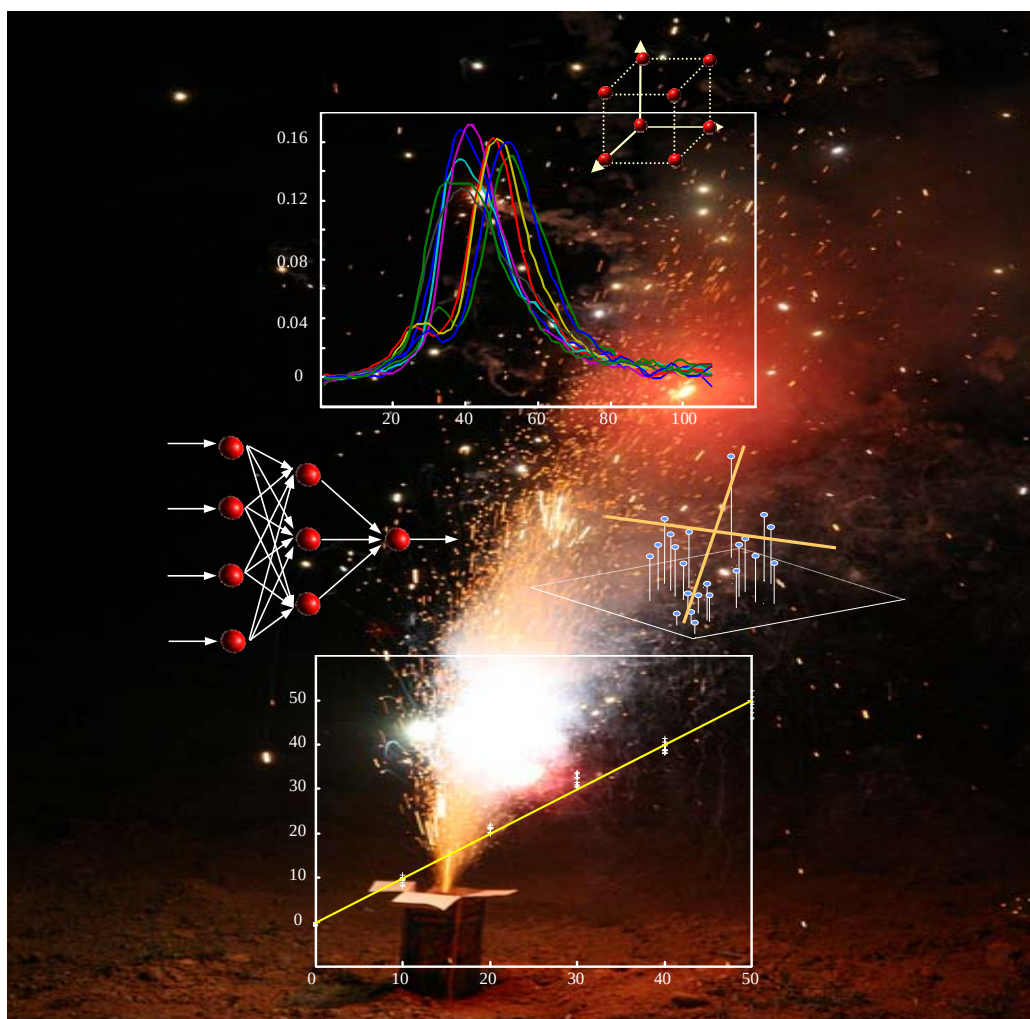


RSC Analytical Spectroscopy Monographs

Edited by J M Andrade-Garda

Basic Chemometric Techniques in Atomic Spectroscopy



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Basic Chemometric Techniques in Atomic Spectroscopy

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Preface

This book is rooted in an informal discussion with three researchers, Dr Alatzne Carlосena, Dr Mónica Felipe and Dr María Jesús Cal, after they had some problems measuring antimony in soils and sediments by electro-thermal atomic absorption spectrometry. While we reviewed the results and debated possible problems, much like in a brainstorming session, I realized that some of their difficulties were highly similar to those found in molecular spectrometry (mid-IR spectroscopy, where I had some experience), namely a lack of peak reproducibility, noise, uncontrollable amounts of concomitants, possible matrix interferences, *etc.*

As many of these difficulties are currently overcome in molecular spectroscopy using multivariate regression methods (or multivariate chemometrics), I proposed that these three ladies should apply them to their spectra. The first reaction on their faces seemed something like ‘ . . . this crazy chemometrician guy . . . ’, but after some discussions we agreed to work together and see what might be achieved. It was not easy to get the spectral raw data that we needed from our old Perkin-Elmer device and Mónica and María spent much time on this until they found a way to do it.

The number of papers we found reporting on the use of multivariate regression in atomic spectrometry was small, and we guessed that this might be because of either a lack of general awareness of the huge potential capabilities of these techniques and/or the difficulties in extracting the spectral data from the spectrometers, something trivial with most instruments dedicated to molecular spectrometry.

We obtained some good results and one morning I read an e-mail from Dr Merlin Fox (Commissioning Editor at the RSC) with a totally surprising proposal: to prepare a monograph on the subject. After reading his e-mail several times and asking him if that was true (some electronic ‘spam’ seemed very possible), Dr Carlосena and I contacted several good scientists in the two fields of atomic spectrometry and chemometrics. I am indebted to all authors

for their constructive words and immediate collaboration, although, maybe, it was the first one we contacted, Professor Alfredo Sanz-Medel (a worldwide-reputed atomic spectroscopist, with several international awards, including the 2007 Robert Kellner Lecture), who really fuelled us to go on. I really want to express my deep and sincere gratitude to each participant in this exciting project. You are not only skilful scientists but also nice persons, enthusiastic workers and, first of all, good friends. Joan, thanks for the nice photograph on the cover, you have a marvelous hobby. Recognition is also due to Merlin Fox for his continuous support and encouragement.

Finally, our thanks to you, the reader. It is the honest desire of the authors to hear from you. We would like to receive your feedback. It is impossible to produce a text like this that satisfies everyone, their expectations and needs. Many things were left out of the book, but if you feel that some more explanations, reviews or information are required, please do not hesitate to contact us. If a new version comes with the winds of the future, your suggestions will be greatly appreciated and, as far as possible, included (and publicly acknowledged, of course).

Jose Manuel Andrade-Garda
A Coruña, Galicia, Spain

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Structure of the Book

It was very clear from the beginning that the main objective of this project would be to present atomic spectroscopists with the basis of the most widely applied multivariate regression techniques. We did not want just '*another book on chemometrics*' and, instead, we challenged ourselves to present some practical material with clear links to common problems in atomic spectroscopy. Although mathematics were avoided as far as possible, a minimum amount was required to present correct explanations and to justify why some issues are tackled in one way rather than in another. We tried to keep technical explanations within the general scientific background that chemists receive in their careers. Besides, in our opinion, atomic spectroscopists should be conscious that things are changing so rapidly in Analytical Chemistry that some sound background on chemometrics is highly advisable. Please, consider it as another tool to be combined with your instruments, not as an end in itself.

In this respect, the first chapter is devoted to a general overview of the most common atomic spectroscopic techniques. The very basics of the analytical techniques are discussed and, most importantly, pros and cons are presented to the reader. Practical difficulties are referred to, their solutions depicted and, when possible, multivariate chemometric solutions pointed out.

The second chapter deals with a critical statement that any analyst and chemometrician has to remember: no good chemometric analysis can be obtained unless the original data are trustworthy. One of the key objectives of chemometrics is to obtain relevant information from the data, but this is possible if, and only if, the data are correct. To obtain reliable data, we can use a suite of dedicated chemometric tools aimed at developing good analytical methodologies. Thus, experimental design, optimization and robustness are cornerstones to assess accuracy during any method development process. Typical methodologies are introduced and discussed, along with extensive literature reviews that combined objective optimization and atomic spectrometry.

Chapter three presents the basic ideas of classical univariate calibration. These constitute the standpoint from which the natural and intuitive extension of multiple linear regression (MLR) arises. Unfortunately, this generalisation is not suited to many current laboratory tasks and, therefore, the problems associated with its use are explained in some detail. Such problems justify the use of other more advanced techniques. The explanation of what the

multivariate space looks like and how principal components analysis can tackle it is the next step forward. This constitutes the root of the regression methodology presented in the following chapter.

Chapter four presents the most widely applied and, probably, most satisfactory multivariate regression method used nowadays: partial least squares. Graphical explanations of many concepts are given, along with the more formal mathematical background. Several common approaches to solve current problems are suggested, along with the golden rule that '*there is not a golden rule*'. The development of a satisfactory regression model can alleviate the typical laboratory workload (preparation of many standards, solutions with concomitants, *etc.*), but only when a strict and serious job is performed with the regression software. Iteration is the key word here, as the analyst has to iterate with his/her data and with the software capabilities. Validation is a key point that can never be stressed sufficiently strongly.

Finally, chapter five goes into a new regression paradigm: artificial neural networks. Quite different from the other regression methods presented in the book, they have gained acceptance because they can handle non-linear systems and/or noisy data. This step forward is introduced briefly and, once again, a review is presented with practical applications in the atomic spectroscopy field. Not surprisingly, most papers referred to deal with complex measurements (*e.g.*, non-linear calibration or concomitant-affected measurements in ETAAS) and/or new analytical atomic techniques (which, therefore, yield very complex data, *e.g.*, X-ray fluorescence in complex systems and several SIMS-based methodologies).

CHAPTER 1

A General Overview of Atomic Spectrometric Techniques

ALFREDO SANZ-MEDEL, ROSARIO PEREIRO AND
JOSÉ MANUEL COSTA-FERNÁNDEZ

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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.

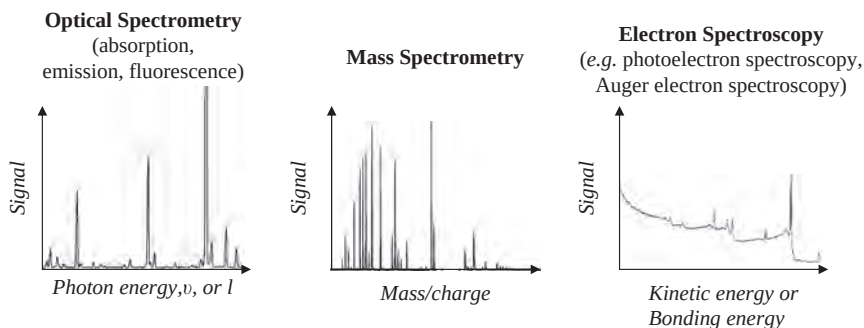


Figure 1.1 Classification of spectrometries according to the detection principle.

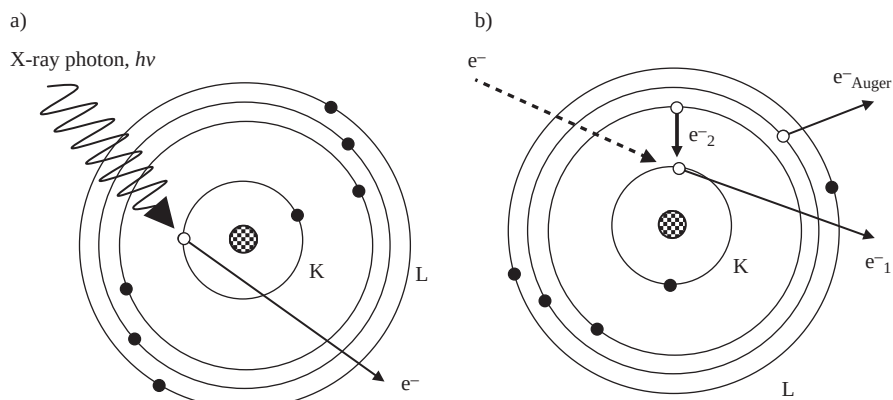


Figure 1.2 Electron spectroscopy. (a) Schematic representation of the XPS process. (b) Schematic representation of the processes for Auger electron emission.

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 $\nu_{12} = (E_2 - E_1)/h$. This process

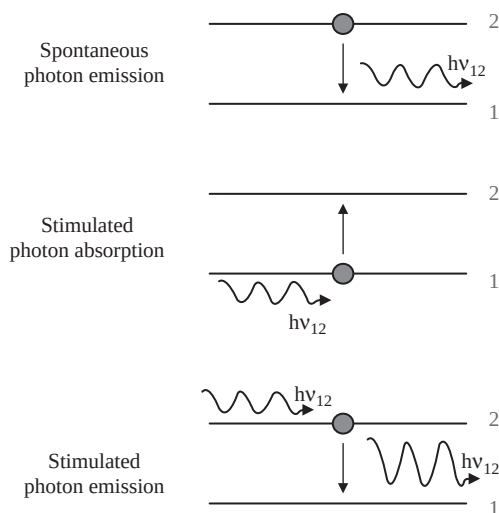


Figure 1.3 Basic interaction processes between matter and interacting electromagnetic radiation.

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

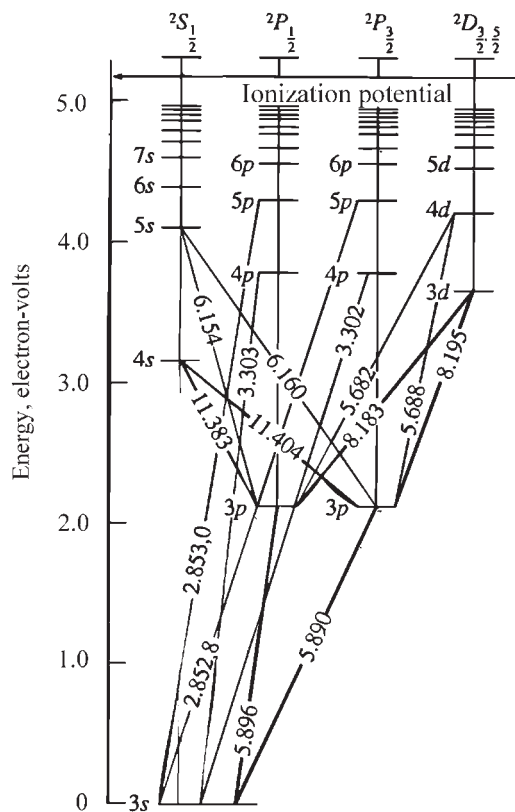


Figure 1.4 Diagram of energy levels and electronic transitions for atomic sodium.

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:

$$T = \frac{I}{I_0} \quad (1.1)$$

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:

$$T = e^{-k'b} \quad (1.2)$$

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:

$$A = -\log T = \log 1/T = k'b \log e = 0.434k'b \quad (1.3)$$

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

$$A = \text{constant} \times b \times N_0 \quad (1.4)$$

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 :

$$A = KbC \quad (1.5)$$

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

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

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:

$$I_F = 2.3K'AI_0 \quad (1.7)$$

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:

$$I_F = 2.3K'KbCI_0 \quad (1.8)$$

$$I_F = k'CI_0 \quad (1.9)$$

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:

$$I_F = kC \quad (1.10)$$

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 an 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.

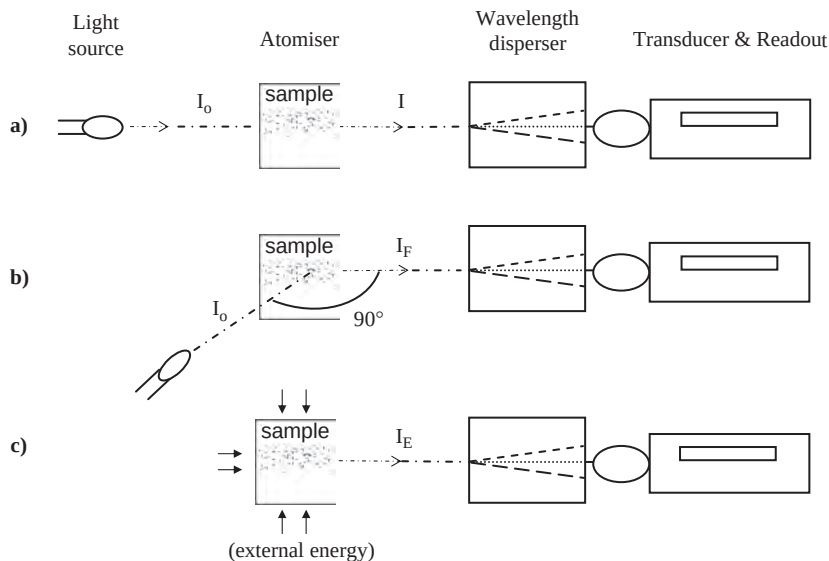


Figure 1.5 Schematics of basic components of analytical techniques based on atomic optical spectrometry. (a) Atomic absorption spectrometry; (b) atomic fluorescence spectrometry; (c) atomic emission spectrometry.

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

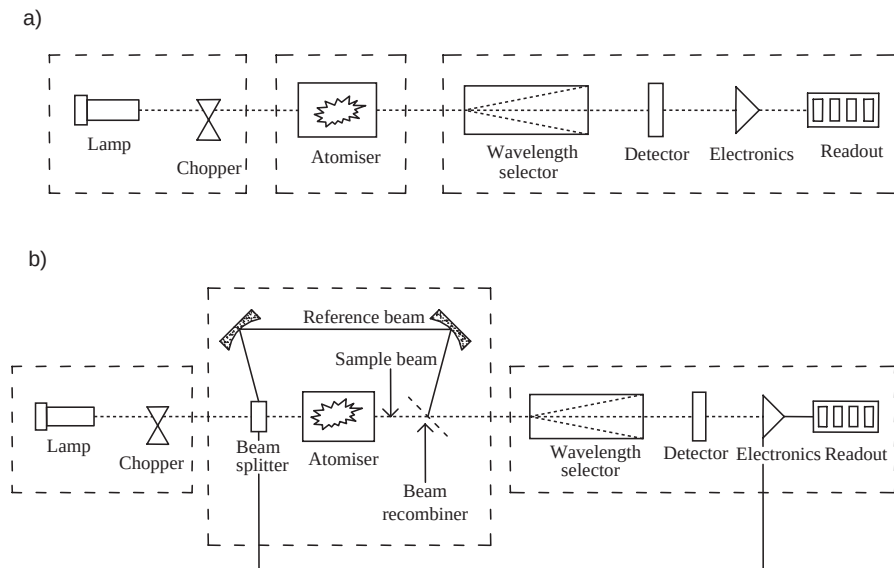


Figure 1.6 Configurations of instruments for atomic absorption spectrometry. (a) Single-beam spectrometer; (b) double-beam spectrometer.

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 $\sim 2100\text{--}2400^\circ\text{C}$, and acetylene–nitrous oxide, with a temperature of $\sim 2600\text{--}2900^\circ\text{C}$.
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

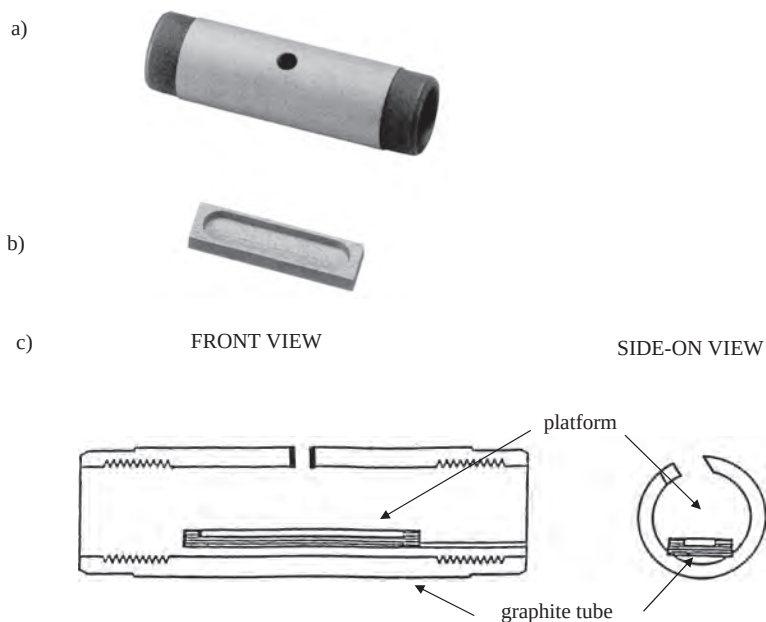


Figure 1.7 Electrothermal atomisation atomic absorption spectrometry. (a) Photograph of a graphite tube. (b) Photograph of a L'vov platform. (c) Schematic front and side-on views of a graphite tube with a L'vov platform.

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

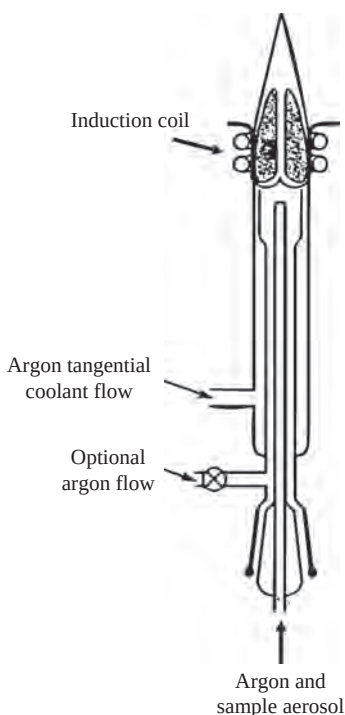


Figure 1.8 Schematic view of an ICP torch.

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 *bremssstrahlung* (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.