A General Overview of Atomic Spectrometric Techniques

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CHAPTER 1

A General Overview of Atomic Spectrometric Techniques

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1.1 Introduction: Basis of Analytical Atomic Spectrometric Techniques

Analytical atomic spectrometry comprises a considerable number of techniques based on distinct principles, with different performance characteristics and hence with varied application scopes, but in all cases providing elemental chemical information about the composition of samples. Figure 1.1 shows that these techniques can be classified into three main groups according to the type of particle detected: *optical spectrometry*, where the intensity of either non-absorbed photons (absorption) or emitted photons (emission and fluorescence) is detected as a function of photon energy (in most cases, plotted against wavelength); *mass spectrometry* (MS), where the number of atomic ions is determined as a function of their mass-to-charge ratio; and *electron spectroscopy,* where the number of electrons ejected from a given sample is measured according to their kinetic energy, which is directly related to the bonding energy of the corresponding electron in a given atom.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are the two main techniques based on electron spectroscopy. In XPS, a source of photons in the X-ray energy range is used to irradiate the sample.

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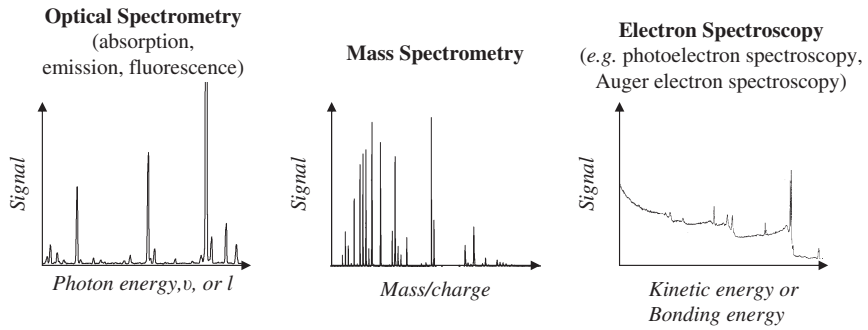

Figure 1.1 Classification of spectrometries according to the detection principle.

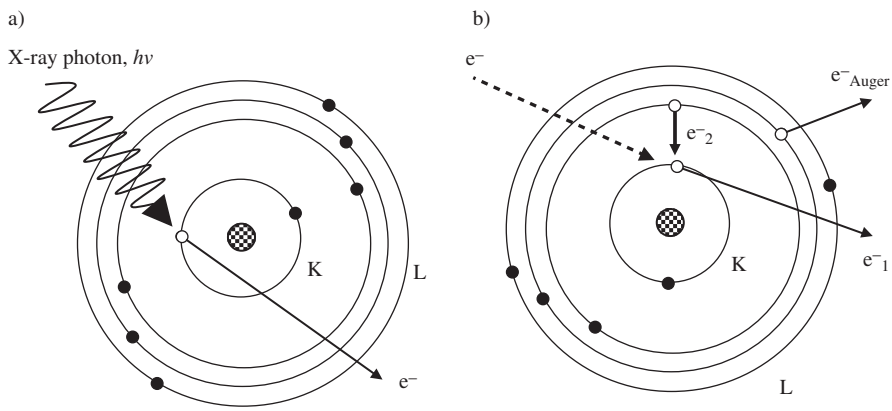

Figure 1.2 Electron spectroscopy. (a) Schematic representation of the XPS process. (b) Schematic representation of the processes for auger electron emission.

Superficial atoms emit electrons (called photoelectrons) after the direct transfer of energy from the photon to a core-level electron (see Figure 1.2a). Photoelectrons are subsequently separated according to their kinetic energy and counted. The kinetic energy will depend on the energy of the original X-ray photons (the irradiating photon source should be monochromatic) and also on the atomic and, in some cases, the molecular environment from which they come. This, in turn, provides important information about oxidation states and chemical bonds as the stronger the binding to the atom, the lower is the photoelectron kinetic energy.

In an Auger process, the kinetic energy of the emitted electron does not depend on the energy of the excitation source. AES consists of a two-step process: first, the sample is irradiated with an electron beam (or, less commonly, with X-rays), which expels an inner electron (e^-_1). In a second step, the relaxation of the excited ion takes place through the fall of a more external electron (e^-_2) to fill the 'hole', and then a third electron (e^-_{Auger}) uses the energy released in that movement to exit the atom (Figure 1.2b). XPS and AES are considered powerful

techniques for surface analysis, with good depth and lateral resolution. However, due to their narrow range of applications in qualitative studies and the scarcity of quantitative analyses, they will not be considered further in this chapter.

The aim of this chapter is, therefore, to introduce briefly the most common quantitative atomic techniques based on both optical and mass spectrometric detection. The main emphasis will be given to conceptual explanations in order to stress the advantages and disadvantages of each technique, the increase in the complexity of the data they generate and how this can be addressed. References to chemometric tools presented in the following chapters will be given.

For these techniques, a dissolved sample is usually employed in the analysis to form a liquid spray which is delivered to an atomiser (*e.g.* a flame or electrically generated plasma). Concerning optical spectrometry, techniques based on photon absorption, photon emission and fluorescence will be described (Section 1.2), while for mass spectrometry (MS) particular attention will be paid to the use of an inductively coupled plasma (ICP) as the atomisation/ionisation source (Section 1.3). The use of on-line coupled systems to the above liquid analysis techniques such as flow injection manifolds and chromatographic systems will be dealt with in Section 1.4 because they have become commonplace in most laboratories, opening up new opportunities for sample handling and pretreatment and also to obtain element-specific molecular information.

Finally, direct solid analysis by optical and mass spectrometry will be presented in Section 1.5. This alternative is becoming more appealing nowadays and implemented in laboratories because of the many advantages brought about by eliminating the need to dissolve the sample. Techniques based on the use of atomiser/excitation/ionisation sources such as sparks, lasers and glow discharges will be briefly described in that section.

1.2 Atomic Optical Spectrometry

Routine inorganic elemental analysis is carried out nowadays mainly by atomic spectrometric techniques based on the measurement of the energy of photons. The most frequently used photons for analytical atomic spectrometry extend from the ultraviolet (UV: 190–390 nm) to the visible (Vis: 390–750 nm) regions. Here the analyte must be in the form of atoms in the gas phase so that the photons interact easily with valence electrons. It is worth noting that techniques based on the measurement of X-rays emitted after excitation of the sample with X-rays (*i.e.* X-ray fluorescence, XRF) or with energetic electrons (electron-probe X-ray microanalysis, EPXMA) yield elemental information directly from solid samples, but they will not be explained here; instead, they will be briefly treated in Section 1.5.

The measurement of analytes in the form of gaseous atoms provides atomic spectra. Such spectra are simpler to interpret than molecular spectra (since atoms cannot rotate or vibrate as molecules do, only electronic transitions can take place when energy is absorbed). Atomic spectra consist of very narrow peaks (*e.g.* a few picometres bandwidth) providing two types of crucial analytical information: the observed wavelength (or frequency or photon energy),

which allows for qualitative analysis, and the measurement of the peak height or area at a given frequency, which provides quantitative information about the particular element sought. The relative simplicity of such atomic spectra and the fairly straightforward qualitative and quantitative information have led to the enormous practical importance of atomic optical spectrometry for inorganic elemental analysis. However, it should be stressed again that to obtain such spectra the analytes must be converted into atoms which will absorb or emit photons of UV–Vis radiation and so an 'atomiser', for example a dynamic medium of high temperature where molecules containing the analyte are broken down into individual gaseous atoms, is needed.

1.2.1 Classification of Techniques: Absorption, Emission and Fluorescence

The interaction processes between UV–Vis photons and the outer electrons of the atoms of the analytes can be understood using quantum mechanics theory. In the thermodynamic equilibrium between matter and interacting electromagnetic radiation, according to the radiation laws postulated by Einstein, three basic processes between two stable energy levels 1 and 2 are possible. These processes, which can be defined by their corresponding transition probabilities, are summarised in Figure 1.3.

- *Spontaneous emission of photons*. This process refers to a spontaneous transition of the electron from the excited state 2 to the lower energy state 1 with emission of a photon of frequency $v_{12} = (E_2 - E_1)/h$. This process

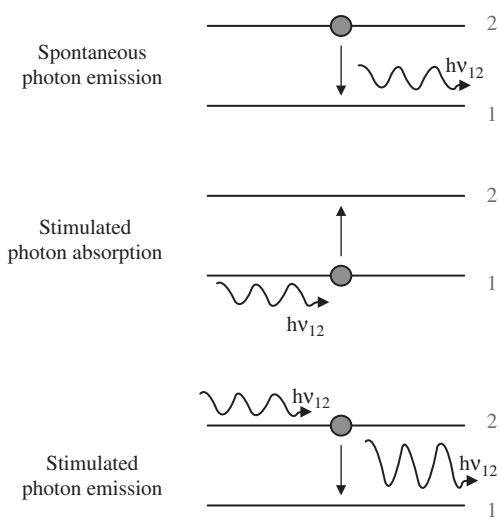

Figure 1.3 Basic interaction processes between matter and interacting electromagnetic radiation.

constitutes the photophysical basis of atomic emission spectrometry, which will be termed here optical emission spectrometry in order to use the acronym OES instead of AES because the latter acronym can be confused with that for Auger electron spectroscopy.

- *Stimulated absorption of photons*. In this case, the electronic transition takes place from state 1 to state 2 in response to the action of an external radiation of the appropriate frequency. Atomic absorption spectrometry (AAS) is based on this process. On the other hand, atomic fluorescence spectrometry (AFS) corresponds to the sequential combination of a stimulated absorption followed by spontaneous emission.
- *Stimulated emission of photons*. This process consists of electronic transitions from the excited energy level to the lower one stimulated by an external radiation of the appropriate frequency $(E_2 - E_1)/h$ and constitutes the basis of the laser (light amplification by stimulated emission of radiation) phenomenon.

Atomic lines can arise from electronic transitions in neutral atoms or in atomic ions (in general, atomic lines for a given element M are denoted M I, whereas their ionic counterparts are denoted M II). The transitions of outer electrons of an atom may be represented as vertical lines on an 'energy level' diagram, where each energy level of the outer electron possesses a given energy and is represented by a horizontal line. For example, Figure 1.4 shows the diagram for the neutral sodium atom (the wavelengths corresponding to the transitions in the diagram are expressed in ångströms, Å). The energy scale is linear in electronvolt (eV) units, assigning a value of zero to the 3s orbital. The scale extends up to about 5.2 eV, which corresponds to the energy necessary to extract the 3s electron and so to produce a sodium ion. All electronic transitions ending on the same energy level are usually called 'series', the most likely ones being those ending in the lowest possible energy level (the ground state) of the electron in the atom.

The light coming from such transitions is separated according to its frequency (or its wavelength, λ) and the intensity observed for each frequency measured electronically (*e.g.* with a photomultiplier tube). Thus, if the observed intensity of the emitted light is plotted against the frequency (or wavelength) of the corresponding transition (line), an 'atomic emission' spectrum is obtained (see Figure 1.1). Similarly, an 'atomic fluorescence' spectrum would be the plot of the measured intensity (coming from atoms excited by appropriate electromagnetic radiation) as a function of the frequency of the emitted radiation. Finally, if stimulated absorption of light in response to an electronic transition between a lower and a higher energy level is measured, a plot of 'percent absorption versus frequency of the light' can be drawn; such a plot represents an 'atomic absorption' spectrum.

The atomic lines in the spectrum appear as vertical lines or 'peaks' due to the nature of the transition involved. That is, in molecules an electronic transition is usually accompanied by simultaneous changes in the molecule vibrational and rotational energy levels; sometimes all the three energy types may change

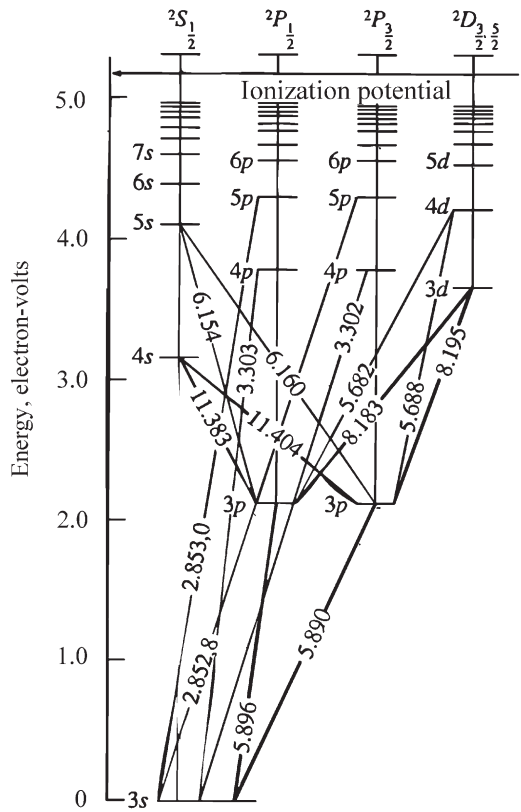

Figure 1.4 Diagram of energy levels and electronic transitions for atomic sodium.

simultaneously in an electronic transition in a molecule. The many transition possibilities allowed in this way and the solvent effect derived from the aggregation state of the sample (the 'excited' sample is in liquid form) determines that in UV–Vis molecular absorption (or emission) the corresponding 'peaks' in the spectrum are widely broadened. Typically, the half-bandwidth of an absorption 'band' in such molecular UV–Vis spectra is around 40 nm (or 400 Å), whereas in atomic 'lines' the half-bandwidth observed, as a result of pure electronic transitions, is a few hundredths of an ångström (typically 0.03–0.05 Å).

Thus, spectral interferences in atomic spectroscopy are less likely than in molecular spectroscopy analysis. In any case, even the atomic 'lines' are not completely 'monochromatic' (*i.e.* only one wavelength per transition). In fact, there are several phenomena which also bring about a certain 'broadening'. Therefore, any atomic line shows a 'profile' (distribution of intensities) as a function of wavelength (or frequency). The analytical selectivity is conditioned by the overall broadening of the lines (particularly the form of the wings of such atomic lines).

The selection of the most appropriate atomic line among all possible transitions for qualitative and quantitative purposes is critical. For most elements, the 'resonance' atomic lines (*i.e.* when the lowest energy level in the corresponding transition is the fundamental or 'ground state' level, $E_0 = 0$) are the most sensitive ones in flames and they are used in the majority of flame methods. However, with plasma sources (commonly used in combination with OES), the choice is more difficult because several emission lines from neutral atoms or atomic ions of the same element may appear useful. Often, the expected concentration range will dictate whether to use a neutral atom resonance line, an ion line or a line arising from transitions between excited atomic states. Resonance lines are useful for trace constituents, but they are susceptible to self-absorption of emitted radiation at high concentrations (this effect is due to an excess of analyte atoms in the ground-state level). Lines of lower relative intensities are often used for minor and major constituents. Moreover, the abundance of nearby, potentially interfering lines from other elements, has to be assessed carefully.

1.2.1.1 Atomic Absorption Spectrometry. Principles of Quantitative Analysis

For quantitative purposes in AAS, a magnitude called transmittance (T) which relates, for a given wavelength, the intensity (measured by the detector) of the light source (I_0) and the intensity not absorbed which has passed through the atomiser or transmitted light (I) is used:

$$T = \frac{I}{I_0} \tag{1.1}$$

The amount of light absorbed is a function of the so-called absorption coefficient (k') and of the optical pathlength in the atomiser cell (b); k' depends on the frequency of the selected analytical line and on the concentration of the analyte absorbing atoms. The general absorbance law (Lambert–Beer–Bouguer law) relates transmittance (and so measured intensities I and I_0) to k' and b through the following equation:

$$T = \mathrm{e}^{-k'b} \tag{1.2}$$

The parameter used in the analytical calibrations by AAS is absorbance (A), which is linearly related to k' (that is, at a given λ, with the atomic concentration of the analyte in the atomiser) and with the length of the optical path:

$$A = -\log T = \log 1/T = k'b \log e = 0.434k'b \tag{1.3}$$

For a given set of experimental conditions in an absorption experiment, we obtain

$$\mathrm{A} = \text{constant} \times b \times N_0 \tag{1.4}$$

N_0 being the analyte atom density (number of atoms per unit volume) in the ground state in the atomiser. The relationship between the atom concentration per unit volume ($N_T \approx N_0$) and the concentration of the analyte in the sample, C, is linear under fixed working conditions for a given line of the analyte. Therefore, we can establish a linear relationship between absorbance and C:

$$A = KbC \tag{1.5}$$

1.2.1.2 Optical Emission Spectrometry. Principles of Quantitative Analysis

Optical emission spectrometry is one of the oldest physical methods of analysis enabling multielement determinations. In this process, free atoms which are generated by thermal dissociation of the sample material are excited or ionised and excited additionally (several collisions or other processes may be responsible for delivering the required energy). The higher the temperature, the higher is the percentage of excited analyte species (at least, in general) and the higher the emission intensity. The Boltzmann equation relates the temperature (T) with the number of atoms in an energy state E_0 and an excited state E_q, provided that the source is in a so-called thermal equilibrium, as

$$n^*/n_0 = \frac{g_q}{g_0} e^{-(E_q - E_0)/k_B T} \tag{1.6}$$

where n_0 is the number of atoms in the energy level E_0, n^* the number of atoms in an energy state E_q, k_B the Boltzmann's constant, g_q and g_0 the statistical weights for each energy state (E_q and E_0) and T the temperature in Kelvin.

The flames commonly used as atomisers have temperatures in the range 2000–3000 K allowing for the analysis of elements such as Na, K and Cs by OES. The flame temperatures are not high enough to excite many other elements, so other atomisers such as spectroscopic plasmas have to be used.

Linear (straight-line) relationships can be easily achieved between the emission intensity of a given transition and the total atomic concentration of the element in the atomisation/excitation system. However, under certain conditions, spectral lines from resonance transitions can display a phenomenon called self-absorption, giving rise to non-linearity in calibration graphs at high concentrations. If changes to the experimental setup cannot correct the problem, it will cause difficulties in classical linear calibration, although they can be solved by multivariate calibration techniques (some of which are introduced in the following chapters).

1.2.1.3 Atomic Fluorescence Spectrometry. Principles of Quantitative Analysis

AFS involves the emission of photons from an atomic vapour that has been excited by photon absorption. For low absorbance signals (and thus for low

analyte concentrations), the following linear relationship applies:

$$I_F = 2.3K'AI_0 \tag{1.7}$$

where I_F is the fluorescence intensity, A the absorbance and I_0 the intensity of the light excitation source. K' depends on the quantum efficiency of the fluorescence process (*i.e.* the ratio between the number of atoms emitting fluorescence and the number of excited atoms). Considering eqn 1.5:

$$I_F = 2.3K'KbCI_0 \tag{1.8}$$

$$I_F = k'CI_0 \tag{1.9}$$

Therefore, I_F depends on the concentration of analyte atoms in the atomiser and on I_0 (in fact, much of the research on AFS as an analytical technique has involved the development of stable and intense suitable light sources). Using a constant light excitation output, linear calibration graphs can be achieved for low analyte concentrations:

$$I_F = kC \tag{1.10}$$

1.2.2 A Comparative View of Basic Instrumentation

The basic components of AAS, OES and AFS instruments are illustrated by the simple schematics shown in Figure 1.5. They need an atomiser to convert the analyte contained within the sample to gaseous atoms. A device is also required to separate the electromagnetic radiations arising from the atomiser and a 'light read-out' system, which is integrated by a transducer or detector (transforming the light intensity into a measurable signal, *e.g.* an electric current), and a electronic read-out system.

In AAS (Figure 1.5a) the external energy is provided by a light source in a straight-line optical axis configuration. Figure 1.5b shows that the basic instrumental components in AFS are the same as in AAS, only the geometry of the arrangement changes as the external light source used for analyte photo-excitation has been rotated 90° (with respect to the straight-line optical axis used in absorption measurements) to minimise the collection of scattered light from the excitation source. Finally, as depicted in Figure 1.5c, OES measurements do not use any external light source since the sample is excited in the atomiser by the energy provided by a flame, a plasma (*i.e.* a hot, partially ionised gas), *etc.*

Based on the configurations in Figure 1.5, many analytical techniques have been developed employing different atomisation/excitation sources. For example, two powerful AAS techniques are widespread: one uses the flame as atomiser (FAAS) whereas the other is based on electrothermal atomisation (ETAAS) in a graphite furnace. Although the flame has limited application in OES, many other analytical emission techniques have evolved in recent decades based on different atomisation/excitation plasma sources.

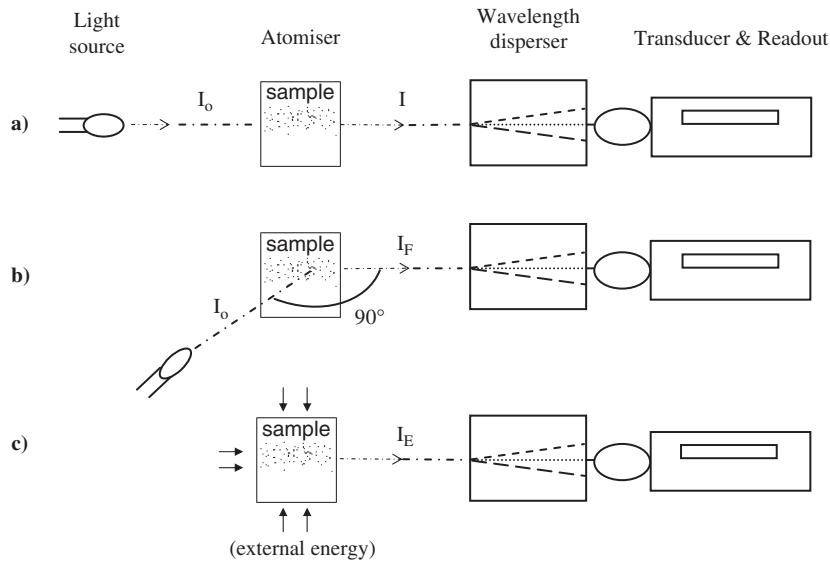

Figure 1.5 Schematics of basic components of analytical techniques based on atomic optical spectrometry. (a) Atomic absorption spectrometry; (b) atomic fluorescence spectrometry; (c) atomic emission spectrometry.

Concerning AFS, the atomiser can be a flame, plasma, electrothermal device or a special-purpose atomiser (*e.g.* a heated quartz cell). Nowadays, commercially available equipment in AFS is simple and compact, specifically configured for particular applications (*e.g.* determination of mercury, arsenic, selenium, tellurium, antimony and bismuth). Therefore, particular details about the components of the instrumentation used in AFS will not be given in this chapter.

1.2.2.1 Atomic Absorption Spectrometry. Instrumentation

Figure 1.6a shows the simplest configuration of an atomic absorption spectrometer, called a 'single-beam spectrometer'. As can be seen, the lamp, the atomiser and the wavelength selector (most wavelength selectors used in AAS are monochromators) are aligned. The selected wavelength is directed towards a detector (*e.g.* a photomultiplier tube), producing a signal proportional to the light intensity. To remove the atomiser continuum emission, the radiation source is modulated to provide a means of selectively amplifying modulated light coming from the lamp while the continuous emission from the atomiser is disregarded. Source modulation can be accomplished with a rotating chopper (mechanical modulation) located between the lamp and the atomiser or by pulsing the lamp (electronic modulation). Synchronous detection eliminates the unmodulated dc signal emitted by the atomiser and so measures only the amplified ac (modulated) signal coming from the lamp.

If a single beam is used, a blank sample containing no analyte should be measured first, setting its absorbance to zero. If the lamp intensity changes when

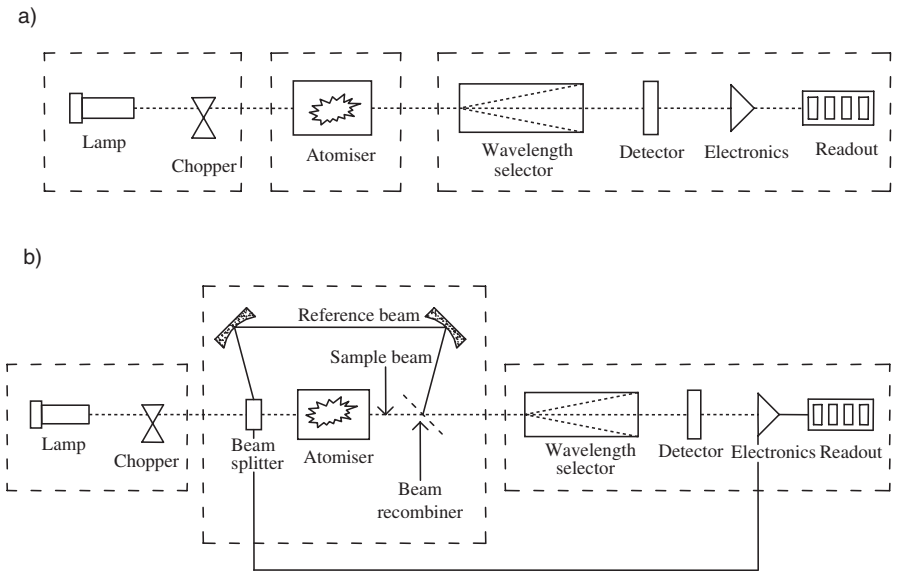

Figure 1.6 Configurations of instruments for atomic absorption spectrometry. (a) Single-beam spectrometer; (b) double-beam spectrometer.

the sample is put in place, the measured absorbance will be inaccurate. An alternative configuration is the 'double-beam spectrometer', which incorporates a beamsplitter so that part of the beam passes through the atomiser and the other part acts as a reference (Figure 1.6b), allowing for a continuous comparison between the reference beam and the light passing through the atomiser.

By far the most common lamps used in AAS emit narrow-line spectra of the element of interest. They are the hollow-cathode lamp (HCL) and the electrodeless discharge lamp (EDL). The HCL is a bright and stable line emission source commercially available for most elements. However, for some volatile elements such as As, Hg and Se, where low emission intensity and short lamp lifetimes are commonplace, EDLs are used. Boosted HCLs aimed at increasing the output from the HCL are also commercially available. Emerging alternative sources, such as diode lasers [1] or the combination of a high-intensity source emitting a continuum (a xenon short-arc lamp) and a high-resolution spectrometer with a multichannel detector [2], are also of interest.

The radiation absorbed or scattered from the light source by atoms or molecules different from the analyte will give rise to a background absorption which will add to the specific absorption of the analyte. Contributions to the background in AAS can arise from spectral interferences due to a spectral line of another element within the bandpass of the wavelength selector (such a possibility is rather uncommon in AAS; besides, such interferences are now well characterised), absorption by molecular species originating from the sample and light scattering from particles present in the atomiser. Therefore, to determine accurately the absorbance due to the analyte, subtraction of the

background from the total absorbance measured in the spectrometer is necessary. In most cases instrumental means of measuring and correcting for this background absorption can be used, such as deuterium or Zeeman-based background correctors [3]. However, instrumental background correction has limitations and it is important to keep in mind that the ideal for background correction should be to be able to measure a true blank solution. Multivariate calibration techniques have very powerful resources to cope with this problem.

Two atomisers are generally used in AAS to produce atoms from a *liquid* or *dissolved* sample:

1. A flame, where the solution of the sample is aspirated. Typically, in FAAS the liquid sample is first converted into a fine spray or mist (this step is called nebulisation). Then, the spray reaches the atomiser (flame) where desolvation, volatilisation and dissociation take place to produce gaseous free atoms. Most common flames are composed of acetylene–air, with a temperature of ~2100–2400 °C, and acetylene–nitrous oxide, with a temperature of ~2600–2900 °C.
2. An electrothermal atomiser, where a drop of the liquid sample is placed in an electrically heated graphite tube which consists of a cylinder (3–5 cm in length and a few millimetres in diameter) with a tiny hole in the centre of the tube wall for sample introduction (see Figure 1.7a). Both ends of the

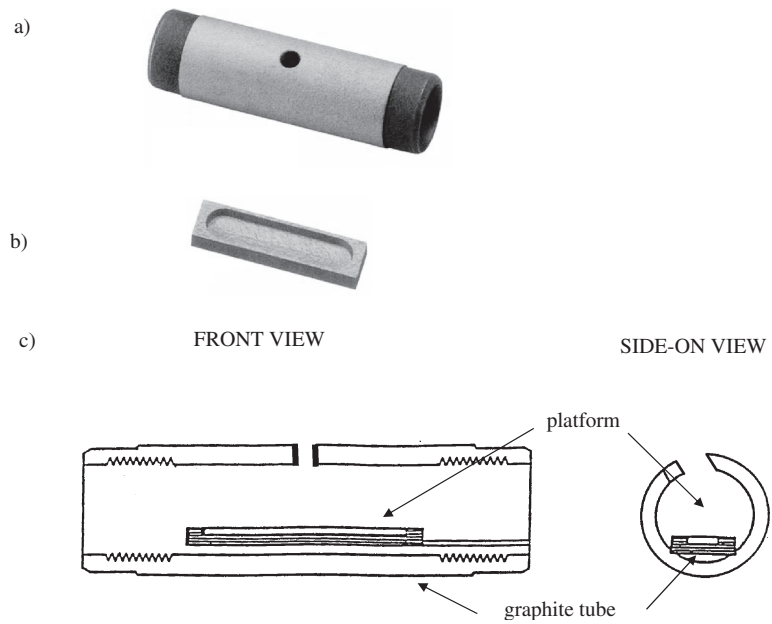

Figure 1.7 Electrothermal atomisation atomic absorption spectrometry. (a) Photograph of a graphite tube. (b) Photograph of a L'vov platform. (c) Schematic front and side-on views of a graphite tube with a L'vov platform.

tube are open to allow the light from the lamp to pass through and for the removal of the sample constituents after the analysis. Atomisers used in commercial ETAAS instruments are most commonly made of pyrolytically coated electrographite. A platform (the so-called L'vov platform) to deposit the sample within the tube is used (Figure 1.7b and c). The platform has a finite heat capacity and is heated primarily by tube radiation, so its temperature will, in principle, be lower than that of the tube wall. Hence the sample deposited on it will be volatilised later in time (relative to direct wall atomisation), at higher gas-phase temperatures which will favour isothermal atom formation, reducing interference effects from temporal non-isothermal conditions typical in wall atomisation.

An ETAAS determination starts by dispensing a known volume of sample into the furnace. The sample is then subjected to a multi-step temperature programme by increasing the electric current through the atomiser body. The heating steps include drying, pyrolysis and atomisation. Unfortunately, during the atomisation step any organic material still present in the graphite tube is pyrolysed, producing smoke which may cause severe attenuation of the light beam. Further, the presence of many salts in the tube can give rise to large background absorbance when atomised at high temperatures. The addition of appropriate chemicals known as matrix modifiers and the use of instrumental methods of background correction have been crucial to overcoming these effects; however, problems still remain for some analytes and some types of samples.

Gaseous and volatilised analytes can also be easily determined by FAAS and ETAAS. For example, the determination of several elements by the formation of covalent volatile hydrides (*e.g.* arsenic, selenium) and cold vapour generation (mercury and cadmium) is feasible with good analytical sensitivity (see Section 1.4.1.1).

Solid sampling can be implemented for both FAAS and, especially, for ETAAS (sample particle size effects are less critical in ETAAS than in nebulisation-based techniques because it offers longer residence times). The availability of commercial instrumentation supporting solids analysis using the graphite furnace has led to its successful application, in particular for fast screening analysis with high sensitivity (absence of any dilution) and minimal risk of contamination [4]. Unfortunately, some problems are associated with direct solid sampling; for example, the small sample sizes required are frequently not representative enough and also matrix-matched standards are usually needed. These inconveniences can be minimised by slurry sampling [5]; however, some limitations remain and a critical one is the need to maintain the stability of the slurry until sample injection. Further, particle size may affect the reproducibility and accuracy if it is non-homogeneous or too large. On the other hand, owing to the absence of a pretreatment step to eliminate the matrix, the molecular absorption signal is often rather high and structured. Another limitation is the probable build-up of carbonaceous residues in the atomiser, reducing its lifetime.

1.2.2.2 *Atomic Emission Spectrometry. Instrumentation*

Flames and plasmas can be used as atomisation/excitation sources in OES. Electrically generated plasmas produce flame-like atomisers with significantly higher temperatures and less reactive chemical environments compared with flames. The plasmas are energised with high-frequency electromagnetic fields (radiofrequency or microwave energy) or with direct current. By far the most common plasma used in combination with OES for analytical purposes is the inductively coupled plasma (ICP).

The main body of an ICP consists of a quartz torch (15–30 mm in diameter) made of three concentric tubes (see Figure 1.8) and surrounded externally by an induction coil that is connected to a radiofrequency generator commonly operating at 27 MHz. An inert gas, usually argon, flows through the tubes. The spark from a Tesla coil is used first to produce 'seed' electrons and ions in the region of the induction coil. Subsequently the plasma forms, provided that the flow patterns are adequate inside the torch, giving rise to high-frequency currents and magnetic fields inside the quartz tube. The induced current heats the support gas to a temperature of the order of 7000–8000 K and sustains the ionisation necessary for a stable plasma. Usually, an aerosol from the liquid sample is introduced through the central channel transported by an argon flow

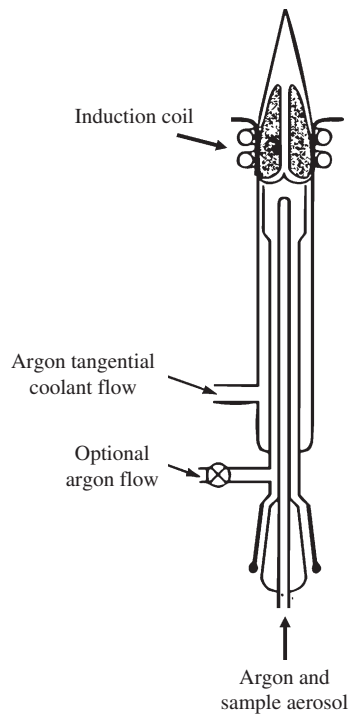

Figure 1.8 Schematic view of an ICP torch.

of about $11\,min^{-1}$. A much higher Ar flow velocity (about $101\,min^{-1}$) is introduced tangentially to prevent overheating. Because of efficient desolvation and volatilisation in the ICP, this atomiser/excitation source is commonly applied for the analysis of dissolved samples. The high temperatures and the relative long residence time of the atoms in the plasma (2–3 ms) lead to nearly a complete solute vaporisation and high atomisation efficiency. Accordingly, although matrix and inter-element effects should be relatively low, it has been observed that sometimes they are significant. Further, the high excitation capacity of this source gives rise to very rich spectra, so a careful assessment of potential spectral interferences is essential. On the other hand, the ICP emission frequently has an important background due to *bremsstrahlung* (*i.e.* continuous radiation produced by the deceleration of a charged particle, such as an electron, when deflected by another charged particle, such as an atomic nucleus) and to electron–ion recombination processes.

For a given ICP-OES instrument, the intensity of an analyte line is a complex function of several factors. Some adjustable parameters that affect the ICP source are the radiofrequency power coupled into the plasma (usually about 1 kW), the gas flow rates, the observation height in the lateral-viewing mode and the solution uptake rate of the nebuliser. Many of these factors interact in a complex fashion and their combined effects are different for dissimilar spectral lines. The selection of an appropriate combination of these factors is of critical importance in ICP-OES. This issue will be addressed in Chapter 2, where experimental designs and optimisation procedures will be discussed. Many examples related to ICP and other atomic spectrometric techniques will be presented.

Concerning the detection of the emitted light, the usual configuration used for signal collection is the lateral view of the plasma. However, nowadays, most instrument companies offer also, at least an ICP system based on axial viewing. For a given system, the use of axial viewing will improve the limits of detection compared with those obtained with lateral viewing, roughly by an order of magnitude. However, axial viewing has a poor reputation in terms of matrix effects and self-absorption phenomena. Chapter 2 presents several examples of the optimisation of ICP detection devices.

The availability of solid-state detectors (such as the charge-coupled detector, CCD) makes it possible to acquire simultaneously significant portions of the spectra or even the entire rich spectra obtained by ICP-OES in the UV–Vis region, thus providing a large amount of data. The commercial availability of ICP-OES instruments with these multichannel detectors has significantly renewed interest in this technique. However, some limitations, such as the degradation of the spectral resolution compared with photomultiplier-based dispersive systems, still remain.

ICP-OES has enjoyed a long-lasting success, with several companies marketing versatile and robust instruments which are being used for various research and routine applications in many laboratories worldwide. However, there is still a demand for improvement. It is expected that most future improvements will be related to more efficient data processing to take full benefit of the available emitted information. In particular, the availability of

the entire UV–Vis spectra should improve the reliability of the analytical results through the use of several lines per element and through a better understanding of matrix effects [6]. Therefore, new alternatives are required for data treatment and calibration. It is the authors' opinion that some of the techniques presented in the next chapters will be of great importance. In particular, several seminal studies have applied multivariate regression to ICP data, and also pattern recognition techniques (*e.g.* principal component analysis, PCA). More details will be presented in the corresponding sections.

Examples of other plasmas which have been used in combination with OES are the following:

- *Microwave-induced plasma (MIP):* this consists of an electrodeless microwave cavity plasma. Like the ICP, an MIP is initiated by providing 'seed' electrons. The electrons oscillate in the microwave field and gain sufficient energy to ionise the support gas by collisions. Large amounts of sample or solvent vapour can result in considerable changes in plasma impedance and thus coupling efficiency. MIPs operate at 2450 MHz (this is the frequency usually available in commercial microwave generators) and at substantially lower powers than ICP devices. The low power levels do not provide plasmas of sufficient energy to get an efficient desolvation of solutions and, hence, MIPs have been used mostly with vapour-phase sample introduction (*e.g.* as detectors for gas chromatography). Sample introduction difficulties have been primarily responsible for the lower popularity of MIPs compared with ICPs.
- *Direct current plasma (DCP):* this is produced by a dc discharge between electrodes. DCPs allow the analysis of solutions. Experiments have shown that although excitation temperatures can reach 6000 K, sample volatilisation is not complete because residence times in the plasma are relatively short (this can be troublesome with samples containing materials that are difficult to volatilise). A major drawback is the contamination introduced by the electrodes.
- *Furnace atomisation plasma emission spectrometry (FAPES):* this consists of an atmospheric pressure source combining a capacitively coupled radiofrequency helium plasma formed inside a graphite tube which contains an axial powered electrode. This miniplasma has rarely been used in analytical atomic spectrometry, probably because of the small number of users and a lack of information about its applications and capabilities [7].

1.2.3 Analytical Performance Characteristics and Interferences in the Different Techniques

This section starts with a discussion of selectivity for the most extended analytical atomic techniques based on optical spectrometry. Then, aspects such as detection limits (DLs), linear ranges, precision, versatility and sample throughput will be presented. The section ends with a brief comparison of the

performances of the most common optical techniques for atomic analysis of dissolved samples.

1.2.3.1 Selectivity

To understand the analytical selectivity of atomic spectroscopic methods, a basic knowledge of the different sources of interferences which may be encountered is essential. Therefore, the concept and relative magnitude of each interference will be described next and compared for the three main atomic detection modes. The following discussion is a sort of basic platform to understand and assess potential sources of error in any atomic technique we might need in our laboratory.

Spectral interferences. These interferences result from the inability of an instrument to separate a spectral line emitted by a specific analyte from light emitted by other neutral atoms or ions. These interferences are particularly serious in ICP-OES where atomic spectra are complex because of the high temperatures of the ICP. Complex spectra are most troublesome when produced by the major constituents of a sample. This is because spectral lines from other analytes tend to be overlapped by lines from the major elements. Examples of elements that produce complex line spectra are Fe, Ti, Mn, U, the lanthanides and noble metals. To some extent, spectral complexity can be overcome by the use of high-resolution spectrometers. However, in some cases the only choice is to select alternative spectral lines from the analyte or use correction procedures.

Physical (transport) interferences. This source of interference is particularly important in all nebulisation-based methods because the liquid sample must be aspirated and transported reproducibly. Changes in the solvent, viscosity, density and surface tension of the aspirated solutions will affect the final efficiency of the nebulisation and transport processes and will modify the final density of analyte atoms in the atomiser.

Chemical interferences. An important type of chemical interference in atomic spectrometry is due to the presence or formation in the atomiser of analyte refractory compounds. These interferences are probably the most serious ones when comparatively low-temperature atomisers (such as flames and graphite furnaces) are employed. The reduction of analyte atoms (which become trapped in the refractory molecule) will bring about a decrease in the analytical signal. Typical examples are phosphate interferences in determinations of Ca and Mg by flame-based methods (phosphates can form and they are only partially dissociated at normal flames temperatures). Another good illustration is the determination of elements such as Al, Si, Zr, Ta and Nb. For these 'refractory' elements, the use of hottest flames than those obtained with air–acetylene is needed, such as nitrous oxide–acetylene flames to allow the dissociation of the corresponding refractory oxides and hydroxides. Apart from 'hottest' atomisers, an alternative way to overcome these interferences is to resort to 'releasing agents' such as chemical reagents (*e.g.* organic chelating compounds, such as 8-hydroxyquinoline) that are able to form compounds with the analyte which are easily dissociated at the usual temperatures of the flame.

Another type of interference that can arise in the atomiser is called 'ionisation interferences'. Particularly when using hot atomisers, the loss of an electron from the neutral atom in metals with low ionisation energy may occur, thus reducing the free atom population (hence the sensitivity of the analyte determination, for which an atomic line is used, is reduced). These interferences can be suppressed in flames by adding a so-called 'ionisation suppressor' to the sample solution. This consists in adding another element which provides a great excess of electrons in the flame (*i.e.* another easily ionisable element). In this way, the ionisation equilibrium is forced to the recombination of the ion with the electron to form the metal atom. Well-known examples of such buffering compounds are salts of Cs and La widely used in the determination of Na, K and Ca by FAAS or flame OES.

In ICP-OES, it has been observed that analyte lines with high excitation potentials are much more susceptible to suffer matrix effects than those with low excitation potentials. The effect seems to be related to the ionisation of the matrix element in the plasma, but in fact it is a rather complicated and far from fully characterised effect [8,9]. Therefore, calibration strategies must be carefully designed to avoid problems of varying sensitivity resulting from matrix effects. A possible approach may be to combine experimental designs and multivariate calibration, in much the same way as in the case study presented in the multivariate calibration chapters.

Temperature variations in the atomiser. Variations in the temperature of the atomiser will change the population of atoms giving rise to atomic absorption, but they affect particularly the population of excited atoms, essential for OES measurements.

Light scattering and unspecific absorptions. Both of these problems occur only in AAS and AFS. When part of the light coming from the lamp is scattered by small particles in the atomiser (*e.g.* droplets or refractory solid particles) or absorbed unspecifically (*e.g.* by undissociated molecules existing in the flame), important analytical errors would be derived if no adequate corrections were made. Scattered and dispersed radiation decrease the lamp intensity and create false analytical signals. Fortunately, both sources of 'false signals' can be easily distinguished from the 'specific' analyte signals which do occur at the analytical line only (and not outside it in the spectrum) and this basic differential feature can be used for correction.

1.2.3.2 Detection Limits, Linear Ranges and Precision

Detection limits (DLs) are the most common figure used to compare analytical techniques (or methods) from the detection power point of view. DLs depend on the analyte and, for some techniques, also on the matrix. Further, DLs depend on the quality of the instrumentation (which is being continuously improved). Therefore, here just some approximate ranges will be given. DLs obtained by AAS are of the order of $\mathrm{mg\,l^{-1}}$ (ppm). These figures are much improved by using ETAAS; in this case, typical DLs are usually lower than $1\,\mu\mathrm{g\,l^{-1}}$ (ppb). ICP-OES can be considered 'half way' as it offers DLs usually

better than in FAAS but poorer than in ETAAS. Considering flame-based techniques, flame OES is advantageous just for alkali metals and, occasionally, calcium. Flame AFS might provide sensitivity similar to or better than FAAS (fluorescence signals have a low background). The limited use of AFS in routine laboratories is not due to technical disadvantages; rather it can be attributed to the fact that it does not offer additional advantages to those from the well-established AAS and OES techniques.

Concerning the linear ranges of calibration, more limited linear (straight-line) ranges are obtained with AAS than with OES and AFS, which span about three orders of magnitude above the corresponding limit of quantification for AAS and five to six orders of magnitude for OES and AFS methods.

In FAAS, relative standard deviations (RSDs) observed for measurements within the linear range are always better than $\pm 1\%$. This value is usually better than the RSDs observed using ETAAS, OES or AFS measurements.

1.2.3.3 Versatility and Sample Throughput

About 70 elements of the Periodic Table can be determined by optical techniques of atomic spectrometry. AAS techniques are basically considered as single element (particularly so for ETAAS, where the lamp and the atomisation conditions have, as a rule, to be selected individually for each element). This feature determines that the sample throughput in AAS (especially with ETAAS) is comparatively low.

In contrast, OES techniques (particularly those using a hot spectrochemical source such as an ICP) are intrinsically multielemental and this offers the possibility of a very high sample throughput in routine analysis. To counterbalance such a clear advantage, AAS techniques are simpler and cheaper than ICP-OES.

1.2.3.4 Comparative Analytical Assessment of the Most Common Analytical Techniques Based on Optical Spectrometry

FAAS, ETAAS and ICP-OES are probably today's 'workhorses' for the routine analysis of dissolved samples. Instrumental development and analytical applications have grown extensively throughout the years. A general comparative assessment is given in Table 1.1. Assuming that any generalisation is risky, it can be stated that FAAS dominates elemental inorganic analysis carried out in rather small laboratories when only a few analytes (probably at $mg\,l^{-1}$ levels) have to be determined. Such long-lasting use can be attributed to several main facts, including its robustness and comparatively low cost, well-established and validated analytical methods and fast analyses (*i.e.* low turn-around time). When sensitivity at the $\mu g\,l^{-1}$ level is required, the technique of choice is ETAAS, even though its simplicity, robustness and speed are worse than those of FAAS. Finally, ICP-OES seems to be the most popular routine

Table 1.1 Comparative advantages and limitations of the most common atomic "workhorses" of dissolved samples analysis by optical spectrometry.

	FAAS	ETAAS	ICP-OES
General advantages	Simple and reliable Most widespread Moderate interferences Ideal for unielemental monitoring in small labs High sample throughput	Sub-ppm ($mg\,l^{-1}$) DLs Microsamples (< 1 ml)	Multielemental High temperature Relatively low matrix interferences High dynamic range
Cost	Low cost	Higher cost	High instrument cost
Limitations	Usually unielemental	Unielemental	Serious spectral interferences
	Sub-ppm ($mg\,l^{-1}$) DLs	Time consuming	Sub-ppm-ppb DLs
	Low temperature (interferences by refractory compounds)	Not so easy to optimize	Expensive to run
	For metal & metalloids	Problems with background For metal & metalloids	Also for some non-metals

technique for inorganic multielemental analysis of dissolved samples, even though the initial investment and subsequent running expenses are much higher than those needed for AAS.

1.3 Atomic Mass Spectrometry

One of the more recent branches of atomic spectrometry, although perhaps the most exciting one, is *atomic mass spectrometry*, which has had a very important impact on science and technology. At present, atomic mass spectrometry is ordinarily performed using inductively coupled plasma ion sources and either a quadrupole or a scanning sector-field mass spectrometer as an analyser. The remarkable attributes of such a combination, being an indispensable tool for elemental analysis, include:

- very low detection limits for many elements;
- availability of isotopic information in a relatively simple spectrum;
- acceptable levels of accuracy and precision.

The success of inductively coupled plasma mass spectrometry (ICP-MS) has resulted in a broad availability of sophisticated instrumentation packages with user-friendly software and sample-analysis 'cookbooks' at reasonable cost [10].

Despite these strengths, ICP-MS has also some important drawbacks, many of them related to the spectral isotopic and/or chemical interferences, which affect analyte signal intensities and, therefore, the applicability of the technique. The complexity of the optimisation of the methodological and operating conditions, the differences in the ionisation rates of the various elements, the sequential isotopic measurements and the limited speed of signal acquisition (a serious drawback in multielemental analysis of fast transient signals) are some other problems to be considered.

In order to overcome, or at least minimise, such drawbacks we can resort to the use of chemometric techniques (which will be presented in the following chapters of this book), such as multivariate experimental design and optimisation and multivariate regression methods, that offer great possibilities for simplifying the sometimes complex calibrations, enhancing the precision and accuracy of isotope ratio measurements and/or reducing problems due to spectral overlaps.

1.3.1 Fundamentals and Basic Instrumentation of Inductively Coupled Plasma Mass Spectrometry

Since the launch of the first commercial quadrupole ICP-MS instrument in 1983, the technology has evolved from large, floor-standing, manually operated systems, with limited functionality and relatively poor detection limit capabilities, to compact, sensitive and highly automated routine analytical instruments. In principle, all ICP-MS systems consist of similar components: a sample introduction system, the ICP ion source, an interface system, the mass analyser, the detector and a vacuum system [8,11].

1.3.1.1 The Sample Introduction System

This is needed to bring the sample into the ICP plasma, where the ions are generated. Solution-based samples are currently introduced via a nebuliser (employed to produce small and narrow aerosol particle size distributions). This system is known to be a critical factor in achieving low detection limits because different designs (pneumatic nebulisers, ultrasonic nebulisers, high-pressure hydraulic design, thermospray or direct injection nebuliser systems, among others) differ in the efficiency of the mass transport (mass of analyte transported to the plasma per unit mass of analyte introduced from the sample). Also, an important body of work in the ICP-MS literature deals with the development of alternative sample introduction systems for both solution and solid sample forms. For example, hydride generation methods, flow injection analysis and slurry nebulisation methods are commonly used.

1.3.1.2 The ICP Ion Source

The ICP system is, in principle, identical with that used for ICP-OES and ICP-AFS, as it described earlier in this chapter. In the ICP, the major mechanism by

which ionisation occurs is thermal ionisation. When a system is in thermal equilibrium, the degree of ionisation of an atom is given by the Saha equation:

$$\frac{n_i n_e}{n_a} = 2\frac{Z_i}{Z_a}\left[2\pi m k_B \frac{T}{h^2}\right]^{\frac{3}{2}} \exp(-E_i/k_B T) \quad (1.11)$$

where n_i, n_e and n_a are the number density of ions, free electrons and atoms, respectively, Z_i and Z_a are the ionic and atomic partition functions, respectively, m is the electron mass, k_B is the Boltzmann's constant, T is the absolute temperature, h is the Plank's constant and E_i is the first ionisation energy.

From the Saha equation, we can see that the degree of ionisation is dependent on the electron number density, the temperature and the ionisation energy of the element of interest. The typical ICP electron densities and temperatures result in all elements with first ionisation potentials below 8 eV being completely ionised and even elements with first ionisation potentials between 8 and 12 eV are ionised by more than 10%. However, ICP is not an efficient ionisation source for elements with ionisation energies above approximately 10 eV. Moreover, both the temperatures and the electron number densities are dependent on the operating conditions of the plasma, in particular the forward power and the carrier gas flow rate, on the solvent loading, on the torch design, on the inner diameter of the injector and on the generation characteristics (frequency). Hence apparently small changes in the operating conditions can lead to a totally different plasma in terms of ionisation efficiencies, therefore affecting the tolerance to solvent loading, sensitivity and susceptibility to matrix effects.

1.3.1.3 The Interface System

An interface is needed for pressure reduction, so that the ions generated in the atmospheric pressure ICP become efficiently transported to the ion lens system of the mass spectrometer where they are focused into the mass analyser. It should be noted that an enormous pressure change is required (reduction by a factor of 10^8–10^{12}) and most of it has to be accomplished over a very short distance (<10 cm) using relatively small vacuum pumps. All modern ICP-MS instruments employ very similar sampling interfaces in which there are a number of common components. The basic layout is shown in Figure 1.9. The plasma expands from the atmosphere through a first orifice on the tip of a metal cone (sampler) to form a 'free jet' into a region whose pressure is a few Torr. Behind the sample cone is the expansion chamber, which is pumped by a single- or double-stage rotary pump producing an operating pressure in the 2–5 mbar range. The cloud of gas atoms, molecules, ions and electrons entering the expansion chamber quickly increases in speed and expands outwards under the influence of the reduced pressure in this region, resulting in the formation of a free jet. Spaced behind the sample cone is a second cone with a smaller orifice in its tip, called the skimmer cone. The centreline flow passes through a molecular beam skimmer into the downstream vacuum system pumped to a pressure of

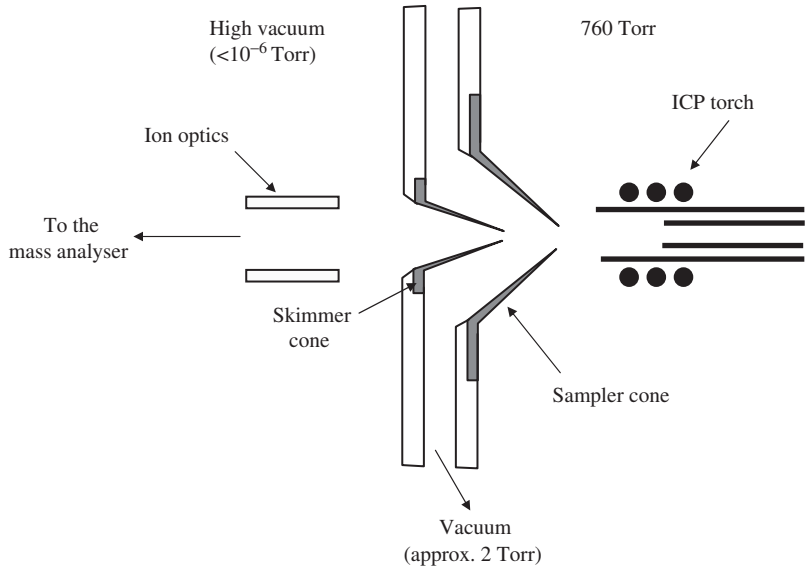

Figure 1.9 Basic layout of an ICP-MS interface.

10^{-3}–10^{-4} Torr. Operating pressures and cone shapes within the sampling interface strongly influence analyte sensitivity, mass response, matrix tolerance and levels of molecular interference. Ion sampling interfaces for ICP-MS have been designed using theory derived from molecular beam studies.

1.3.1.4 Ion Optics

Once the ions have entered the skimmer tip, it is necessary to extract and focus them into the analyser by subjecting the charged ions to constant electric fields. In order to construct an effective ion optical array, it is necessary to calculate the path followed by the ions in the electrostatic fields. We can resort to a number of mathematical models, such as SIMION, for a better understanding and optimisation of the ion-optical design for ICP-MS and the processes involved [12].

1.3.1.5 The Mass Analyser, the Detector and the Vacuum System

The mass analyser sorts the ions extracted from the ICP source according to their mass-to-charge ratio (m/z). The mass spectrum is a record of the relative numbers of ions of different m/z, which is characteristic of the analyte compound (see Figure 1.1). Functionally, all mass analysers perform two basic tasks:

1. separation of ions according to their mass-to-charge ratio;
2. measurement of the relative abundance of ions at each mass.

Most work in ICP-MS has been conducted using quadrupole-based mass spectrometers. The quadrupole mass filter is comprised of four parallel electrically conducting rods. Opposite rods are connected and parallel rods are supplied with a dc voltage, one pair being held at $+U$ V and the other set at $-U$ V. The first set of rods is supplied with an rf voltage and the second set of rods is supplied with an rf voltage out of phase by 180°. This combination results in the formation of an oscillating hyperbolic field in the area between the rods. Ions, when inside the quadrupole, are forced to follow certain trajectories that are dependent on the geometry of the field, the amplitude and the angular frequency of the alternating potential, the magnitude of the dc bias applied to the rods, the m/z of the ions, the initial conditions (position and velocity) and the phase angle with which the ions enter the field. Hence the quadrupole mass analyser has the ability to transmit certain ions and reject others depending on the stability of their path. Stable ions are transmitted through the length of the quadrupole whereas unstable ions hit the rods. The mass spectrum is scanned by varying the amplitude of the potential and the magnitude of the dc bias applied to the rods, while maintaining a constant ratio between those parameters. Quadrupole mass analysers are essentially sequential instruments, although they can be used to scan rapidly over 200 m/z in around 1 ms. Such a system typically provides a resolution of 0.5–1 atomic mass unit (amu).

However, nowadays some other different mass spectrometers are used for ICP-MS: 'time-of-flight' (TOF) systems for multielemental analysis of transient signals, ion trap analysers for ion storage, multicollector instruments for precise isotope ratio measurements and double-focusing sector field mass spectrometers for high mass resolution, but still the majority of instruments are equipped with quadrupole filters, which are simpler and cheaper.

We should not forget that an appropriate detector, a Faraday cup or a secondary electron multiplier equipped with a conversion dynode, is needed for ion detection. Most commercial instruments are equipped with a secondary electron multiplier, which can be operated in a low amplification mode, the analogue mode, and with a high gain, the counting mode, where each ion is counted. With this dual mode, a linear dynamic range of up to nine orders of magnitude can be achieved, so that major and minor components of the sample can be measured in one run.

Finally, successful operation of the mass analyser requires a collision-free path for ions. To achieve this, the lens system, mass analyser and detector are operated in a high-vacuum environment (below 10^{-6} Torr).

1.3.2 Analytical Performance Characteristics and Interferences in ICP-MS

The mass spectrum generated with an ICP-MS system is extremely simple (see Figure 1.1). Each elemental isotope appears at a different mass (*e.g.* ^{27}Al would appear at 27 amu) with a peak intensity directly proportional to the initial concentration of that isotope in the sample solution. A large number of

elements ranging from lithium at low mass to uranium at high mass are simultaneously analysed typically within 1–3 min. With ICP-MS, a wide range of elements at concentration levels from ppt to ppm can be measured in a single analysis.

Detection limits reported for the analysis of solutions by ICP-MS depend strongly on different variables, particularly the mass analyser, the sample matrix and the analyte under investigation. Moreover, small variations in many different instrumental parameters (including those affecting the plasma generation and the efficiency of ion sampling or transmission) can govern the sensitivity and detection limits when working with ICP-MS. However, for most elements, typical DLs in solution are in the range 0.1–10, 1–100 and 0.01–0.1 $ng\,l^{-1}$ for the quadrupole filter, the time-of-flight and the sector-field-based MS systems, respectively. In most cases, these DLs are 100–1000 times superior to those achieved routinely by plasma emission (ICP-OES) and fluorescence (ICP-AFS) spectrometry [13].

1.3.2.1 Quantification Procedures

Quantitative analysis in ICP-MS is typically achieved by several univariate calibration strategies: external calibration, standard addition calibration or internal standardisation. Nevertheless multivariate calibration has also been applied, as will be presented in Chapters 3 and 4.

Conventional external calibration uses pure standard solutions (single- or multielement) and is therefore unable to compensate for matrix effects, fluctuations or drifts in sensitivity. Matrix effects can be compensated for by using matrix-matched calibration solutions. In this case, the degree of compensation depends on the proper matrix adjustment.

Different mathematical approaches have been applied to enhance the performance of external calibrations in ICP-MS. To some extent, the observed drifts can be compensated for by regularly repeating the calibration or by repeated measurement of one standard, which allows for a mathematical drift correction [14]. Also, external calibration by weighted linear regression offers significant advantages over simple regression, especially for the determination of analytes at low concentrations. Confidence intervals are equivalent to those obtained by simple regression for analyte concentrations around 10 times the limit of quantification or lower. On the other hand, accurate results can be obtained even though calibration ranges are not adapted to the analyte concentration, which implies working with sufficiently wide calibration intervals where the main contribution to total uncertainty arises from the calibration itself.

Standard addition calibration is more robust and reliable than conventional external calibration, but is more time consuming and costly if it is applied separately for each sample. A major advantage of standard addition is the correction of multiplicative matrix effects such as alteration of nebulisation efficiency. The intensities of all samples (and spiked samples) change by the same factor, which leads to an altered calibration slope. However, for additive

effects, such as interferences caused by the matrix, the calibration line is shifted parallel and the intercept changes, which results in biased analyte concentrations. In some cases, this bias can be avoided (or indeed identified) by choosing another isotope and comparing the results for each. Standard addition has no inherent compensation for instrumental drifts in the ICP-MS system. However, a reduction of the drifts, which limit the applicability of standard addition for ICP-MS, was achieved by applying a chemometric method (a bracket approach, where the spiked sample is measured between two different measurements of the sample) [15].

Internal standard (IS) calibration requires ratioing of an analytical signal to an IS which has very similar characteristics to that of the analyte of interest (an element which is similar to the analyte either in mass, ionisation potential or chemical behaviour). Quantitative analysis applying internal standardisation is the most popular calibration strategy in ICP-MS, as improvements in precision are obtained when the technique is appropriately used. Of course, the validity of this calibration method requires that one ensures a good selection of the correct internal standard. For this purpose it is possible to resort to chemometric methods [16].

An alternative to quantitative analysis by ICP-MS is **semiquantitative analysis**, which is generally considered as a rapid multielement survey tool with accuracies in the range 30–50%. Semiquantitative analysis is based on the use of a predefined response table for all the elements and a computer program that can interpret the mass spectrum and correct spectral interferences. This approach has been successfully applied to different types of samples. The software developed to perform semiquantitative analysis has evolved in parallel with the instrumentation and, today, accuracy values better than 10% have been reported by several authors, even competing with typical ones obtained by quantitative analysis. The development of a semiquantitative procedure for multielemental analysis with ICP-MS requires the evaluation of the molar response curve in the ICP-MS system (variation of sensitivity as a function of the mass of the measured isotope) [17]. Additionally, in the development of a reliable semiquantitative method, some mathematical approaches should be employed in order to estimate the ionisation conditions in the plasma, its use to correct for ionisation degrees and the correction of mass-dependent matrix interferences.

1.3.2.2 Interferences in ICP-MS

Spectroscopic interferences have been recognised as one of the main limitations of the most often used quadrupole-type ICP-MS since its initial development. Such interferences, which appear when an interfering species has the same nominal m/z as the analyte, may be subdivided as follows.

1. *Isobaric overlaps* appear when isotopes of different elements have the same nominal mass. Many of them can be overcome by choosing an alternative less interfered isotope of the element of interest, although a sacrifice in sensitivity may result.

2. Some elements in the low mass range, such as Ce and Ba, have second ionisation potentials low enough to yield significant quantities of *doubly charged* ions. In general, mass resolutions between 2000 and 10 000 are required to separate them.
3. *Molecular (polyatomic) ions* are the main source of spectral overlaps in ICP-MS. Ions from the plasma gas (such as Ar^+ and Ar^{2+}) can result in spectral overlaps with $^{40}Ca^+$ and $^{80}Se^+$, respectively. Acids used to digest and preserve samples can also result in intense signals from molecular ions that can overlap with major isotopes of some elements (*e.g.* $^{15}N^{16}O^+$ from HNO_3 has the same nominal mass as $^{31}P^+$). Molecular oxides formed from elements present in the sample are also common. Polyatomic interferences are more difficult to correct for, as they are less predictable because they depend on the abundance of at least two isotopes and also depend strongly on the sample (analytes and matrix) and the operational parameters of the ICP-MS system.

Some of the most prominent spectral interferences can be resolved with a resolution from 4000 up to 10 000, depending on the analytical problem. It can be tempting to calculate the resolution necessary to resolve two masses based only on their exact masses and the specified resolving power of the instrument. However, the resolution required will depend on the relative magnitude of the spectral overlap and analyte ion signals. For example, to resolve the overlap of $^{37}Cl^+$ and $^1H^{36}Ar^+$, a resolution of 3900 would be sufficient when considering the exact masses alone. However, as can be seen in Figure 1.10, a resolution of 10 000 is needed to provide baseline resolution of the two peaks (because the $^1H^{36}Ar^+$ ion is much more intense).

ICP-MS instruments based on a quadrupole mass analyser typically provide a mass resolution not better than 0.6 mass units, clearly insufficient for many applications. The development of high-resolution ICP-MS, in the late 1980s, made it possible to resolve analytes from interferences using a double-focusing instrument on the basis of a magnetic and an electric sector field. Additional time is required to acquire these data, but the chances of overlooking a potential overlap are greatly diminished. High mass resolution is one of the most important features of double-focusing instruments, but not the only one. When working at 'low' resolution, they also show a higher sensitivity, as compared with quadrupole devices, and have much lower background noise. However, the trade-off for increasing resolution in sector-based mass spectrometers is a decrease in sensitivity. Typically, the sensitivity decreases by at least a factor of 6–8 when the resolution is increased from 4000 to 10 000.

Although this technology is effective in resolving a wide range of polyatomic interferences, the increased cost associated with this type of instrumentation (more than twice the price of a quadrupole instrument) limits its use in most routine laboratories, hence alternative methods of interference reduction have been sought for. The use of chemical extraction and chromatography (in order to separate the analyte from the matrix prior to analysis) or the operation of the ICP-MS under so-called 'cool plasma' conditions, allows the elimination of

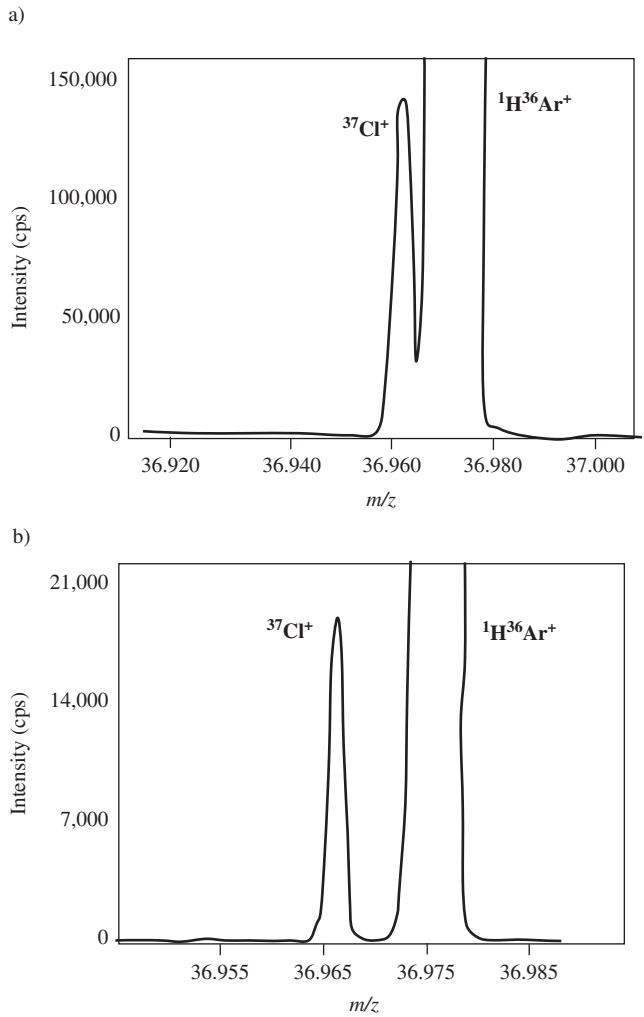

Figure 1.10 Mass spectra near $^{37}Cl^+$. (a) Resolution of 4000 (signal of peak $^1H^{36}Ar^+$ about 20 000 000 cps). (b) Resolution of 10 000 provided by sector-based mass spectrometer (signal of peak $^1H^{36}Ar^+$ about 3 000 000 cps).

many polyatomic ion interferences. However, several drawbacks still remain with these modes of operation: they are sometimes difficult to optimise and are suitable for only a few interferences.

More recently, the advent of the collision/reaction cell technology has revolutionised commercial quadrupole ICP-MS systems. A gas, such as hydrogen, helium or ammonia, is introduced into the reaction cell (placed inside the mass spectrometer and preceding the analyser quadrupole), where it reacts and dissociates or neutralises the polyatomic species or precursors. Through collision and reaction with appropriate gases in a cell, interferences

such as $^{40}Ar^{+}$ can be almost completely eliminated while leaving analyte ions (*e.g.* ^{80}Se) relatively unaffected.

However, often these possibilities are not available or not applicable, due to either a lack of appropriate technology or financial or personnel constraints. Alternatively, we could also apply a wide variety of multivariate methods and chemometric approaches to correct or minimise for ICP-MS spectral interferences (some of them are referred to in Chapter 2, when discussing experimental design and optimisation), particularly when the ratio of overlap ion signal to analyte ion signal is not too large. The general mathematical strategy to correct for isobaric interferences in atomic mass spectrometry is subtraction on the contribution of interfering isotopes from measurements of non interfering isotopes. In the case of polyatomic interferences from two or more species on a particular mass, the chemometric approaches require consideration of correction factors calculated using the natural isotope abundances of the atoms from which the interference is formed. In such a situation, the complexity of the mathematical approach is high. In the following chapters different tools will be introduced that can be applied in order to solve this problem of ICP-MS (*e.g.* multivariate methods, which have been applied by several authors for the correction of spectral and non-spectral interferences [18]).

1.3.3 Isotope Ratio Measurements and Their Applications

The scope of isotopic analysis is extremely wide nowadays and natural or induced variations in the isotopic composition of target elements are being investigated for several purposes, including bioavailability studies, nuclear chemistry, age determinations and environmental, geological and clinical applications. Precise and accurate isotope ratio measurements have traditionally been carried out by thermal ionisation mass spectrometry (TIMS). However, the capability of ICP-MS (a technique that is easier to handle, with a higher sample throughput and widespread availability) to provide isotopic elemental information permits not only the determination of isotopic ratios but also the use of isotope dilution and its corresponding improvement in accuracy (of special interest for quantification purposes). Also, isotopic patterns are extremely useful in ICP-MS to confirm the identity of sought-for elements.

As the precision of the ICP-MS isotope ratio is poor compared with the precision using TIMS, the range of applications for ICP-MS have traditionally been limited to measuring induced changes in the isotopic composition of a target element (for example, to calibrate by means of isotope dilution). However, the introduction of multicollector ICP-MS systems to enhance precision and accuracy in isotopic analysis opened up novel applications.

1.3.3.1 Precision and Accuracy in Isotope Ratio Measurements by ICP-MS

When performing accurate isotope ratio measurements with ICP-MS, the following issues should, at least, be considered.

Required precision. This will lead you to the instrument you need. Quadrupole ICP-MS is easy to use, robust and relatively inexpensive. In general, these instruments permit good precision of isotopes ratio measurements ranging from 0.1 to 0.5%. Applying high-resolution ICP-MS precision in isotope ratio measurements can generally be improved by a factor of 5–10 (mainly because of the flat-topped peak shapes and fewer spectral overlaps obtained with these high-resolution instruments). Multicollector ICP-MS systems increase precision due to the collection of all isotopes of interest simultaneously in a multicollector array and so they provide an opportunity to measure the isotopic composition of many elements more accurately than other ICP-MS instruments.

Spectroscopic interferences. These can affect the ion intensity of an isotope and, therefore, the isotope ratio measurement. One would try to minimise such interferences by resorting to any of the techniques and technologies, and also the mathematical correction strategies, described in the previous section.

Mass discrimination. In ICP-MS devices, ions of different mass-to-charge ratios are transmitted with different efficiencies and therefore the instrument produces different responses for ions of different masses. This systematic error is called mass discrimination. Typically, the mass discrimination for ICP-MS instruments is about 1% per mass unit (at mass 100). As the ion kinetic energy is dependent on the mass, any energy-dependent process in the instrumentation (*e.g.* sampling of ions from the ICP, transfer of ions, mass separation and ion detection) will contribute to the mass discrimination. Accurate isotope ratio measurements require mathematical corrections for mass discrimination. External calibration is frequently used, offering sufficient accuracy. For this, isotopic reference materials with known isotopic composition or samples in which the element has a known natural isotopic composition are used. The correction factor for mass discrimination (the so-called K-factor) can be easily calculated based on the 'true' value (given by the certified isotope ratio) and the 'observed' value (that is, the measured isotope ratio including the bias caused by mass discrimination). However, with reduced uncertainty (*e.g.* using a multicollector ICP-MS instrument), complex mathematical models should be used for appropriate mass discrimination correction.

Detector dead time. This is the time required for the detection and electronic handling of an ion pulse. If another ion strikes the detector surface within the time required for handling the first ion pulse, the second ion will not be detected and, hence, the observed count rate will be lower than the actual value. If this is not corrected for, inaccurate isotope ratio results will be reported. In ICP-MS, several mathematical methods should be applied for its evaluation and correction.

Data acquisition parameters. Precision and accuracy in the measurement of isotope ratios can be improved if the number of measurements is increased (*e.g.* if the measurement time is increased). Various measurement protocols can be applied and those whereby the time actually spent on measuring the isotope ratios of interest is maximised are preferable. The data acquisition parameters of an ICP-MS device that can be changed to improve the isotope ratio precision

are the integration time (dwell time) per acquisition point, the number of acquisition points per spectral peak and the number of sweeps, among others. Many of these parameters have been optimised using chemometric approaches. Many examples will be given in Chapter 2. The measurement time can sometimes be used more efficiently by increasing the acquisition time for the less abundant isotope(s) relative to that of the most abundant isotope(s). Finally, simultaneous monitoring of all the isotopes is performed in multicollector ICP-MS instrumentation, which results in a superior isotope ratio precision, similar to that offered by state-of-the-art TIMS. A multicollector ICP-MS system is operated in a static mode during the measurements, which means that neither the accelerating field nor the strength of the magnetic field is changed during data acquisition.

1.3.3.2 Isotope Dilution Analysis

Inductively coupled plasma isotope dilution mass spectrometry (ICP-IDMS) is a well-known analytical technique based on the measurement of isotope ratios in samples where their isotopic composition was altered by the addition of a known amount of an isotopically enriched element.

ICP-IDMS has high potential for the routine analysis of trace elements if accuracy is of predominant analytical importance [19]. In contrast to other calibration approaches, IDMS does not directly suffer from long-term changes or drifts in instrument sensitivity. Moreover, provided that isotopic exchange between the sample and spike is ensured, losses of analyte do not affect the analytical results. Additionally, IDMS can also be used to prevent the final analytical result being affected by analyte losses during sample pretreatment.

In the last few years, we have seen the application of isotope dilution methodologies to some new analytical fields. One of these is 'elemental speciation', where the aim is to determine individual chemical species in which an element is distributed in a given sample. IDMS has also proved its usefulness in element speciation, in which either species-specific or species-unspecific spikes can be used. For example, species-specific IDMS is nowadays used in several laboratories as an effective tool to validate analytical procedures for speciation and to investigate and document eventual interconversion between species. In addition, the study of induced variations in the isotopic composition of a target element can also provide insight into various (bio)chemical and physical processes; isotopic analysis is, therefore, also of increasing importance in biological studies.

The principle of isotope dilution analysis is surprisingly simple. It relies on the intentional alteration of the isotope abundance of an endogenous element in a given sample by the addition of a known amount of an enriched isotope of the same element (spike). Therefore, the element to be analysed must have, at least, two stable isotopes that can be measured free of spectral interferences in a mass spectrometer. This principle is illustrated in Figure 1.11 for an element containing two different isotopes, a and b. As can be observed, the a isotope is the most abundant one in the sample whereas the spike is isotopically enriched in the b isotope. It is clear that the abundances of the two isotopes

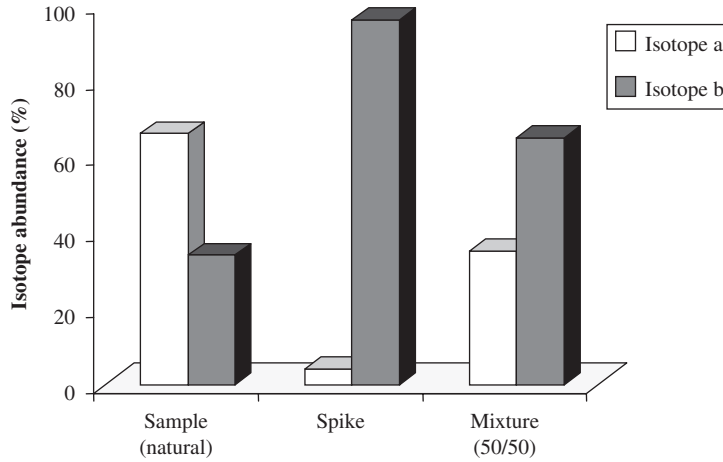

Figure 1.11 Illustration of the principle of isotope dilution analysis for an element containing two different isotopes (a and b).

and, hence, the isotope ratio in the mixture will be intermediate between those in the sample and the spike and it will depend both on the amount of spike added and on the initial amount of the element in the sample. These relationships can be expressed mathematically using the isotope dilution equation, which can be written in different forms depending on the complexity of the application [20].

IDMS is based on measurements of masses and isotope ratios only. Some important advantages, compared with other calibration strategies, such as external calibration and standard additions, are that instrumental instabilities such as signal drift and matrix effects will have no influence in the final concentration in the sample, high accuracy and small measurement uncertainties are enabled, possible loss of substance of the isotope-diluted sample will have no influence on the final result and there is no need to resort to an external instrumental calibration or standard additions to the sample.

Isotope dilution analysis is now internationally regarded as a reference or highly qualified primary method thanks to all these advantages.

1.4 Flow Systems with Atomic Spectrometric Detection

The coupling between flow injection (FI) systems and atomic spectrometric detectors is a strategy now well established for inorganic elemental analysis. Flow injection analysis (FIA) is a powerful, convenient analytical tool highly suitable for automating sample pretreatment, which is often required before measuring by atomic spectrometry (including sampling dissolution and/or dilution, matrix removal, preconcentration, *etc*.). Additionally, flow manifolds can simplify the well-known problem of sample introduction to atomisers or

even reduce/minimise interferences (*e.g.* by coupling on-line separation techniques before the detector). All these facts explain the great importance of FI systems as practical troubleshooters when coupled to atomic spectrometric detectors.

1.4.1 Flow Injection Analysis and Atomic Spectrometry

The basics of an FI experiment are very simple. A discrete volume of a sample is injected into a continuous liquid stream. The sample becomes mixed with the carrier stream by a number of processes collectively known as 'dispersion' and is conducted to the detector, where the analyte is monitored on-line. Some reagents can also be added to the FI system and merged with the sample (before arriving at the detector) at a confluence point (they perform sample conditioning, analyte derivatisation, *etc.*). As a result of the dispersion processes involved in an FI manifold, the concentration–time profile of the analyte at the detector results in a peak. Depending on the experimental conditions, the peak may be skewed or may be close to a symmetrical Gaussian shape. The design of an FI system requires consideration and optimisation of different operational parameters, many of them interrelated, by using appropriate chemometric tools (*e.g.* the simplex method). Examples will be given in Chapter 2.

Flow systems are developed mainly for liquid samples and their complexity can range from simple to very complex manifolds to deal with ultratrace amounts of the target analyte in complex matrices, which often require on-line separation/preconcentration steps. As a wide variety of chemical manipulations can be carried out in an FI manifold, the scope of the FI applications is enormous. Not only liquid samples, but also both gas and solid samples, can be also introduced into the liquid flow manifold if special adaptations are made. Gas samples simply require impermeable tubing. Solids can be either introduced into the system and leached with the help of auxiliary energy (*e.g.* ultrasound) or introduced as slurries.

Concerning the requirements of the detector, it is important to stress that interfacing a detector with an FIA system yields transient signals. Therefore, desirable detector characteristics include fast response, small dead volume and low memory effects. FI methods have been developed for UV and visible absorption spectrophotometry, molecular luminescence and a variety of electrochemical techniques and also for the most used atomic spectrometric techniques.

A large part of the success of the combination of FI and atomic spectrometry is due to its ability to overcome interference effects. The implementation of some pretreatment chemistry in the FI format makes it possible to separate the species of the analyte from the unwanted matrix species (*e.g.* by converting each sample into a mixture of analyte(s) and a standard background matrix, designed not to interfere in the atom formation process and/or subsequent interaction with radiation in the atom cell). Often such separation procedures result also in an increased analyte mass flux into the atom source with subsequent improvements in sensitivity and detection limits.

In general, FI procedures are used in conjunction with atomic spectrometry for any of the following purposes:

1. The use of discrete sample volumes to provide improved tolerance of the detector to dissolved solids, organic solvents and sample viscosity. FI provides on-line dilution and a suitable means of handling slurried samples.
2. Retention of the analyte on a solid-phase extractant, followed by dissolution in a clean matrix (such as dilute nitric acid) to remove interferences and preconcentrate the analyte.
3. To implement an easy and automated means for chemical vapour generation procedures (hydride generation for arsenic, selenium, *etc*., and cold vapour mercury), which allows for a reduction on the interferences caused by first-row transition metals (such as copper and nickel). FI methods may be readily coupled with almost all the atomic-based spectroscopic techniques (including graphite furnace atomisers).
4. Manifolds have been described for the addition of internal standards in order to automate the standard additions method.
5. In addition to solid-phase extraction and chemical vapour generation, other sample pretreatment procedures (including liquid–liquid extraction, precipitation, dialysis and even distillation) can be automated and coupled to the spectrometer.

In principle, all these capabilities will enhance the performance of any type of atomic spectrometry, independently of the nature of the spectroscopic technique used (*e.g*. a procedure that separates trace elements from a large volume of a highly saline medium and releases them into a smaller volume of dilute nitric acid can be used in conjunction with any type of spectrometer).

Nowadays, the outstanding advantages of using flow manifolds as sample preparation systems for atomic detectors have been demonstrated for a variety of techniques. Characteristic examples of the instrumentation required and typical applications are presented in a comprehensive monograph dedicated to FI and atomic spectrometric detectors [21].

1.4.1.1 Coupling FI Systems to Atomic Detectors

The on-line interface of flow manifolds to continuous atomic spectrometric detectors for direct analysis of samples in liquid form typically requires a nebuliser and a spray chamber to produce a well-defined reproducible aerosol, whose small droplets are sent to the atomisation/ionisation system. A variety of nebulisers have been described for FAAS or ICP experiments, including conventional cross-flow, microconcentric or Babington-type pneumatic nebulisers, direct injection nebuliser and ultrasonic nebulisers. As expected, limits of detection have been reported to be generally poorer for the FIA mode than for the continuous mode.

Alternatively, one can resort to the introduction of analytes as gaseous derivatives, which offers special advantages in atomic detection (*e.g.* improved detection limits, reduction of matrix effects and simplicity of the coupling to the atomic detector). Flow injection is a particularly useful procedure for the implementation of chemical vapour generation (CVG) methods. These procedures are based on the generation of a volatile chemical derivative of the species of the analyte (*e.g.* conversion of an analyte to its hydride, often by means of a tetrahydroborate reduction), removal of the generated volatile species from solution to the gaseous phase (by a gas–liquid separation device) and transport of the released compound by a carrier gas flow to the atomiser/detector. In terms of the number of analyses performed by CVG, the determination of mercury by the generation of the monatomic elemental vapour is by far the most widely used procedure. However, considerable attention has been also paid to the generation of the volatile species of arsenic, selenium and cadmium. For CVG in a typical flow system, a constant flow of sample solution is mixed with a constant flow of reducing solution (*e.g.* tetrahydroborate) and of the purge gas. Liquid and volatile generated gaseous species are then separated in a gas–liquid separator yielding two outlet flows. The gaseous analyte with hydrogen and purge gas flows to the atomiser/detector, while the liquid effluent is drained. Clearly, many different experimental parameters should be optimised in this design (*e.g.* the nature and concentration of the reducing reagents, the liquid flows of sample and reagents, the flow of the carrier gas or the nature of the gas–liquid separator), in order to ensure efficient generation of the volatile analyte and its transport to the spectrometer. Again, as multiple variables should be optimised (many of them interdependent), multivariate optimisation methods are critical. An important aspect of the FI–CVG procedure is that after appropriate optimisation of the experimental setup, certain interferences can be minimised.

Flow systems for volatile analyte generation have also been coupled to other atomic excitation sources for optical emission, atomic fluorescence and mass spectrometric detection (*e.g.* ICP-OES, ICP-MS, AFS, MIPs and AAS). Using this approach, it is possible to trap the volatile analyte hydride in the interior of a graphite furnace, thereby allowing a preconcentration prior to atomisation. Hydride generation is also a powerful tool for the elimination of matrix interferences in ICP-QMS. As a typical example, by using on-line flow hydride generation coupled to ICP-QMS, the sensitive determination of Se in biological or environmental matrices can easily be carried out, avoiding most of the isobaric interferences typically present on several of its most abundant isotopes.

Finally, we should consider that the intrinsic discontinuous nature of the ETAAS technique has limited the interest in interfacing basic continuous flow manifolds to this detector. However, several flow approaches offer special attraction for their combination with ETAAS, particularly:

- separation and preconcentration by on-line column sorption and solvent extraction;

- formation of volatile derivatives of the analyte and their preconcentration on a graphite tube;
- slurry sampling.

1.4.1.2 FIA Strategies for Calibration and Standardisation in Atomic Spectrometry

The contribution of flow analysis to improving the performance of atomic spectrometry is especially interesting in the field of standardisation. FIA can provide a faster and reliable method to relate the absorbance, emission or counts (at a specific mass number) to the concentration of the elements to be determined. In fact, flow analysis presents specific advantages to solving problems related to the sometimes short dynamic concentration ranges in atomic absorption spectrometry, by means of on-line dilution. The coupling of FI techniques to atomic spectrometric detectors also offers tremendous possibilities to carry out standard additions or internal standardisation.

However, it is worth noting that the basic advantage provided by FIA to atomic spectrometry is the ability to provide data on different wavelengths or mass numbers as a function of time for the same sample or standard injected, comparable to hyphenated gas chromatography–mass spectrometry (GC–MS) or two-dimensional nuclear magnetic resonance techniques. In this respect, the systems are unaffected by multiple spectral interferences which have no real detrimental effect on calibration apart from decreased signal averaging. Standardisation is theoretically still possible by a second-order standard additions method when matrix effects are present in the samples, provided that different instrumental responses are obtained for a standard solution of an analyte and a solution of the same analyte in the presence of other matrix compounds. Appropriate mathematical methods should be employed for such second-order calibration, simply by treating the signal as a function of time or introducing simple non-chromatographic separation methods based on FI principles.

1.4.2 Chromatographic Separations Coupled On-line to Atomic Spectrometry

In the past, most analytical problems related to environmental or biological systems were addressed by measuring the total concentrations of the elements. However, at present, there is an increasing awareness of the importance of the chemical form in which an element is present (*e.g.* the oxidation state, the nature of the ligands or even the molecular structure) since its chemical, biological and toxicological properties critically depend on it. Hence there is a clear need for rapid and robust analytical tools to perform chemical speciation, and atomic spectroscopy is undoubtedly one of the most important tools for such studies.

Many analytical strategies and methods have been described for elemental speciation. However, the so-called hyphenated (coupled or hybrid) techniques,

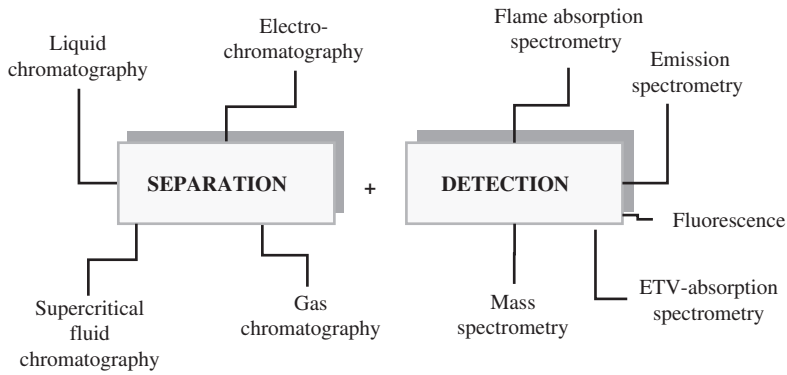

Figure 1.12 Species-selective hyphenated techniques for speciation analysis.

consisting in the on-line coupling of an efficient separation technique [such as GC, high-performance liquid chromatography (HPLC) or, more recently, electrophoresis] with a sensitive and element-specific atomic detector (usually an atomic absorption, emission or mass spectrometer) have become a fundamental tool for speciation analysis [22]. Some of the hyphenated techniques available for species-selective analysis in biological and environmental materials are summarised schematically in Figure 1.12. The choice of the hyphenated technique depends primarily on the objective of the research. In addition, speciation analysis in environmental and/or biological samples faces two main challenges because of the usually low concentrations of the analytes (below $1\,\mu g\,g^{-1}$) and the complexity of the matrix itself.

The success of an analytical speciation approach depends critically on the achievement of a good separation between the different species of the element. The chromatographic technique should guarantee that each signal corresponds to only a particular species. Despite the need for thermally stable and volatile analytes, GC remains the preferred sample introduction technique for the time-resolved introduction of analytes into an atomic spectrometer thanks to its high resolution and sensitivity, caused by the quasi-100% sample introduction efficiency and virtually no energy losses for the vaporisation and desolvation of the mobile phase. Although not so advantageous as GC in terms of detection limits and resolution, HPLC and capillary electrophoresis (CE) are the common choice for sample introduction into a plasma to determine species that either are non-volatile by themselves or that cannot be volatilised by a derivatisation reaction. The wide variety of separation mechanisms and mobile phases that preserve the species identity and also the coupling simplicity (in particular, the compatibility of the mobile phase composition and flow rate) to accepted standard nebulisers made HPLC–ICP-MS coupling an established procedure.

The choice of the detector becomes crucial when the concentration of analyte species in the sample is very low and low limits of detection are required. For element-specific detection, the major atomic spectrometric techniques, flame AAS, OES, AFS and ICP-MS, are specially suited as chromatographic

detectors. An important problem when coupling the separation technique to the atomic detector consists on interfacing the chromatographic system and the atomic spectrometer, as the separation conditions may not be compatible with those required by the detector in terms of flow rate and the mobile phase composition. Usually, chromatography and spectrometry can be coupled on-line. However, the preference for a highly sensitive discrete atomisation technique such as electrothermal vaporisation (ETV) with atomic absorption spectrometric detection (ETAAS) or with ICP-MS detection may justify off-line coupling.

On-line coupling between a gas chromatograph and an atomic spectrometry detector is fairly simple. Typically, the output of the CG capillary column is connected to the entrance of the atomisation–ionisation system simply via a heated transfer line. When separation is performed by liquid chromatography (LC), the basic interface is straightforward: a piece of narrow-bore tubing connects the outlet of the LC column with the liquid flow inlet of the nebuliser. Typical LC flow rates of 0.5–2 ml min^{-1} are within the range usually required for conventional pneumatic nebulisation.

HPLC–AAS was the first hyphenated technique employed to determine metal–protein complexes. Although AAS is not a truly multielement technique, some instruments can measure up to four elements simultaneously, which is sufficient for a number of practical speciation applications. FAAS can be coupled with HPLC directly. This technique is compatible both with the flow rates and with the mobile phase composition (including organic solvents) commonly used in HPLC. Main applications include AAS detection of complexes with metals that yield intense responses in AAS (Cd, Zn, Cu) and species that can be converted on-line into volatile hydrides (*e.g.* As, Se, Cd). ETAAS is more sensitive than FAAS but its coupling is not so straightforward. The off-line ETAAS analysis of metallothionein-bound metals by fraction collection after HPLC separation has been a common approach. Use of an autosampler and flow-through cells allows for a high degree of automation, leading to a quasi-on-line coupling.

Microwave-induced plasma optical emission spectrometry (MIP-OES) is very sensitive for volatile species containing metals. Hence its use has been also proposed as a detector in the development of hyphenated techniques for speciation. GC–MIP-OES has been successfully applied for the speciation of alkylmetal species of low molecular weight (Hg, Sn and Pb compounds) in many different environmental applications [23].

Because MIPs are formed at low temperatures, liquid samples cannot be introduced because they extinguish the plasma, even small amounts of organic vapour. However, the on-line coupling of HPLC to MIP-OES has been described for the speciation of mercury and arsenic compounds. Continuous cold vapour (CV) or hydride generation (HG) techniques were used as interfaces between the exit of the HPLC column and the MIP, held in a surfatron at reduced pressure [24].

When ultrasensitive detection is required, ICP-MS is virtually the only technique capable of coping, in an on-line mode, with such trace element

concentrations. Due to the multielement capability and high sensitivity of ICP-MS, along with the possibility of measuring different isotopes of a given element, its coupling to high-resolution separation techniques is well recognised as one of the most powerful tools for elemental speciation. HPLC and GC couplings are especially simple since the gas or liquid flows can be directly introduced into the ICP torch with only slight disturbances of the plasma, without any splitting or dilution process. In contrast, CE requires sophisticated interfaces and nebuliser systems in order to coupling it to an ICP-MS.

In addition, the isotope specificity of ICP-MS offers a still underexploited potential for improved accuracy when quantifying via the use of isotope dilution techniques. The application of isotope dilution analysis (IDA) in elemental speciation allowed for the development of highly accurate and precise quantification approaches for the determination of a wide range of elemental species even when analysing complicated matrices [25]. When several species of the same element need to be analysed, each compound can be enriched in a different isotope of the element, opening up a unique capability for quantification: multiple spiking species-specific IDA. Resorting to this powerful approach requires rather complex mathematical treatments. In fact, depending on the availability of the isotopically enriched species and the complexity of the speciation problem, a more or less sophisticated and specific mathematical approach must be developed to quantify the processes and, finally, the concentrations [26].

In all these hyphenated techniques, many different experimental parameters affecting the chromatographic separation, the interface and the detector should be carefully optimised. The use of mathematical approaches for adequate optimisation and development of the hyphenated systems is unavoidable (see Chapter 2 for many examples).

1.4.3 Detection of Fast Transient Signals

When discrete amounts of analyte (sample) are carried into a stream of a flowing fluid (a gas or a liquid carrier), analyte signals do not reach a steady state and transient time-dependent signals are obtained. Data acquisition is a discontinuous process which can be characterised by the number of data collected per unit time (acquisition frequency) and the time spent sampling each datum (sampling period). The acquisition frequency must be adapted to the signal to be sampled; too low a frequency can result in a loss of information, too high a frequency can overload the system without improving the measurements. The adjustment of such parameters is of particular importance when detecting transient signals.

Transient signals are typically obtained in atomic spectrometry when samples are introduced by flow injection techniques or when the spectrometer is used as an element-specific detector in hyphenated techniques. Inductively coupled plasma mass spectrometry has nowadays become the detection technique of choice for multielement-specific detection in speciation as it allows multielemental

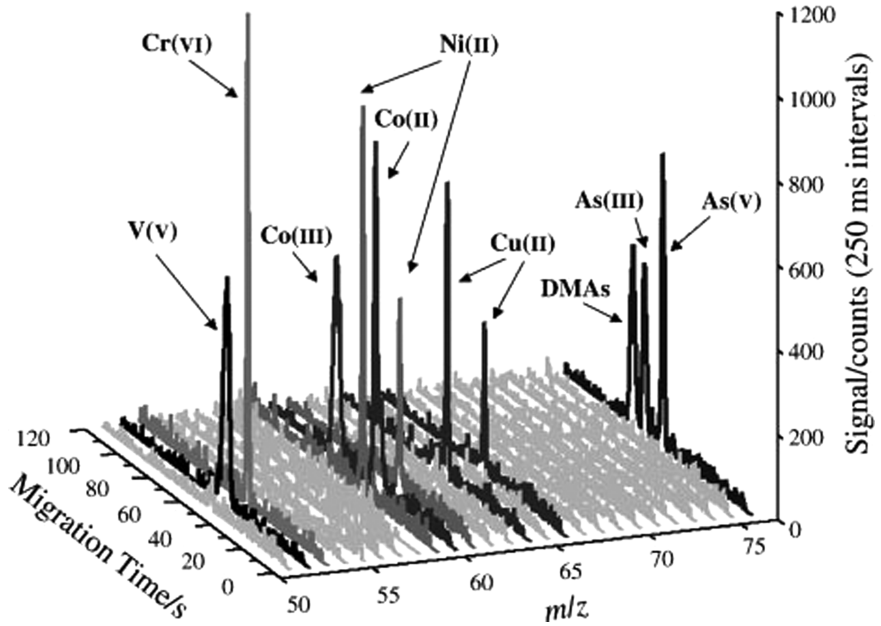

Figure 1.13 CE-ICP-TOFMS separation and multielemental detection of V(V), Cr(VI), Co(II), Co(III), Ni(II), Cu(II), As(V), As(III) and DMAs cyanide complexes. Reproduced from J. M. Costa, N. Bings, A. Leach and G. M. Hieftje, *J. Anal. At. Spectrom.*, 2000, **15**, 1063–1067, with permission.

analysis in a great variety of sample types and is virtually the only technique capable of achieving the stringent detection limits required in most practical cases.

When using ICP-MS as an elemental detector in hyphenated techniques, simultaneous detection of more than one analyte in the short transient signals generated by the chromatographic separations is typically required (*e.g.* see Figure 1.13). In such a situation, data acquisition parameters play a crucial role to enhance the detection limits and also the precision and accuracy. The same applies to isotope and isotope ratio measurements made using transient signals. Data acquisition in such systems is controlled by the number of points or channels per spectral peak, the number of sweeps (the number of scans along the mass spectrum to obtain a single reading) and the dwell time (the time spent counting ions per channel). It is essential to optimise those parameters carefully, which depend on the nature of the ICP-MS system, the nature of the transient signal (duration and intensity) and the number or isotopes to be monitored simultaneously. To obtain a reliable profile of the transient signals, it is common practice to work in the peak hopping mode using a single point per mass, one sweep per reading and a dwell time shorter than 100 ms.

Hyphenation between a chromatographic separation system and an ICP mass spectrometer often leads to transient signals of very short duration (from

less than 5 s for GC up to about 60 s for LC). However, the best precision for the measurement of isotope ratios by ICP-MS is obtained using steady-state signals of several minutes or even longer, instead of short transient signals. Thus, the simplification of the sample preparation procedure achieved by the on-line coupling of a separation technique may be offset by a reduction in precision resulting from measurements made on short transient signals.

The common mass spectrometers used in ICP-MS today are scanning-based analysers, such as the quadrupole mass filter (ICP-QMS). Unfortunately, they suffer from important performance limitations when used as detectors of short transient signals (*e.g.* those generated in speciation analysis) derived from their inability to perform true simultaneous multielemental analysis. With scanning-based instruments, individual mass-to-charge ratios are measured in a sequential mode, from one isotope to the next. As a result, some difficulties (in terms of precision, sensitivity or accuracy of isotopic and isotope ratio measurements) are expected when fast transient or time-dependent signals (such as those produced by electrothermal vaporisation, laser ablation, chromatography or capillary electrophoresis) are used to determine a large number of analytes in a single peak.

The precision attainable in ICP-MS is limited by counting statistics and can be improved by increasing the integration time, which implies increasing the dwell time and/or the number of sweeps. For a fixed number of sweeps, increasing the dwell time is beneficial in reducing noise and hence improving limits of detection, although the number of points per peak is also reduced and the peak profile may not be described properly. Furthermore, the multielemental nature of ICP-MS adds another level of complexity to the monitoring of transient signals, because the number of readings has to be distributed between the different isotopes measured. This means that the mass range ratio of an analysis can be increased only by sacrificing sensitivity and precision. Furthermore, the measurement of sequential m/z values at different points within the time-dependent concentration profile of a transient signal can result in peak distortions and quantitation errors commonly referred to as 'spectral skew'. Finally, non-simultaneous ion extraction in scanning mass analysers hampers the use of ratioing techniques to reduce multiplicative noise associated with sample introduction and plasma fluctuation.

To minimise these shortcomings of scanning ICP-MS instruments, important efforts have been made to investigate other types of mass analysers. Particularly, time-of-flight mass spectrometry (TOFMS) should be well suited for the measurement of time-dependent transient signals [27]. In TOFMS spectrometers, all m/z values are extracted simultaneously (as a packet of ions) for mass analysis so that the 'spectral skew' usually associated with the measurement of transient signals is eliminated (see Figure 1.14). It has been pointed out that simultaneous ion extraction compensates for the effects of drift and multiplicative (flicker) noise components in the source by using ratioing techniques. Not surprisingly, ICP-TOFMS has been used already for multielemental detection in transient signals derived from several hybrid techniques, including CE and GC, for speciation purposes. A comparison between the performance

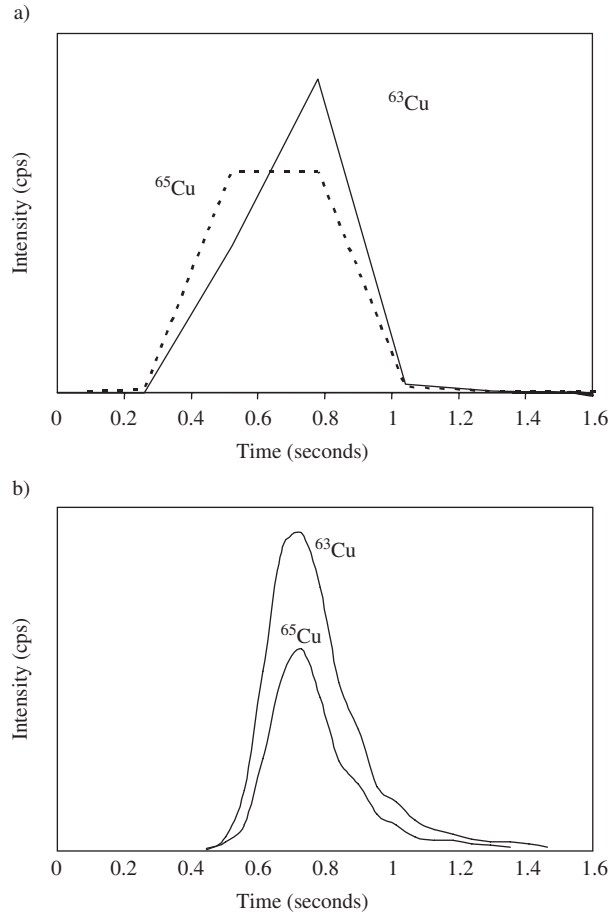

Figure 1.14 Transient signals for ^{63}Cu and ^{65}Cu produced by an electrothermal vaporization device and detected with (a) a quadrupole-based ICP-MS instrument and (b) a ICP-TOFMS instrument, when five isotopes were measured simultaneously.

of different ICP-MS systems (based on quadrupole and TOF mass analysers) [28] demonstrated that the best precision in isotope ratio measurements was obtained using ICP-TOFMS when transient signals faster than 8 s FWHM were monitored or when the number of isotopes to be measured was above 15. Conversely, the quadrupole mass analyser offered similar precision to ICP-TOFMS for transient signals of about 10 s or more, even when 25 isotopes were measured. In such measurements, the accuracy using a TOF mass analyser was slightly superior to that observed using an ICP-QMS instrument, probably as a result of the sequential nature of the Q-mass analyser.

However, the main limitation of ICP-TOFMS at present is, perhaps, its comparatively low sensitivity: detection limits for ICP-TOFMS are roughly one

order of magnitude poorer than those reported for ICP-QMS, monitoring a single m/z under similar conditions [28]. On the other hand, as speciation of too many elements in a single chromatographic (or electrophoretic) peak is seldom needed, it appears that the ICP-QMS stands up in a general comparison for speciation analysis purposes.

As discussed above, ICP-IDMS is becoming a highly valuable method for trace element and element-speciation analysis. For ICP-IDMS the highly precise and accurate isotope ratio measurements that are currently required can be made by resorting to multicollector-ICP-MS.

The main limitation of ICP-IDMS is that isotope ratio measurements in transient signals generated by hyphenated techniques suffer from significant drifts. The main source of bias in the measured isotope ratios is in the ICP–MS (and not in the chromatographic separation) [29]. When the precision of the hyphenated chromatography–multicollector-ICP-MS method is compared with those of other quadrupole ICP-MS-based techniques, it can be clearly stated that this approach is more powerful than any quadrupole-based method which detects the ions sequentially. However, even using multicollector-ICP-MS as an element-specific detector, the precision of isotope ratio measurements in such transient signals, compared with the results from continuous sample introduction, is reduced by about one order of magnitude [29].

All isotope ratio measurements have to be corrected for instrumental mass bias by normalising to an invariant isotope of the same element (internal correction) or, whenever the internal approach cannot be applied, to a well-characterised isotope standard material (external correction). However, the external correction method requires the mass discrimination of an element being identical for the sample and the standard, which is not always the case. A large benefit of the hyphenated chromatography–ICP-MS system is that all measurements of standards and real samples can be carried out with exactly the same matrix – the eluent of the HPLC system.

1.5 Direct Analysis of Solids by Spectrometric Techniques

Advantages brought about by the direct analysis of solid samples as compared with the analysis of dissolved samples include a shorter total analysis time (prior dissolution steps are not required), low cost (chemical reagents are not used), less risk of contamination and less destruction of the sample. In addition, some techniques can extract information about chemical speciation (*e.g.* XPS provides information about oxidation states and chemical bonds) and spatial composition, *i.e.* information with lateral resolution allowing mapping of the surface and analysis with depth resolution, of particular interest for thin-film analysis.

A few representative and widely used techniques based on optical and mass spectrometry for direct solid analysis have been selected for further explanation here. As was stated in the introductory section (see Section 1.1), analytical

techniques based on electron spectroscopy, although offering high interest for surface identification, will not be described in this chapter.

1.5.1 Elemental Analysis by Optical Spectrometry

Very often, techniques for direct solid analysis are classified into two groups according to whether they provide bulk information (of interest for homogeneous samples) or analytical information with lateral and/or depth resolution.

1.5.1.1 Bulk Analysis Techniques

Spark-source optical emission spectrometry (SS-OES) and XRF are well-established routine techniques, providing bulk information, which play an important role nowadays in industrial process monitoring (raw materials and final products). Whereas SS-OES is clearly an atomic technique, where atoms are formed directly from the solid sample by virtue of the high energy of an electrical spark, the inclusion of XRF among the atomic techniques deserves some explanation. In this latter technique, the sample is investigated for its composition at room temperature and so atoms are not formed during the analysis. In XRF, a primary beam of X-rays is used to excite and eject electrons from inner shells of the atoms (*e.g.* K or L shells) of a solid. After such excitation, electrons of the outer shells fall spontaneously to fill in the 'holes' originated and the difference in the energy between the two levels is released in the form of electromagnetic radiation (fluorescent or secondary X-rays), providing elemental information.

SS-OES is used mainly for the analysis of electrical conductors. The surface of the sample is first ground flat and placed against the spark stand, where it is flooded with argon. The spark includes two phases: the first consists on a low-energy discharge produced by a primary circuit which applies a potential in excess of 10 kV for a few microseconds to ionise the argon and create a conducting plasma. As soon as the plasma is formed, the second phase starts, melting the sample and evaporating it at the spark's point of impact. The elements present in the plasma are excited and emit their characteristic spectra. The total duration of both phases of the spark is only a few milliseconds. Unfortunately, matrix effects, self-absorption and even self-reversal problems are usually observed in SS-OES.

In general, analytical techniques based on the use of electromagnetic radiation for excitation purposes allow for the direct analysis of any solid sample independently of its conductivity; however, thin conductive coatings and/or other charge-balancing techniques are usually required when using charged particles for excitation. Therefore, direct analysis of conducting and insulating samples with XRF is feasible. Regrettably, XRF suffers from severe matrix effects and this constitutes its most serious drawback. Matrix correction models are being developed to compensate for the absorption of light from other

elements in the solid sample and also for secondary fluorescence coming from atoms of the analyte excited by light emitted by excited atoms of other elements in the sample.

1.5.1.2 Techniques Providing Lateral and/or Depth Information

Three techniques with spatially resolved information capabilities have been selected here for some further explanation: EPXMA, laser-induced breakdown spectroscopy (LIBS) and glow discharge optical emission spectrometry (GD-OES). Figure 1.15 summarises the lateral and depth resolution provided by the techniques described in this section. It is worth noting that the closer to the bottom left corner the technique is located, the higher (and so better) is the depth resolution.

As for XRF, gas atoms are not formed during EPXMA. In EPXMA, an electron probe is used to excite and eject electrons from the solid, yielding excited ions which relax and emit X-radiation. Electron guns can be focused easily on small areas of the solid surface, although exciting electrons cannot go too deep into the solid. Hence this technique obtains analytical information with some spatial resolution. The technique is prone to serious matrix interferences, like XRF.

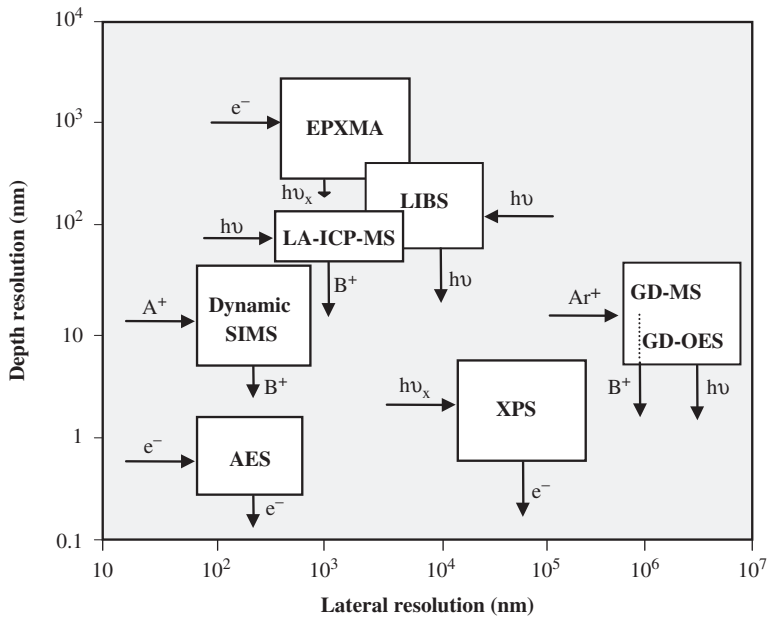

Figure 1.15 Comparison of the lateral and depth resolution allowed by different optical and mass spectrometric techniques used for direct solid analysis (A^+, B^+, incident and emitted ions, respectively; e^-, electrons; $h\upsilon$, photons). XPS and AES are included in the graph for comparison.

The generation of a GD takes place typically in a low-pressure chamber through which argon flows continuously. The device consists of a grounded anode and a cathode (the sample). An electric current ionises the discharge gas, forming a plasma and yielding argon ions which are attracted towards the sample surface producing the sputtering (removal) of atoms, electrons and ions. The atoms of the analyte are excited and ionised through collisions in the plasma and, therefore, measurement by OES and MS is feasible. The uniform formation of craters on the sample surface leads to a good depth resolution [30] (see Figure 1.15). GD-OES offers fairly good detection limits (mg kg^{-1}) and high sample throughput. Further, the sputtering and excitation processes are rather separated, giving rise to minimal matrix effects as compared with other direct solids analysis techniques and this simplifies the quantitation of depth profiles. However, problems in depth quantitation still remain; for example for the analysis of multilayered samples containing layers of very different composition (from one layer to another, the composition of a given element can change from a very low concentration to almost 100%; therefore, if a highly sensitive emission line is chosen, self-absorption can occur). Moreover, algorithms need to be developed to correct for the effect of some light elements (such as hydrogen, nitrogen and oxygen) which can produce serious effects in the calibration curves.

LIBS operates by focusing a laser on to a small area at the surface of the specimen. The laser ablates a tiny amount of material, in the ng–pg range, which instantaneously generates a plasma plume with temperatures of about 10 000–20 000 K and breaks down the material into excited and ionic species. At that time, the plasma emits a continuum of radiation which does not contain any useful information about the species present within it, but after a very short time the plasma expands at supersonic velocities and cools. At this point, the characteristic atomic emission lines of the elements can be observed. The delay between the emission of continuum radiation and characteristic radiation is of the order of 10 μs, making it necessary to gate the detector temporally. LIBS is useful for the remote direct analysis of both conductors and insulators. Because a very small amount of material is ablated during the LIBS process, the technique is considered essentially non-destructive or minimally destructive. Typical data in LIBS exhibit high relative standard deviations. This is due, in part, to either the non-linear nature of the interaction producing the plasma, matrix effects and sample heterogeneity [31].

1.5.2 Elemental Analysis by Mass Spectrometry

Three direct solid analysis mass spectrometric techniques allowing for lateral and/or depth resolution have been selected in this section: laser ablation (LA) coupled to ICP-MS, secondary ion mass spectrometry (SIMS) and GD-MS.

LA–ICP-MS is suitable for the direct analysis of materials such as metals, semiconductors, ceramics and insulators at trace and ultratrace levels (detection limits ~ 1 ng g^{-1}) without sample preparation. The MS detection mode makes it possible isotope analysis and also isotope dilution methods using

stable tracers to improve the accuracy and reproducibility of the analytical results. Unlike LIBS, LA–ICP-MS separates the ionisation step from the sampling step. In LA–ICP-MS, a short-pulsed, high-power laser beam is focused into the sample surface in an inert gas atmosphere (*e.g.* Ar) under normal pressure. The ablated material is transferred by an Ar gas stream into the ICP ion source of an ICP-MS instrument for atomisation and ionisation purposes. Therefore, both steps can be independently controlled and optimised. Further, in LA–IPC-MS a dry sample is introduced into the plasma, which results in a lack of polyatomic interfering species caused by the interaction of water and acid species with the argon plasma. However, limitations still occur and most of them come from the laser-based sampling process [32], for example, the occurrence of non-stoichiometric effects in the transient signals, defined as elemental fractionation. Moreover, matrix effects and non-linear calibrations are other frequent limitations of LA–ICP-MS.

In dynamic SIMS, a primary ion beam of energy, ranging from 0.5 to 20 keV, is used to sputter-remove successive layers of the sample in a well-defined area ranging in size from, typically, 1×1 mm to $10 \times 10\,\mu$m. This yields elemental information on the surface region from a few nanometres to several hundred micrometres in depth. The detection limits of the technique are in the ppm–ppb range. Unfortunately, quantification by SIMS is bedevilled by matrix effects. They arise because the particle emission and ionisation processes take place 'simultaneously'. If we were able to decouple sputtering from ionisation (ionisation occurring after the neutrals were moved away from the surface), the ion yield would be independent of the matrix and quantification would be easier.

Instruments based on GD-MS coupling have been employed most commonly for the quantitative analysis of trace and ultratrace amounts in high-purity materials. However, it has been demonstrated that, as in GD-OES, quantitative depth profile analysis by GD-MS is possible [33]. At present, a GD-MS prototype which allows the depth quantification of thin layers on conducting or insulating materials is being developed for commercial purposes [34].

Figure 1.15 shows the lateral and depth resolution achievable with the three mass spectrometric techniques described in this section. As can be seen, the depth resolution obtained with the GD techniques is similar to that with dynamic SIMS (with the additional advantage of less matrix effects in the GD sources). However, the lateral resolution obtained with SIMS is much better because the primary ion beam in SIMS is highly focused whereas in a GD the limitations in the source design make it necessary to sputter a sample area with a diameter of 1–4 mm. On the other hand, the depth resolution obtained with techniques based on lasers is not yet as good as with SIMS or GDs.

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