete destruction of the organic material without loss of analytes.[581] The ash is then leached with dilute hydrochloric acid or nitric acid. Care is needed to make sure that losses due to siliceous ash residue or by adsorption on the wall of the crucible are avoided. The addition of hydrofluoric acid might be helpful to avoid such residues[582] while the choice of an adequate crucible material is of prime importance to avoid adsorption losses. Since the most important retention losses have been reported for silica and porcelain vessels, platinum vessels are generally recommended. Losses have been observed also for volatile elements, such as Hg, As, Se and Cd, but often can be circumvented by the addition of ashing aids. High blank values, which are difficult to control, at least when standard muffle furnaces are used instead of special furnaces (e.g. equipped with quartz walls), often limit the applicability for samples with low trace metal contents. Nowadays dry ashing is only applied sporadically, since other digestion procedures are faster and better.

Oxidative wet digestions are used far more frequently than dry ashing or fusions for subsequent analysis by FAAS or GFAAS. These can be performed in open vessels, with reflux condensation if required, or in closed containers under pressure (autoclaves). Open vessel digestions have a number of disadvantages, which should exclude them from the list of recommended procedures, especially (a) low sample throughput and (b) incomplete digestion due to low reaction temperatures, (c) high consumption of reagents creating high costs, large amounts of waste and environmental pollution by fumes, (d) high risk of contamination due to the amount of reagents and the exposure to the laboratory environment and (e) the possibility of analyte losses due to volatilization. In order to reach the necessary oxidation power with open-vessel digestions, strongly oxidizing, high-boiling acids such as perchloric acid, sulfuric acid and phosphoric acid are often used as digestants. These acids are more difficult to clean up than lower boiling acids and are thus more strongly contaminated. Further, the use of such acids cannot be recommended in combination with determination by GFAAS for many reasons: these acids (a) penetrate the graphite lattice and often remain in the tube after pyrolysis, leading to (b) reduction of the lifetime of the graphite tube and to (c) background interferences by molecular absorption. In the case of perchloric acid, volatile chlorides can be formed, leading to analyte loss during pyrolysis and/or atomization especially for main group III elements (aluminum, gallium, thallium).[583–585] Even in FAAS these acids create some problems, either by reducing the uptake rate of the nebulizer because of their high viscosity or by other interference effects.[586] By using low-boiling mineral acids, complete destruction of the organic material is not often possible by open digestion. However, it has frequently been shown that many elements can be extracted from biological materials, even with diluted mineral acid, without complete destruction of the organic material.[587] In any case, such methods

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cannot be generalized and have to be verified for the matrix being investigated. In general, animal materials cause fewer problems than plant materials, and elements such as Ca, Cd, Cu, K, Mg, Mn, Na, Pb and Zn can be more easily extracted than Al, Cr, Fe, P and Si.

While the application of high-boiling acids for AAS is problematic, it is the oxidation power which is needed to decompose totally the complex organic matrix of some of the environmental samples. Of the mineral acids that are compatible with AAS (e.g. HNO_3, H_2O_2, HCl and HF), only the first two develop sufficient oxidation power but, because of their low boiling points, the oxidation power is not enough for complex matrix-containing substances, which are difficult to digest, such as fat. In order to raise the boiling point of these acids and therefore their oxidation power, the wet digestion procedure can be performed under pressure. There are many advantages of a pressure dissolution compared with open acid dissolution.[588] Since the pressurized decomposition vessel represents a closed system, the loss of volatile elements is avoided, in addition to the risk of contamination from the laboratory environment. Depending on the pressure which the system can withstand, either temperatures in the region of 200 °C (medium pressure, ≈80 bar) or >300 °C (high pressure, ≈130 bar) are possible. Under such harsh conditions, the total decomposition of complex matrices is possible, and organic materials can be decomposed with very little residual carbon remaining in the digest (<1%). The disadvantage of pressure digestion in autoclaves ('bombs') is the small amount of organic matter which can be treated. The special problem with biological materials is that large amounts of gaseous products (CO_2) are formed during the digestion. As a result, the maximum sample mass that can be loaded into such pressure vessels is limited to about 200–500 mg for a vessel volume of about 100 mL for medium-pressure systems and about 1 g for high-pressure systems. Using a medium-pressure system, operated at 170–180 °C, the optimum digestion time for biological materials with nitric acid is about 3 h.[589] For a high-pressure digestion system, the effective digestion time can often be reduced to about 1.5 h. About 2 mL of nitric acid are generally sufficient for a pure carbon content of 100 mg, independently of the type of biological sample. For determining the maximum sample mass, one has to consider that the carbon content of dried biological material varies between 35 and 50% for plant materials and between about 45 and 55% for animal materials with the exception of oils and fats that have carbon contents between 74 and 78%. Nitric acid alone is sufficient for complete digestion under high pressure for most elements and biological sample types.[589] Some samples (e.g. some plant samples, mussels) contain high amounts of silicate, requiring the addition of hydrofluoric acid. For more details, introductory papers and review articles on pressure digestion should be consulted.[588,590]

Since the end of the 1980s, these various digestion techniques have been increasingly replaced by microwave-assisted acid digestions which are frequently performed in closed containers and under low (up to 40 bar) to medium pressure (up to 80 bar).[408,591] The major advantages compared with conventional digestion techniques include the reduced time and reagent requirements, the lower blank values, the reduced risk of analyte losses, the possibility of automation and the ability to digest a number of samples at the same time. When comparing the time required for a conventional pressure digestion (CPD) and for a MWD, one has to consider that the digestion time is drastically reduced in a microwave system. This is shown in Table 11.

The most important difference is the fast heating for MWD. In addition to the time advantage for MWD, there is also an advantage with respect to the wear of materials. The digestion vessels in CPD are under heat and pressure stress for a much longer time than the vessels in MWD systems. Therefore, the vessels in CPD systems wear out earlier, and contamination due to sorption/desorption processes are more pronounced than in MWD systems.

The time gain with MWD is further reduced when the digestion cannot be performed in a single step. This is the case when either the gases produced during the digestion must be vented or reagents have to be added after the first step in order to complete the digestion. Especially under low-pressure conditions, the oxidation power of nitric acid is not sufficient for all types of material. Materials rich in fat are especially difficult to decompose[592] and often require the addition of additional oxidants such as hydrogen peroxide.[593,594] Stronger oxidants such as sulfuric acid and perchloric acid are (besides their incompatibility with GFAAS) also not very useful in MWD. Typically, they develop their oxidizing power at such high temperatures (above 250 °C) that the polymeric material often used for the vessels breaks down. When a single-step digestion is the target for method development, the method requires careful optimization

Table 11 Comparison of the time involved in MWD and CPD (in minutes)

Preparation step	MWD	CPD
Preparation of the digestion (weighing of the sample material, adding the acids, capping the vessels)	10	10
Digestion period (heating)	10–20	180–210
Cooling period	5–10	20
Preparation of the determination	5–10	5–10
Cleaning of vessels	5–15	10–20
Total time	35–65	225–270

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with respect to the matrix. Chemometric techniques have been applied for this purpose.[595] State-of-the-art MWD systems having temperature and/or pressure sensors for each vessel require much less method development and optimization, since the digestion can be automatically operated under optimum conditions.[426,427] Some systems use quartz vessels that can be used at temperatures above 200 °C and allow pressures up to 80 bar.

In addition to these widely used digestion procedures a number of techniques have been proposed that have not come into general use, but can occasionally be of interest as comparative techniques or for a special combination of analytes and matrices. A comparison of such techniques with respect to their characteristics is given in Table 12. Since FAAS and GFAAS methods do not require the highest digestion quality with respect to completeness of the destruction of organic materials, even the incorporation of MWDs into flow systems has been successfully performed for some biological materials. A review of such methods was presented by Burguera and Burguera.[596] Solubilization of materials with tetramethylammonium hydroxide (TMAH) has been used successfully, sometimes under microwave assistance,[597] especially in combination with speciation. Other less frequently used techniques are based on combustion in a stream of oxygen in a closed system[592,598] or on intense infrared (IR) irradiation. Details of these and other techniques can be found in treatises and review papers on sample digestion.[599,600]

4.3.3 Methods for Flame Atomic Absorption Spectrometry

In general, digestion of solid material is always combined with dilution. Under normal conditions, when using acid digestion, 200–500 mg of biological material are usually decomposed in about 5 mL of acid, the digest being then diluted to 10–20 mL. Hence the dilution factor is about 40 for such decomposition, if not higher. Following such dilution and remembering that a technique should only be applied in its optimum working range, FAAS is suitable without reservation only for the direct determination of major components such as potassium, sodium, calcium and magnesium and minor components such as copper, iron and zinc. In some cases manganese can also be determined by FAAS in biological materials. Under given conditions it is also possible to determine aluminum, chromium, nickel and silicon. The use of the nitrous oxide–acetylene flame is a prerequisite for most of these elements to obtain correct results. Table 13 presents a number of recent applications.

For other trace elements in biological materials, the sensitivity of FAAS is generally not sufficient. For such cases, preconcentration has often been used in combination with FAAS, especially before 1980. Since today more sensitive direct methods, using for example GFAAS, are available, such preconcentration methods cannot be recommended any longer.

These classical preconcentration techniques take on a fully new dimension when they are performed automatically and on-line in a closed FI system. The most often used methods of preconcentration with such FI/FAAS

Table 12 Digestion methods for biological materials[a]

Method	Contamination	Completeness	Throughput	Costs	Comment
Dry ashing (450–550 °C)	+++	++/+++	++	+	Usually less applicable for low contents and high precision
Combustion	++/+	+++	++	++	Low sample throughput
Open acid digestion, automated system	++/+ ++	++ ++	+++ ++++	++ ++	Medium to high sample throughput
Open microwave-assisted	++	++	++++	++	High sample throughput
Pressure digestion PTFE < 200 °C	++/+	++	++	++	Digestion quality mostly sufficient (at least for AAS)
Microwave-assisted pressure digestion, <200 °C	++/+	++/+	+++/++++	++	Digestion quality not always sufficient
Microwave-assisted pressure digestion, <250 °C, quartz vessel	+	++/+++	++	++	Digestion quality mostly sufficient (at least for AAS)
High-pressure digestion, >300 °C	+	++++	++	++++	Optimum digestion quality but costly
UV-photolysis	+	++	++	++	Restricted applicability, but possibility of on-line digestion in FI systems

[a] +, Small; ++, medium; +++, high; ++++, very high.

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Table 13 Selected publications on the analysis of biological materials by FAAS

Analyte	Sample material	Remarks	Ref.
Ca, Cr, Cu, Fe, Mg, Mn, Zn	Biological reference materials	Comparison with ICPOES	601
Ca, Fe, K, Mg, Zn	Biological reference materials	Comparison of CPD and MWD	602
Ca, Fe, K, Mg, Mn, Na, Zn	Biological reference materials	Solubilization with TMAH	597
Ca, K, Mg, Mn	Biological reference materials	MWD	603
Ca, Mg	Various	Interlaboratory trial, dry ashing	604
Ca, Mg	Foliage	Dry ashing	605
Ca, Mg, K	Pine needles	MWD	606
Ca, Mg, K, Na, Cu, Fe, Mn, Zn	Tree rings	Open acid digestion	607
Ca, Na	Fruits, vegetables	La + K as buffer	608
Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	Medicinal plants	Comparison of digestion methods	609
Cd, Cr, Fe, Mn, Pb, Zn,	Moss and bark	Polluted bioindicators	610
Cd, Pb	Seaweed	Comparison of digestion methods	611
Fe	Potatoes	Speciation study	612
Rb	Biological materials	Overview of Rb in the food chain	613
Zn	Marine organisms	Reference materials	614

techniques for the analysis of biological materials are sorbent extraction on packed microcolumns,[615–618] precipitation/coprecipitation[619,620] and sorption in knotted reactors.[621,622] More important than high enrichment factors is the high rate of sample throughput that can be achieved with these on-line techniques, making them very suitable for FAAS. Enrichment factors of 16–40 with a sample throughput of 120–180 h^{-1}[622,623] appear to be much more sensible than enrichment factors of 90–180 at a sample throughput of only 13 h^{-1}.[624] In addition, if the enrichment time is too long, the susceptibility to interferences and the risk of errors increase, such as the breakthrough of the column.

4.3.4 Methods for Graphite Furnace Atomic Absorption Spectrometry

Digests of biological materials contain about 5–50 mg of the original matrix per milliliter of solution. Since about 50% of the biological matrix is hydrocarbons, which were oxidized and removed as gases during the digestion, the remaining matrix is of the order of 2–30 mg mL^{-1}. This salt content is much higher than for fresh water and the highest concentrations may reach those of seawater. This means that for those cases where the analyte concentration is low, as in seawater, the analysis of biological materials approaches the complexity of seawater analysis. For this reason, the direct analysis of biological materials has greatly benefited from the development of the STPF concept and the instrumentation associated with it. It is accepted nowadays that accurate results can be obtained for the direct analysis of many biological materials by strictly applying this concept and by excluding all forms of contamination. For example, As, Cd, Cu, Fe, Pb, Sb, Se and Zn have been determined by using platform atomization and applying Pd–Mg as modifier and B, Cr, Mn by using Mg as a modifier. The vast amount of literature in this area has been reviewed in the form of a monograph by Tsalev[565] covering the publications up to 1993 and by Welz and Sperling[2] covering publications until 1997.

The number of publications on extraction techniques has decreased markedly owing to the clear advantage of the direct determination of trace elements by GFAAS with respect to simplicity, sample throughput and accuracy. The application of such techniques can be restricted to those cases where the concentration of the element is not sufficiently high for a direct determination. Preconcentration is often required for noble metals such as gold,[625,626] palladium and platinum,[598,627–630] but also for a number of other trace elements such as beryllium,[631] bismuth,[632] cobalt[633,634] and nickel[635] under certain conditions.

Although biological materials are relatively easily dissolved or digested, direct solids analysis has frequently been described (about150 publications during 1975–99). Problems with atomization interferences and background correction, reported in early publications since 1975, have been largely overcome by ZBC and the STPF concept. Introduction of air or oxygen during pyrolysis allows for in situ ashing and helps to avoid carbon build-up in the graphite furnace. Intercomparison studies have shown that direct solid analysis of biological materials is often able to produce accurate results, even when using only samples masses in the range 1–5 mg. When samples are properly homogenized, relative standard deviations in the range <10–20% are typical. When 5–10 subsamples are analyzed by direct solid sampling, confidence intervals for the mean result are in general within about ±10% as precise as the determination of a digest with 2–3 subsamples.

Of special interest is solid sampling for the distribution analysis of biological structures (e.g. birds feathers, human hair, special regions in organs), very small samples (e.g. insects), or for the investigation of the homogeneity

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of samples. A disadvantage of solid sampling GFAAS is that not all modern furnaces allow for the introduction of solid samples and often special equipment is needed.

This and other disadvantages can be overcome by the use of suspensions of powdered samples (slurry) in a solvent such as water or dilute acid. Using an automated slurry sampler incorporating an ultrasonic probe for homogenization just prior to dispensing the sample volume into the furnace, fully automated analysis is possible with characteristics very similar to those in solution analysis. Homogenization by ultrasonic agitation is very effective, so that practically all types of biological samples can be suspended in dilute nitric acid with the addition of Triton X-100 as a wetting agent. By using a slightly wider sampler capillary (0.8 mm i.d. instead of the standard 0.4 mm i.d.), particles $< 600\,\mu m$ can be dispensed without major problems. Table 14 gives an overview of elements determined in biological materials by either solid- or slurry-sampling GFAAS.

A complete overview of these techniques can be found in a monograph edited by Kurfürst.[478]

4.3.5 Methods of Speciation Analysis for Biological Materials

Being part of the biosphere, living organisms take part in the environmental cycling of elements. Owing to the metabolism of living organisms, trace elements can be present in biological materials in a large variety of chemical forms. To identify the physiologically active forms, to store and transport of species and to find sensitive indices of the status of trace elements are the main purposes of most environmental investigations into speciation in biological systems. In general, in the investigation of toxic effects, the speciation of small molecules is of concern (e.g. methylmercury), whereas in the investigation of biological functions the determination of large molecules has priority (e.g. vitamin B_{12}).

As in other areas of speciation analysis, the methods of sample collection, pretreatment and storage of biological materials for speciation studies are critical. Not only must a representative sample be collected without contamination, but also the distribution and integrity of the chemical species has to be maintained. Changes in parameters such as temperature, ionic strength, pH, pE, oxygen level, irradiation with UV light, to which the sample is exposed during and after sampling, can influence the speciation of elements. In general, it is essential to choose those analytical conditions which do not differ markedly from those found in the original system, in order to minimize such influences.

Most of the speciation studies on biological materials have been carried out with wet tissue, which is either extracted as fresh material or has previously been dissected and rapidly frozen. Extraction can be performed by blending the sample as a paste or slurry with the selected solvent or solvent mixtures[637] using an Ultra Turrax homogenizer or ultrasonication. Other techniques, such as supercritical fluid extraction (SFE) or microwave-assisted leaching have been applied for this purpose. Using selective extraction procedures for separation, 'first-order speciation' is sometimes possible, especially when the number of species present is limited or when a group parameter is sufficient for the characterization. The most often performed speciation analysis of biological materials is the determination of methylmercury. However, this determination is only rarely done by using GFAAS. The most frequently described technique is extraction of methylmercury chloride or methylmercury bromide from acidic solution with toluene (e.g. fish tissue). The extract can then be analyzed directly by GFAAS after addition of dithizone or thiosulfate acting as a modifier.[638]

The determination of inorganic and organic arsenic compounds is also of great interest. A review of methods for arsenic speciation in environmental and biological samples has been published by IUPAC.[59] Again, since the GFAAS technique cannot be easily coupled with separation techniques such as HPLC, arsenic speciation analysis by using GFAAS has not found wide application. By using extraction with KI–toluene, the more toxic species As(III), As(V), monomethylarsenic

Table 14 Biological matrices and elements investigated by solid-sampling and slurry-sampling GFAAS [information from the literature[2,478,636]]

Matrix	Elements determined by solid-sampling GFAAS	Elements determined by slurry-sampling GFAAS
Animal tissues	Cd, Cs, Hg, Ni, Pb	B, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Si, Sn
Biological reference materials	Ag, As, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Mo, Rb, Se, Tl, Zn	Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Se, Sn, Zn
Human materials (hair, nails)	Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, La, Mg, Mn, Ni, Pb, Pt, Se, Zn	Al, Ag, B, Cd, Co, Cr, Mn, Ni, Pb
Plant tissues	Cd, Co, Cu, Fe, Mg, Ni, Pb, Tl	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl, Zn
Marine and aquatic samples	As, Cr, Fe, Mn	As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se

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acid and dimethylarsenic acid can be separated from the nontoxic arsenobetaine. Determining arsenic in the extract by GFAAS then gives the total toxic arsenic concentration.[639,640]

Organotin compounds are of interest because of their toxicity. This applies in particular to tributyltin oxide, which is used as an antifouling paint. The separation of this compound from mussels and other marine organisms starts with the extraction from the homogenized tissue mixed with hydrochloric acid by using an organic solvent such as *n*-hexane. Mono- and dibutyltin compounds can be removed with dilute sodium hydroxide solution, and the tributyltin oxide is back extracted in nitric acid. The tin concentration in the extract is determined by GFAAS.[543,544,641,642] Another tin compound of interest is the pesticide tricyclohexyltin hydroxide (Cyhexatin). Residues in apples can be determined directly by GFAAS after extraction with chloroform.[643]

Bioavailable chromium has been determined in cereal products, vegetables and oil seeds by extraction with ethanol and determination by GFAAS after a digestion of the extract.[644] When the extraction of the material alone is not selective for the species, a separation technique such as liquid chromatography (LC) has to follow. Of the LC techniques available, fractionation according to size [SEC or fast protein liquid chromatography (FPLC)] has been most frequently used.

For selenium speciation, the determination of the organic compounds and the distinction between inorganic selenite and selenate are of interest. Ion chromatography has been applied to separate selenite and selenate, and FAAS and GFAAS were used for on-line detection, depending on the required sensitivity for the analysis of feedstuffs and selenium additives in animal feeds.[645] A greater number of inorganic and organic selenium species can be separated by coupling FPLC with GFAAS via an ultralow volume fraction collector. By using this approach for the determination of selenium species in plant tissues, a sensitivity was obtained that is comparable to that obtained by LC/ICPMS.[646,647] Again, extraction of such Se species from the biological tissues is a critical step.[648]

Chromium speciation, which is of great importance because of the high toxicity of Cr(VI), has not been widely applied to biological materials. Metal-free HPLC equipment and fast procedures are a prerequirement for obtaining undisturbed speciation; FPLC was successfully used to separate different Cr complexes extracted from cabbage xylem.[649] Positively charged chromium(III) species and kinetically labile complexes are not retained on the column, while the relatively stable chromium(III)–EDTA and –oxalate complexes and chromium(V) are retained and separated. Determination of chromium in the individual fractions was performed off-line by GFAAS.

For the separation of various lead species in biological materials, fractionated wash procedures using organic solvents and acids of varying strengths have been applied.[650,651] The investigation of roots, foliage and other plant components, and the dissection of leaves into subcellular fractions with the corresponding compartmentalization of the lead content, have been described.[651] In many cases GFAAS is used as the determination technique for the sum determination of volatile lead, that is, tetraalkyllead compounds in marine organisms.[650]

Metallothioneins and other high molecular weight species are often determined by LC separation with various AAS detectors. A review of coupled techniques used for such analysis has been presented by Lobinski et al.[652] The major interest is in cadmium,[653–661] but other elements such as copper,[655,658,661–663] zinc,[658,661] lead,[655] magnesium,[663] nickel, silver[661] and thallium[660] are also determined. It is of particular interest to determine to which protein the metal is bound; gel filtration and gel permeation chromatography are especially suitable for separating various metal-binding proteins. The determination of the metal concentrations in the eluate is carried out either by on-line coupling with FAAS or by GFAAS. Likewise for this application, the difficulty of coupling HPLC with AAS detectors is apparent. On-line coupling with FAAS is possible when the nebulizer aspiration rate is reduced to about $2\,mL\,min^{-1}$, but the sensitivity is relatively poor.[654,658,664] Sensitivity can be improved by using high-efficiency nebulizers for interfacing, such as the thermospray nebulizer.[653,655,663] GFAAS offers the required sensitivity but it can only be applied off-line[656,657] by using a fraction collector or quasi-on-line by a flow-through interface,[537] both with limitations with respect to resolution and versatility as already mentioned (see section 4.1.5).

Other techniques which have been used in combination with AAS detection are ultrafiltration,[665,666] ultracentrifugation[667,668] and supercritical fluid chromatography (SFC).[659]

ABBREVIATIONS AND ACRONYMS

AA	Atomic Absorption
AAS	Atomic Absorption Spectrometry
APDC	Ammonium Pyrrolidine Dithiocarbamate
ASV	Anodic Stripping Voltammetry
BCR	Bureau Communautaire de Référence
BOC	Baseline Offset Correction
CPD	Conventional Pressure Digestion
CPG	Controlled-pore Glass
CRM	Certified Reference Material
CVAAS	Cold Vapor Atomic Absorption Spectrometry

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DDDC	Diethylammonium Diethyl-dithiocarbamate
DDTC	Diethyldithiocarbamate
DQO	Data Quality Objectives
EDL	Electrodeless Discharge Lamp
EDTA	Ethylenediaminetetraacetic acid
EEC	European Economic Community
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
FI	Flow Injection
FPLC	Fast Protein Liquid Chromatography
GAP	Good Analytical Practice
GC	Gas Chromatography
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GLP	Good Laboratory Practice
HCL	Hollow-cathode Lamp
HGAAS	Hydride Generation Atomic Absorption Spectrometry
HPLC	High-performance Liquid Chromatography
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ICPOES	Inductively Coupled Plasma Optical Emission Spectrometry
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
LC	Liquid Chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
MWD	Microwave-assisted Digestion
OES	Optical Emission Spectrometry
PFA	Perfluoroalkoxy
PIXE	Particle-induced X-ray Emission
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QC	Quality Control
QTA	Quartz Tube Atomizer
SFC	Supercritical Fluid Chromatography
SFE	Supercritical Fluid Extraction
S/N	Signal-to-noise Ratio
STPF	Stabilized Temperature Platform Furnace
THGA	Transversely Heated Graphite Atomizer
TMAH	Tetramethylammonium Hydroxide
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
ZBC	Zeeman Effect Background Correction

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