Analytical Techniques for Trace Element Determination

DOI: 10.1515/psr-2017-8002

1 Introduction

A lot of elements occur in different matrices at low levels of content, and a lot of these elements were not detectable by analytical methods for a long time. The knowledge about their presence appeared with the development of analytical technology and caused the origin of the term “trace elements.” Trace element defined by IUPAC [1] is any element having an average concentration of less than about 100 parts per million atoms or less than 100 mg/kg. In the second half of the 20th century, together with rapid increase of detection capabilities of analytical techniques, a new term of ultratrace elements appeared. Even though the term exists and is commonly used, there is no rigid definition. Ultratrace concerns elements at mass fraction below 1 ppm.

The knowledge of trace and ultratrace elements is very important in various fields of science, industry, and technology. Ultralow concentrations of elements might be as well essential as hazardous doses for organisms; some traces can dramatically change properties of designed devices. Therefore, the need for accurate measurements at low amount of contents is required and very important.

The common use of extremely sensitive instrumentation needs the adequate control of contamination and verification of the accuracy of determination. The gain of analytical sensitivity multiplied contamination as well as other problems. Therefore, correct precautions should be taken to determine trace elements in the parts per billion concentration range and below. Errors during trace and ultratrace elemental analysis can be caused by improper sampling, storage, sample preparation, and, finally, by analysis itself. Therefore, an accuracy of an analytical determination should be always established.

Collecting a representative sample without contaminating is a key to the meaningful analysis and Thiers’ words from 1957 “unless the complete history of any given sample is known with certainty, the analyst is well advised not to spend his time analyzing it” [2] is always up to date.

Nowadays, there are a large number of available analytical techniques allowing for trace and ultratrace analysis of elemental composition. For the trace elements that are present in parts per million concentration range, the most widely used technique is probably atomic absorption spectrometry with flame atomization. For ultratrace elements present in concentration of parts per billion and below, the number of suitable techniques drops due to the required analytical sensitivity. The determination of trace elements is commonly held with potentiometry, voltammetry, atomic spectrometry, X-ray, and nuclear methods. Electrochemical methods can measure either free ions in solution (potentiometry) or free ions together with ions bound in labile complexes (voltammetry), and they can also provide analysis of the oxidation state of some of the elements. Atomic spectrometric techniques are very sensitive and can be used to measure the total element content within a sample; however, accuracy of these techniques can be affected by the matrix of the sample. X-ray and nuclear techniques provide very low limit of detections and matrix insensitivity and are used for comparison of results due to their principles fundamentally different from those of the other analytical techniques. Therefore, they are less likely to be prone to the same systematic biases. Benefits and losses of each technique should concern the number of analytes possible to measure with the use of the technique, occurrence of interferences and difficulties, detection limits, throughput of samples, and expenses.

The determination of trace elements and contaminants in complex matrices often requires extensive sample preparation and/or extraction prior to instrumental analysis. A large number of samples that need to have determined the concentration of essential and toxic elements belong to food [3, 4], environmental [5, 6], clinical and biological [5–7, 7–9] samples. Routinely, the determination of trace metals has been carried out by inductively coupled plasma atomic emission spectrometry (ICP AES), inductively coupled plasma mass spectrometry (ICPMS), electrothermal atomic absorption spectrometry (ETAAS), and flame atomic absorption spectrometry (FAAS). However, matrix of many samples (biological, clinical, environmental, etc.) is complex and consists of high amounts of soluble solid substances and large amounts of inorganic compounds (i.e., salts of Ca, K,
Na, Mg, chlorides, phosphates, sulfates). The direct analysis of these kinds of samples gives many difficulties in sample introduction, nonspectral and spectral interferences in measurements by atomic absorption spectroscopic methods, inductively coupled plasma atomic emission or mass spectrometry. Therefore, samples have to be mineralized before analysis to destroy the organic matter or at least diluted to decrease the content of concomitant substances.

2 Spectroscopic techniques

2.1 Atomic absorption spectrometry

FAAS is one of the most conventional techniques for the determination of trace metal ions because of the relative simplicity and inexpensiveness of equipment. In this technique, a sample is introduced into a flame where it is dissociated into constituent atoms. Electromagnetic radiation in the UV/Vis part of the spectrum is directed through the flame and partially absorbed by the atoms. Methodology for most elements is well known and allows to use the FAAS technique to determine trace elements directly in various samples’ materials [10–12]. However, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples and suffers from the matrix interferences. Several procedures have been developed for preconcentration and separation of traces of metals required prior to instrumental determination to lower the detection limits, to improve the precision and accuracy of analytical results, and to bring the analyte concentration into the dynamic range of the detector. The preconcentration methods like solvent extraction, ion exchange, adsorption, and coprecipitation were frequently used for trace analysis of lead, cadmium, copper, cobalt, chromium, nickel, tin, gold, palladium, iron, and zinc in different research materials [13–20]. The coprecipitation method is useful for the preconcentration of trace metal ions and is one of the most useful ways for the preconcentration as well as separation of trace elements from the sample matrix. For the determination of Cr(III), Cu(II), Fe(III), Pb(II), Pd(II), and Zn(II) in food samples, the use of Ni(II)-α-benzoin oxime as a coprecipitation agent can be successfully applied without too much prolongation of the procedure [21]. Liquid–liquid extraction transferring analyte from the aqueous sample to a water immiscible solvent is widely used for samples’ preparation. Cloud point extraction (CPE), similar to liquid–liquid extraction, transferring analyte from the aqueous sample to a water immiscible solvent, is widely used for samples’ preparation and coupled with AAS technique. CPE is based on the property of surfactants to form micelles, which under certain conditions (temperature and concentration) separate into two phases: a surfactant-rich phase of a small volume and a large aqueous phase. Hydrophobic complexes of metallic elements present in such media are trapped in the hydrophobic micellar core and extracted in the surfactant-rich phase, which is directed to AAS detector. The small volume of the surfactant-rich phase obtained after the CPE methodology seems to be ideal for coupling with electrothermal AAS, even though there are applications of CPE coupled with FAAS [16]. Nevertheless, the above-mentioned methods are time consuming and require at least some chemical additives and complex equipment. Miniaturization of liquid extraction methods can be achieved by a drastic reduction of the extractant phase volume by single-drop microextraction, hollow fiber liquid-phase microextraction, and dispersive liquid–liquid microextraction (DLLM) allowing for separation and preconcentration of organic and inorganic contaminants in a single step. Due to the need of a sample volume between 2 and 4 mL for FAAS analysis, a microsample injection system (MIS) in case of small volumes obtained after preconcentrations methods might be applied [17, 22]. Online separation and preconcentration based on the adsorption of an analyte on an appropriate material representing the solid phase (SP) and then followed by an elution step directing the solution to the FAAS detector allows the use of wide range of sorbents, chelating agents, and eluents; it is also easily implemented and controlled. The analytes can be retained in their complexed or ionic forms on sorbents or functionalized with specific ligands. The online separation or preconcentration system requires stable material packed in minicolumns placed immediately after the injection valve or its sampling loop. Due to the high enrichment factor, high recovery, low cost, low consumption of organic solvents, and the ability to combine with different detection techniques, an SP extraction (SPE) has been commonly coupled with FAAS. The analytical parameters such as selectivity, affinity, and capacity depend on the sorbent chosen for SPE. Different materials can be used as sorbents for online preconcentration: modified silica gel, modified chitosan resins, chelating resins, magnetic nanoparticles, carbon materials, cellulose, and egg shell membrane.

Due to the high surface to volume ratio, easy derivatization procedures and unique thermal and mechanical stability carbon nanotubes (CNTs) have attracted a lot of attention. CNTs have diameters from fractions to tens of nanometers and lengths not bigger than several micrometers. The surface areas range from 150 to 1,500 m$^2$/g, which is a basis for serving as good sorbents. To improve selectivity, CNTs can be functionalized with different organic molecules. However, CNTs need to be modified with a specific ligand to improve the performance of sorbents by increasing the sorbent capacity and selectivity [15]. The chelating resins are superior in selectivity to
solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation, and physical adsorption. The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen, and sulfur. The properties of selectivity and sorption of these resins can be affected by different factors: chemical activity of the complexing group, the nature and kind of the metal ions, the pH of the solution, ionic strength, or polymeric matrix [23].

Among other carbon materials, carbon dots ( CDs) turned out to be a selective and sensitive method to separate and determine Cr in various samples. Due to the unique physical and chemical properties, CDs functionalized can facilitate the adsorption of analytes in consequence of electrostatic interaction, anion exchange, chelate interaction, or physical structure and can be employed in SPE as separation and preconcentration material in online or offline modes. Novel water-soluble CDs capped with branched polyethyleneimine polymer with dispersed particle extraction coupled with slurry sampling technique and followed by FAAS detection were employed on Cr(VI). CDs modified with cationic surfactant promoting small droplets generation during the aspiration and nebulization processes acted as a selective sorbent for separation and preconcentration of Cr(VI) enhancing the sensitivity of its determination [19].

An interesting solution for FAAS technique for elemental analysis is modification of instrumentation and the use of thermospray flame-furnace (TS-FF) AAS improving the efficiency of sample introduction. In this case of TS-FF consisting of a nickel tube, a sample solution is nebulized via a ceramic capillary to a standard burner head of an FAAS instrument, onto which the tube is placed [24]. Comparing to a standard FAAS systems, the TS-FF introduces a complete sample to the atomizer and provides a much longer residence time of the sample in the flame. As a result, the sensitivity of measurements may increase by an order of magnitude [25].

For the determination of elements forming hydrides or volatiles species (As, Bi, Ge, Pb, Se, Sb, Sn, Te, Hg, Cd, Co, Cu, Ag, Au), a chemical vapor generation (CVG) system is applied for various samples. The direct transfer of the volatile compounds to any atomizer eliminates the need of other steps but atomization, thus improving the sensitivity. In contrast to ETAAS, the FAAS technique is compatible with the online generation systems of volatile species. Analytes are easily preconcentrated before atomization by trapping directly on the flame atomizer. Even though there are solutions of coupling CVG for both techniques: FAAS and ETAAS [26].

ETAAS differs from FAAS by the use of much higher atomization temperatures, which reach up to 3,000 K. FAAS is typically used for determining low concentrations of elements (e.g., Al, Ca, Co, Cr, As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) [27–32] and can be applied without the need of earlier preconcentration of analytes. Measurements commonly apply to only one or two elements [33, 34]. However, relatively small quantities of solid and liquid samples may be analyzed. The technique, similarly to FAAS, has various types of interferences including background absorbance, matrix effect on atomic absorbance values, and differences of the chemical form in elements. There are various tools used to eliminate or to reduce these interferences: preliminary mineralization of a sample, separation of elements to be determined from interfering components, chemical modifiers, Zeeman effect background correction, and devices with separated zone of evaporation and atomization including graphite “filter furnace” (FF) atomizer and a L’vov platform.

Graphite is the most commonly used material in ETAAS. Due to the porosity of its surface, various species in the subsurface agglomerate in tubes are present. As a consequence, several corrosion changes have been observed when tubes were exposed to different compounds. Due to the surface and in-depth corrosion of tube and platform, their total lifetime can be significantly reduced. Usually, chemical modifiers are applied to the graphite furnace by adding to the solution with or after the sample or standards. But chemical modifiers can be also applied as a metal deposit on the graphite tube surface or on the L’vov platform acting as a permanent modifier and making the pyrolysis and atomization steps possible without repeating the treatment of the tube or platform. It was demonstrated that electrodeposited noble metals could serve as permanent modifiers by intercalation and remaining near the surface region of the tube for the total tube’s lifetime. This observation developed permanent performance of various modifiers [35]. There are several permanent modifiers recommended – noble metals as well as their mixtures of less volatile metals: palladium, molybdenum, magnesium, molybdenum-iridium, molybdenum-ruthenium, vanadium, iridium, ruthenium, vanadium-iridium, vanadium-ruthenium, tungsten, tungsten-vanadium, and tungsten-magnesium [36]. In case of liquid samples, palladium and tungsten were used successfully [37–39], while the direct determination of antimony in solid samples was ineffective [40]. Problems in the determination of arsenic and antimony result from background spectral interferences and may be resolved by the selection of alternative analytical lines by the use of high-resolution-continuum source (HR-CS) ETAAS or by the application of a combination of Zeeman background correction together with the selection of an appropriate modifier.

In comparison with a platform, graphite FF atomizer provides increase in sensitivity. Filtration of atomized sample through the porous graphite improves performance of the FF atomizer because during this process molecular species are eliminated from the atomization volume. A wider range of sample volumes, which can be introduced into the graphite FF atomizer, provides additional advantage of this atomizer compared with the platform. The use of FF with Pd-Mg chemical modifier in the determination of Pb, As, and Cd during direct
ET AAS analysis in various food samples provided a nearly twofold increase in sensitivity in comparison with a conventional heated graphite furnace with a platform. Additionally, it significantly eliminated matrix effects including background absorbance [29].

The main disadvantage of ETAAS and FAAS analysis of solid samples is the sample pretreatment, which is often the most time consuming and problematic (e.g., incomplete dissolution, precipitation of insoluble analyte, loss of elements during heating, contamination) step. The total concentration of analyte can be determined after acid digestion or alkali fusion. Microwave-assisted sample dissolution has been employed commonly for sample dissolution but barring some obvious advantages it still causes some problems (cost, short lifetime of digestion vessels, explosions, losses and contamination, long time of cooling, small sample throughput, corrosion of microwave parts, constant supervision during the digestion), which are exaggerated during trace elements analysis. The ideal method for the analysis of solid samples would eliminate the sample dissolution, minimizing the sample preparation and improving the analytical results. Solid sampling can be applied to materials of different physical structures, whereas slurry sampling is dependent on the size and structure of the particles to be analyzed. In both cases, the use of an appropriate modifier mixture and optimized pyrolysis and atomization temperatures eventually avoids background absorption caused by the complex matrix. Slurry or solid sampling with ETAAS method has been extensively used for analysis of biological materials, sediments, and soils slurries in order to simplify sample preparation and to avoid problems associated with sample dissolution procedures [34, 41, 42]. The ETAAS method with solid sampling into a graphite furnace ensures the rapid and reliable determination of metals in soils or precipitates providing strict control of the sampling efficiency, particle size, number of particles present in the injected volume, analyte homogeneity, suspension medium, slurry concentration, stirring and sample depth. Analyses of environmental samples by solid sampling used either two-stage atomization with the use of permanent modifiers or slurry sampling. ETAAS analysis of volatile elements (as arsenic or antimony), which evaporate as oxides in the temperature of graphite furnace higher than 400 °C, need the use of chemical modifiers (e.g., noble metals: palladium, nickel and magnesium nitrates, high melting of tungsten or zirconium carbides or mixtures of some of them) stabilizing analyte and facilitating the removal of the matrix by the increase of the temperature of atomization. Even ETAAS with the injection of sample suspensions into a graphite furnace ensures the rapid and reliable determination of metals; it is worth mentioning that it significantly shortens the life of tubes and lowers the sample throughput. The use of ultrasound-assisted extraction procedure can allow to avoid these problems because the sample matrix is not introduced into the atomizer, avoiding the buildup of carbonaceous residues or silicates on the graphite platform [43].

HR-CS AAS is an innovation that improves the performance of AAS. After the introduction of AAS technique in 1955 by Walsh, the use of spectral line instead of CS was necessary due to required spectral resolution, which was not achieved with the available monochromators at that time [44]. Together with efficient background corrector (like least-square background correction), it has been applied to the analysis of many analytes in a great variety of samples [45–47].

HR-CS AAS is a valuable tool due to the visibility of the spectral environment of the analytical line at high resolution. With the use of line source ETAAS with Zeeman effect background correction, a high signal indicating the presence of spectral interference for lead in fertilizer samples is observed. Due to this interference, there is no possibility in the determination of lead at 217.0 nm because of the presence of phosphorus monoxide (PO) under the magnetic field and splitting of the rotational lines of the molecular spectrum. The background absorption without and with magnetic field is not the same, resulting in background correction errors. HR-CS ETAAS is a tool that allows for investigation of these interferences due to the visibility of the spectral environment of the analytical line at high resolution. With the use of HR-CS ETAAS, it is possible to detect the presence of spectral interferences (S and N) and storage of the spectra of diatomic molecules with rotational fine structure that coincide temporally and spectrally with the analyte absorption [46]. To eliminate the fine structured background using least-squares background correction, it is mandatory to identify the molecule that is responsible for the spectral interference. Then, the reference spectrum of the interfering molecule is recorded and subtracted from the sample spectrum and a spectrum of pure analyte is obtained. The fine structured background depends on the chemical composition of each sample. In case of arsenic, the spectral interferences were corrected using a reference spectrum obtained from NaCl and PO, while in the case of selenium NO and PO reference spectra were used to correct the interferences [48]. In both cases, it was possible to obtain accurate results. Sulfur and nitrogen-containing molecules were responsible for the fine-structured background, which was completely corrected in case of lead determination. Using the most sensitive line at 217.001 nm, some unknown spectral interferences were observed. The use of HR-CS ETAAS made it possible to verify that the digestion of samples did not avoid the presence of spectral interferences since digested samples presented fine-structured background similar to the samples prepared as slurry. Comparing HR-CS ETAAS and line source ETAAS with Zeeman effect background correction, the results can be considered similar, indicating that the latter technique was able to correct the herein found spectral interferences to a reasonable extent [46].
2.2 Inductively coupled plasma atomic emission spectrometry

ICP-AES, also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), provides an excellent scope for the determination of trace elements with high sensitivity. This is due to very high temperatures (up to 8,000 K) of plasma used for atomization of analyte present in a sample. The ICP is created by argon gas, which is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern toward the magnetic field of the radio-frequency coil. A stable plasma is generated as the result of the collisions between the neutral argon atoms and the charged particles. While the sample is introduced to the plasma, it immediately collides with the electrons and charged ions and is broken down into charged ions. Various molecules break up into their respective atoms, which then lose electrons and recombine repeatedly in the plasma. Excited atoms emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample and detected by a photomultiplier or a semiconductor detector.

Even ICP-AES has similar limits of detection to FAAS; it can detect many elements simultaneously and has a much larger dynamic range. On the other hand, an ICP-AES suffers from a lot of interferences and is much more expensive than the AAS technique. Since the condition of ICP is changed by matrix elements from sample solution, signal intensities derived from analytical elements might be influenced. In analysis of high-viscosity solutions, injection volume of sample might be not constant, which may result in not reproducible analytical results or higher limit of detection. Therefore, the investigation of the influence of matrix elements and high viscosity of sample must be indispensable for accurate, sensitive, and reproducible determination by ICP-AES. One of the solutions to reduce the influence of some matrix elements might be vaporization of Cl− and CO32− ions, decreasing the viscosity of a sample, and lowering the pH of samples or decomposing organic compounds present in a sample. This could be obtained by the use of H2SO4–fume treatment [49].

Not without significance is the level of limit of detections that makes this technique not suitable for direct analysis of extremely low element levels. Therefore, prior to detection with ICPAES, an effective preconcentration step is required, similarly like in FAAS analysis described earlier [50, 51]. Various factors affecting the preconcentration process such as sample volume, concentration of the eluent, sample and eluent flow rates, as well as the accuracy of the method have to be always optimized and investigated in this case.

2.3 Inductively coupled plasma mass spectrometry

ICP-MS is widely used in routine multi element determination at the trace and ultratrace level in liquid samples with different matrix composition. The use of separation and enrichment techniques for analytes improves its limits of detection from the level of sub-μg/L even to sub-ng/L. Due to the excellent sensitivity, low detection limits, possibility of isotopic determination, and small sample volume ICP-MS, wide dynamic range is widely used in clinical and biological [52–54], food [55, 56] environmental, geological, industrial analysis [57–59], and in a variety of different tasks [60]. Most of the elemental analysis with the use of ICP-MS described in the literature concerns easy available materials [61–63], but a great number belongs also to the limited samples [64].

In the ICP-MS technique, the sample is ionized in the same type of argon plasma as in the ICPAES technique. At the first stage of the process, the liquid sample is nebulized with an effective nebulizer transforming it into a fine aerosol, which is then transported with argon to ICP torch. In the plasma, nebulized water matrix and chemical compounds are evaporated, molecules dissociated into atomic constituents, and then ionized into positively single-charged ions. Ions are extracted from the argon plasma into mass analyzers: quadrupole (QMS), double focusing sector field (SFMS), and time of flight (TOFMS). In mass analyzer, ions are separated according to their mass-to-charge ratio or energy-to-charge ratio in double focusing SF instruments. The separated ion beams are detected by photomultiplier or Faraday cups.

Among a large variety of sample introduction systems developed for ICP-MS, the most common and most economical is liquid solution nebulization. Therefore, there is a need of previous digestion of solid samples that is a very important stage for the whole analytical procedure. There are a lot of different liquid sample introduction systems developed [65–67]. The most frequently used for mineralized samples is pneumatic nebulizer (concentric, cross-flow, V-groove, sonic spray, or multi-microspray) combined with spray chamber (double pass, single pass, and cyclonic) with a solution uptake rate of 0.5–2 mL/min and very low transport efficiency (1–20 %) [68]. Higher sample introduction efficiency is provided by high-efficiency nebulizers like ultrasonic nebulizers [69, 70] or electrothermal vaporization, which allows for in situ sample preparation and preconcentration [71, 72]. Due to the trace element determination in micro- or nanoliters of sample, there are also micronebulizers available with solution uptake rate of 0.1 μL/min, which is a great advantage because of reduction of contamination problems (memory effects, deposition, clogging) or some interferences caused by solvents or possibility of coupling with techniques like electrophoresis requiring low sample consumption.
Besides the very high expenses, the ICPMS technique has a lot of advantages: sensitivity, very low limit of detections, throughput, multielemental analysis, and isotopic information, even though it suffers from atomic and molecular isobaric and multielemental interferences [73, 74]. This can be overcome simply by the choice of noninterfered isotope in case of multi-isotopic elements, by the subtraction of blanks, appropriate sample preparation [75], the use of mathematical correction [76], cold plasma conditions [77], by the use of collision or reaction cell technology [78–81], or by the use of high-resolution mass spectrometers that resolve elements and interferences. In order to overcome some physical interferences, an internal standard, standard addition method, the choice of sample introduction system, or simply dilution of the sample is frequently used [62, 82–84]. Extremely important for the achieved detection limits (LODs) as well as precision (RSD) of measurements is the kind of mass analyzer used in the ICPMS system. Samples with complexed matrix are the source of many interferences. Due to the low resolution commonly used, quadrupole analyzers have a lot of limitations compared to the systems with high-resolution mass analyzers [85–88].

Some of the most repeatable and accurate analytical measurements achieved today are thanks to the conjunction of an ICPMS with an isotopic dilution quantification methodology (Table 1).

**Table 1**: Overview of analytical performance of selected techniques used for trace elements determination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte</th>
<th>Technique</th>
<th>LOD [μg L⁻¹]</th>
<th>RSD [%]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food, natural waters</td>
<td>Cr(III), Cu(II), Fe(III), Pb(II), Pd(II), Zn(II)</td>
<td>Coprecipitation FAAS</td>
<td>0.1–5.3</td>
<td>&lt;5</td>
<td>[20]</td>
</tr>
<tr>
<td>Tap water, groundwater, industrial effluent</td>
<td>Cr(VI), Pb(II)</td>
<td>DLLM MIS-FAAS</td>
<td>0.037–0.054</td>
<td>&lt;4</td>
<td>[22]</td>
</tr>
<tr>
<td>Fruit (apple, grape, nectarine, green beans, cantaloupe)</td>
<td>Cu(II)</td>
<td>Functionalized CNTs FAAS</td>
<td>0.65</td>
<td>3</td>
<td>[15]</td>
</tr>
<tr>
<td>Environmental (water samples)</td>
<td>Cr (VI)</td>
<td>CD FAAS</td>
<td>0.21</td>
<td>2.8</td>
<td>[19]</td>
</tr>
<tr>
<td>Water, biological (hair, nail, liver)</td>
<td>Zn(II)</td>
<td>Flow injection FAAS</td>
<td>2.2</td>
<td>&lt;1.2</td>
<td>[23]</td>
</tr>
<tr>
<td>Fruit juices, seawater</td>
<td>Cu</td>
<td>Chelating resign TS-FAAS</td>
<td>0.15</td>
<td>2.7–6</td>
<td>[25]</td>
</tr>
<tr>
<td>Wine, beer, milk, kefir, yoghurt, juice, lemonade Juices, alcoholic beers</td>
<td>Pb, As, Cd</td>
<td>FF-ETAAS</td>
<td>0.1–2.0</td>
<td>3–6</td>
<td>[27]</td>
</tr>
<tr>
<td>Vegetable oil, fat samples</td>
<td>Sn(IV)</td>
<td>CPE FAAS</td>
<td>0.33</td>
<td>2.1–6.2</td>
<td>[16]</td>
</tr>
<tr>
<td>Vinegar</td>
<td>Mn, As, Pb, Cu, Cd, Zn</td>
<td>FF ETAAS</td>
<td>4–0.8</td>
<td>3–8</td>
<td>[28]</td>
</tr>
<tr>
<td>Water, biological (hair, nail, liver)</td>
<td>Cd</td>
<td>ETAAS</td>
<td>0.004</td>
<td>1.07–2.33</td>
<td>[32]</td>
</tr>
<tr>
<td>Body fluids</td>
<td>Cr, Ni, Al, V</td>
<td>SPE ICPAES</td>
<td>0.01–0.39</td>
<td>1.2–2.2</td>
<td>[50]</td>
</tr>
<tr>
<td>Body fluids</td>
<td>Al, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, V</td>
<td>ICPEAS H₂SO₄ fume ICPEAS SF ICPMS</td>
<td>1–2</td>
<td>1</td>
<td>[49]</td>
</tr>
<tr>
<td>River water</td>
<td>Pb, As, Cu, Hg</td>
<td>Stripping voltammetry</td>
<td>0.07–0.4</td>
<td>2–12</td>
<td>[113]</td>
</tr>
<tr>
<td>Tap water</td>
<td>As(III)</td>
<td>Boron-doped diamond stripping voltammetry</td>
<td>1.5</td>
<td>4.56</td>
<td>[111]</td>
</tr>
<tr>
<td>Freshwater and seawater</td>
<td>Ir(III)</td>
<td>Catalytic adsorptive stripping voltammetry</td>
<td>0.002</td>
<td>6</td>
<td>[117]</td>
</tr>
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</table>

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2.3.1 Isotopic dilution inductively coupled plasma mass spectrometry (ID-ICP MS)

The capability of measuring precise and accurate isotope ratios by ICPMS is applied in the determination of element concentrations by the isotope-dilution (ID) technique, which is regarded as a primary method of measurements. ID ICPMS provides the possibility of absolute quantification for elements with two or more isotopes in any sample material. One or two enriched isotope tracers of the element of interest in known concentrations are added to the sample. The determination is performed after precise mixing by measuring changed isotope ratios in the sample spike mixture compared to those in the sample and highly enriched isotope tracer. The precision and accuracy of the trace element concentrations determined by ID ICPMS are in the low percentage range [72, 89–91]. Other advantages of the IDMS technique are no need of the preconcentration or dilution factor once complete isotope equilibration between the sample and the spike has been achieved and no influence of the instrumental sensitivity on the final value for the element concentration [92, 93]. IDMS is well documented for total elemental analysis.

2.4 Laser ablation ICPMS

Direct solid sampling is possible with an ICPMS system due to the laser ablation (LA) application. This technique is based on surface ablation of sample material by the use of focus laser beam. First, the sample is placed in a special ablation cell isolating it from the ambient environment. Then, the material is ablated and the formed dry aerosol is introduced to the plasma with the aid of a gas stream allowing for surface analysis or depth analysis of studied materials. Different ablation cells with different internal volumes and geometries mainly depending on the sample sizes influence the overall transport efficiency and signal profile. Volume of ablation cell affects mainly the dispersion of the signal [94].

LA ICPMS is not completely accepted for quantitative analyses mainly due to the fractionation effects and the persistent lack of adequate reference materials for the wide variety of samples [95, 96]. Laser wavelength, pulse duration, power, and spot size influence fractionation during the LA process. The size of the aerosol determines the particle size distribution of the generated aerosol because of its chemical composition, transport efficiency and decomposition in the ICP. The thermal character of the LA process might lead to the formation of agglomerates and molten spherical particles of different sizes in dependence of the laser wavelength. Matrix effects may be induced in the ablation process, during aerosol transport to plasma, or in the ionization process in the plasma. Therefore, the calibration of LA ICPMS has to provide the capabilities to compensate these differences among samples and standards in order to obtain quantitative data. There are several calibration strategies for LA ICPMS; among them are internal standard method, external calibration, standard addition, isotope dilution, or matrix matched standards [96–98]. Additionally, the use of isotope dilution mass spectrometry in combination with LA ICPMS allows an accurate, precise, and time-effective quantitative analysis of trace elements in powdered samples using different isotope dilution calibration strategies.

LA ICPMS is becoming one of the most important direct analytical techniques for the rapid and sensitive determination of stable and radioactive isotopes on solid surfaces [99]. LA ICPMS avoids wet decomposition of a sample as well as the risk of contamination during sample preparation. In fact, it needs little or no sample preparation and offers a very good sample throughput and reduced spectral interferences. A significant feature of LA is the high spatial resolution between 10 and 100 μm for nanosecond lasers and below 1 μm for femtosecond lasers, with very low sample uptake of picograms. This microdestructive character of the technique is important in case of unique samples [100–103]. LA ICPMS has been used to produce images of element distribution in various materials, mainly in clinical and biological samples [104]. The challenging task of LA ICPMS for future applications is the analysis of a single cell or particle with interesting applications in life and material science.

3 Electrochemical techniques

Potentiometry using ion-selective electrodes (ISEs) and stripping voltammetry using polarographic techniques are two principal methods for trace detection.
Potentiometric sensors are passive electrochemical devices in which changes in the equilibrium voltage are monitored under zero current conditions. The equilibrium potential of the device is ideally described as a Nernstian function of the activity of the target ions to be measured.

ISEs are chemical sensors for the selective determination of ions in complex matrixes and have been applied for many years in clinical chemistry for the measurement of electrolyte concentrations in blood or plasma. Electrodes are available for the most important clinically relevant ions, for example, Na⁺, K⁺, Cl⁻, Ca²⁺, and H⁺. Most of the potentiometric devices had limits of detections in the micromolar range, but numerous new developments of sensor arrays, new reference electrodes, polyion sensing, new ionophores, miniaturization for liquid chromatography, and capillary electrophoresis detectors significantly improved lower detection limits, broadening the range of application like trace metal analysis in environmental and biological samples [105–109].

The LOD for ISEs is defined as the activity at which the extrapolated Nernstian response, for the target ion, intercepts with the extrapolated potentiometric response from an infinitely dilute solution. Possible biases existing in ISE measurements come from the super-Nernstian or sub-Nernstian response of the ISE in the low concentration and from the presence of interfering ions in solution; the nonideal aspects of this technique can be eliminated by special electrode design, use of new ion-selective materials, and robust calibration of the system. The elimination of the effect of interfering ions is challenging by calibration since the composition of the calibration solutions and filling solutions may vary from the sample. In this case, improved electrode and materials design can provide better results.

Stripping voltammetry is a powerful analytical technique for trace metal detection. Its uniqueness comes from remarkably low detection limits, high sensitivity, and the ability to detect trace metal elements in different oxidation states. Another advantage that should be mentioned is portability of the instrumentation and the ability to perform rapid analysis as well as low costs for basic instrumentation and operation [110]. The problem that occurs is due to the common use of mercury film electrode that should be avoided because of its toxic soluble salts. Mercury electrode was substituted by the use of some nonmercurial electrodes, for example, electropolymerized polymer film, bismuth, antimony, and silver or gold electrodes [111–113]. Gold electrodes in different forms have been used to detect heavy metals by stripping analysis: solid disc electrodes, films on glassy carbon, graphite or platinum, microelectrodes, modified gold electrodes, gold nanoparticles, and screen-printed electrodes. Many voltammetric studies, including stripping methods, have focused on the modification of the electrode surface or use of a chelating/complexing agent to increase the detection limit. With this aim, different complexing have been used [114].

Stripping voltammetry consists of two steps. An electrolysis/deposition step where the analyte is accumulated at the surface of the working electrode during a certain period either by faradic process (anodic or cathodic) [110, 115] or nonfaradic (adsorptive) [116, 117] process. This preconcentration phase can be as long as required, depending on the concentration of analyte in solution. Low element concentrations will require long accumulation step to buildup enough material on the electrode. The accumulation increases with time, not with concentration of an element in the sample, which allows achieving very low detection limits. This first step of preconcentration is followed by a stripping step removing the previously accumulated metal back into the solution by the means of applying an anodic potential sweep. The current generated during the stripping is directly proportional to the concentration of the metal present in the water sample. During the electrolysis, the analyte is reduced at the working electrode together with any other element that can be reduced at this deposition potential. If a low deposition potential is used in acidic conditions, hydrogen is formed at the working electrode surface by the reduction of protons and oxidants are produced at the auxiliary electrode. The hydrogen generation is problematic as it blocks the electrode surface, affects the reproducibility, and increases the noise of the voltammograms. The very few attempts that have been made to measure in such conditions were mostly directed toward the determination of As(V), which is only reducible in acidic conditions. To avoid hydrogen bubbles blocking the electrode, a rotating electrode was developed with the old disk placed on the side to facilitate the removal of hydrogen. The gold disk needs to be polished and cleaned after only 10 measurements. In this regard, the wire electrode has been more successful by using a gold film deposited on a platinum wire electrode. Stripping voltammetry is limited in acidic conditions to relatively high deposition potentials because of the interfering effects of the hydrogen produced at the working electrode. A simple procedure performing reliable, sensitive, and reproducible trace metal analysis and smooth stripping signals made at gold microwire electrode was obtained after applying a simple electrochemical conditioning procedure of using a vibrate electrode instead of stirred or stagnant conditions, which resulted in that hydrogen did not block the electrode in mild acidic conditions (pH <1) [118]. Vibrations at 200 Hz help in removing the hydrogen bubbles.

Determination of more than one metal using stripping analysis is difficult due to the possibility of overlapping peaks, which can occur in the narrow potential range where metals are reduced or oxidized. The multielement detection of As, Cu, Pb, and Hg was performed in the presence of oxygen by differential pulse anodic stripping voltammetry with the use of gold vibrating microwire electrode, which allowed us to performed analysis without deoxygenation that simplified the use of stripping and decreased the measurement time [113].
The combination of a vibrator with a gold microwire electrode resulted in a very small stable and reproducible diffusion layer thickness, which improved the sensitivity and reproducibility of the results, allowing making determination with a very short deposition time. The use of HCl 0.1 M with NaCl 0.5 M was found optimum in terms of peak resolution, shape, and sensitivities, and additionally was found similar to the seawater properties, which raised the range of research objects. Possible effects of Al, Cd, Cr, Fe, Mn, Ni, Sb, and Zn in different concentrations from 1.0 μg/g to 1,000 μg/g on 1.0 μg/g/L of a mixture of As, Cu, Hg, and Pb did not cause any significant interferences. Arsenic was the element that suffered the most from these interferences; however, concentrations of interfering metals tested were very high compared to their expected levels in real samples.

Adsorptive processes can further lower detection limits of stripping voltammetry to the picomolar concentration levels and are very useful for saline matrices like seawater and estuarial water samples as well as for speciation studies. In adsorptive stripping voltammetry, the analyte is adsorbed on the working electrode by means of a nonelectrolytic process prior to the voltammetric scan. This procedure avoids the main difficulties of anodic stripping analysis with metals with a strong tendency to form intermetallic compounds, with low solubility on mercury electrode (e.g., Ni). For trace metals, the method is based on the formation and accumulation of a metal complex on the working mercury electrode and subsequent measurements of the reduction peak of the accumulated complex. The formation of a monomolecular complex layer on electrode increases the sensitivity of voltammetric measurement because the metal is not dissolved in the mercury [114, 116, 117, 119].

Despite many advantages of electrochemical detection, there is a great limitation in sample throughput and its size, which is at least 10 mL. Reducing sample size would ensure the extension to limitedly available samples, concurrently reducing reagent consumption and analysis time. Sample size reduction in voltammetry has been achieved by miniaturization and the development of dedicated electrodes. Microfluidic devices featuring solid-state microelectrodes have been developed significantly reducing sample requirement. Detection capabilities, precision, and accuracy are similar to typical solutions but application might be broadened to a range of limited availability of samples. The electrochemical route allows on-chip integration of the control instrumentation to produce self-contained truly portable microanalytical systems. The introduction of new modified electrodes, the development of novel derivatization schemes, the integration of additional functional elements (preconcentration) on a single microchip platform, and the coupling of new detection schemes and assays enhance the power of electrochemical detectors for microscale analytical systems [120, 121].

4 Other techniques used for trace analysis

4.1 Techniques uses X-ray

Due to its very low limit of detections and matrix insensitivity, X-ray methods have been widely used for trace analysis in geological materials, steels, cements, archaeological samples, forensic samples, and environmental samples such as airborne particulate matter [122]. A commonly used technique is X-ray fluorescence (XRF) used to analyze for all elements. The sensitivity of XRF depends on the energy of the incident radiation, the geometry of the instrument used, and the efficiency of the detector. The precision of XRF measurements is limited by the statistics of the detected photons. The LODs depend on the sensitivity of the instrument and the background level of the sample matrix. Typical XRF precision is better than 0.1 % and typical LODs are few g/cm² for particulate material for a wide range of elements.

In total reflection XRF (TXRF), the incoming radiation is incident on the sample at less than the critical angle and is totally reflected. The low background levels result in improved LODs and even 2 pg may be detected for a variety of elements with a counting time of 1,000 s. Using synchrotron radiation sources (SR), TXRF with polychromatic beam for sample excitation allows for lowering detection limits to even 0.03 pg/m² and the use of more intense photon fluxes will lower them by several orders of magnitude [123].

For these techniques, samples need to be in a form of thin film and that is a reason for low matrix effects conversely to the above-mentioned techniques. Quantification is performed by the addition of a single element, not present in the sample itself, as internal standard and a calibration curve valid in all matrices. The lack of robustness in these calibration methods leads to large systematic errors that are significant compared to the very low amounts being analyzed.

X-ray emission may be induced by heavy charged particles (particle-induced X-ray emission). Calibration is often by means of thin-film standards or using fundamental physical parameters in conjunction with an experimentally determined efficiency curve. LODs of ng/cm² have been claimed for particulate material on ambient air filters for a range of elements.
4.2 Activation analysis

Activation analysis refers to the identification and quantitative determination by use of radionuclides produced from a target element. It requires very little or no sample preparation, is nondestructive in nature and largely unaffected by the sample matrix, and allows for multielemental determination.

Neutron activation analysis (NAA) is the most common variant in which neutrons are used to irradiate and to activate the sample. When the measurement is carried out without prior chemical separation, the method is called instrumental NAA (INAA). As a result of a nuclear reaction between the neutron and the isotope of the element of interest, radionuclides with characteristic half-lives may be produced emitting radiation of varying energies that may be measured by a suitable detector and are characteristic of the element form that they were produced. In INAA, the decomposition of the radioactive sample is not necessary; the method is also nondestructive, which in case of unique objects is a valuable feature.

Acknowledgment

This article is also available in: Matusiewicz, Bulska, Inorganic Trace Analytics. De Gruyter (2017), isbn 978–3–11-037194–9.

References


