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A Practical Approach to Quantitative Metal Analysis of Organic Matrices Using ICP-OES

1.1 Introduction and Basic Overview

When salts of certain metals in solid or in solution are subjected to thermal energy associated with flames, characteristic mono- and multicolours are produced. This colour characteristic used for metal identification gave rise to the birth of a science commonly known as spectroscopy and was discovered by Isaac Newton (1643–1727) during his study of the solar spectrum and made possible by his invention of a triangular dispersing prism. The Isaac Newton prism was used to disperse the emission light from a flame into bands, which could be used to characterise two elements in the same solution (Figure 1.1). A common event seen on a wet day is the separation of white light from the sun passing through raindrops (a prism) high in the sky, being diffracted and separated into colours and forming attractive rainbows.

This procedure has long been used to qualitatively detect the presence of alkali and alkaline elements such as sodium, potassium and calcium. Henry Fox Talbot (1800–1877) noted that when the wick of a candle was dampened in a solution containing table salt (NaCl) an intense yellow colour formed in the flame which he correctly associated with sodium metal. The identification of colour(s) is attributed to the thermal energy caused by a heat source, which raises electrons in atoms to a higher energy state. These electrons cannot remain in this excited state for too long and will emit energy in the form of light to return to the more stable, ground state. The disadvantage of this procedure is that it is limited to single alkali or alkaline earth elements in the flame.

The flame will visually impart colours when selected elements such as sodium (yellow), potassium (blue) and calcium (predominantly red with a little green and blue)

are placed at the base of the flame with the aid of a previously acid cleaned platinum wire. A mixture of near similar levels of metals in the flame would emit colours that would confuse detection with the naked eye unless one element is predominant. Prussian chemist, Robert Wilhelm Eberhard Bunsen (1811–1899) and German physicist, Gustav Kirchhoff (1824–1887) discovered this metal/colour phenomenon when they studied the behaviour of metal salts in a flame made from a mixture of air and coal-gas and attributed these colours to line spectra from the elements rather than compounds using a simple apparatus that consisted of a prism, slits and magnifying glass. They soon discovered that elements when heated would emit light at the same wavelength they absorbed, producing bright lines in the spectrum. Thus by heating an unknown compound and examining the spectrum, scientists could identify the elements that made the compound. This formed the basis of the modern science of spectroscopy. They carried out tests of different salts containing the same metallic element to give the same colour. This simple analogy concluded that no matter what the element is compounded to, the same colour would result. Sodium chloride gave the same yellow colour as sodium sulphate, sodium nitrate, sodium phosphate, etc. Similarly consistent colours were obtained for other alkali and alkaline elements and their compounds.

Later, German physicist Joseph von Fraunhofer (1787–1826) discovered ‘dark lines’* [1] and with the advent of more sophisticated optics he was able to attribute these lines (bands) to characteristic wavelengths. An early practical example of this is the separation and identification of lithium (Li) and strontium (Sr) in solution. In the Li and Sr example, one line or band is the wavelength for Li and the other for Sr. However, it is worth noting here that Li^+ emits only one waveband while Sr emits several and despite this they are still identifiable for each element. Elements giving multiple colours (as calcium, above) illustrated the presence of several lines associated with a particular element. Kirchhoff and Fraunhofer were the first to observe these lines that are now assigned to wavelengths in modern spectroscopy.

It was not until the early 20th century, with the advent of astronomy and atomic physics, that the science of quantitatively measuring metals in solutions became possible [2,3]. Atomic emission was the first to emerge, quickly followed by atomic absorption spectroscopy (AAS) and, later (~mid 1960s), by atomic fluorescence. These methods were attributed to the effects that occur when most metals achieve a sufficiently high temperature and most compounds decompose into atoms in the gas phase. In atomic spectroscopy, samples are vaporised sufficiently at temperatures as low as 1800°C and as high as 9000°C, and atomic concentrations are determined by measuring absorption or emission at characteristic wavelengths against calibration curves prepared from standards of the elements under testing. The high selectivity and sensitivity of wavelengths caused by the absorption or emission of the atoms, and the ability to distinguish between elements made possible by modern sophisticated optics in a complex matrix, was the beginning of the study of developing methods for the quantifying of metals in sample solutions by atomic spectroscopy.

*Fraunhofer lines are when white light containing all wavelengths is passed through a cool version of a gas of an element and the photons from the light interact with atoms. Assuming some of the wavelengths from the light have correct frequency to promote an electron of that element to a higher energy level, photons at this frequency are absorbed by the gas causing “gaps” in the spectra giving rise to “dark lines”.

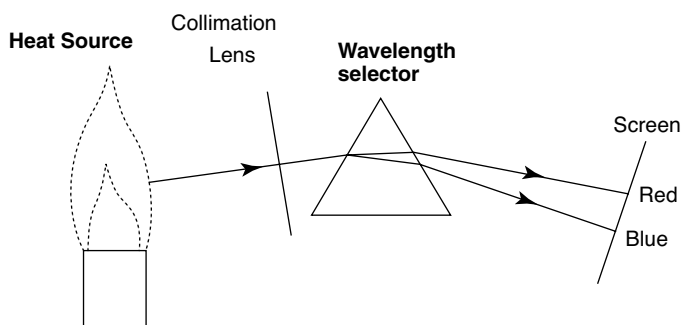


Figure 1.1 Simple diagram showing separation of combined multiple wavelengths using a light dispersion prism

The fact that light emitted from thermally treated elements caused interference patterns and could be diffracted, illustrated that they must behave with wave characteristics. In 1841, James Clerk Maxwell discovered the electromagnetic theory of radiation, which showed that light consists of photons with oscillating electric field (E) in a magnetic field (B) travelling rapidly through space. Maxwell also showed that the combined electric field and magnetic field vibrate at right angles to each other, to which the photon is propagating in a straight line (Figure 1.2). However, for the sake of simplicity it is easier to consider waves as sine waves and the photons can be explained in terms of properties of sine waves. The successive distances between the peaks or troughs are equal, and measured as lambda, λ .

The atomic spectra of most elements originate from the transition of electrons from the ground state to the excited state, giving rise to what are commonly called resonance lines [4]. The diagrams in Figure 1.3 are transitions – selected lines for sodium and potassium and the wave-numbers associated with each transition. Some elements in the periodic table contain very complicated electronic structures and display several resonance lines close together. The widths of most atomic lines are extremely small (10^{-6} nm), and when broadened in various ways the width never exceeds 10^{-2} nm [5]. Fortunately, the modern optics available on the latest instruments can isolate lower bandwidths.

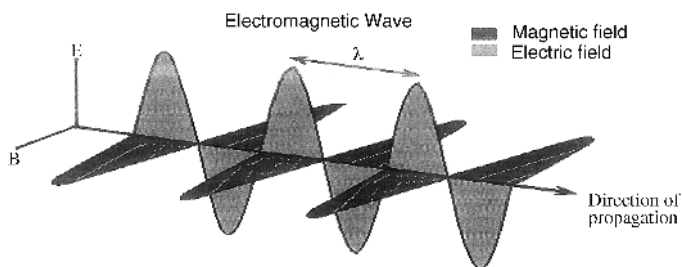


Figure 1.2 Maxwell's electromagnetic radiation diagram

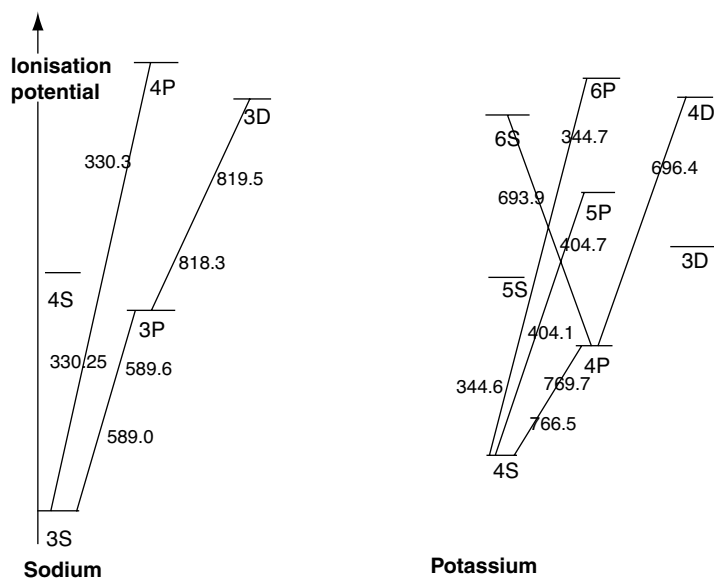


Figure 1.3 Energy levels and wavenumber (nm) diagram for sodium and potassium

1.2 Schematic Representation of the Energies Generated by Atomic Spectroscopic Methods

The three main types of energies applied for the excitation, ionisation and emission steps used for elemental analysis can be shown schematically, as in Figure 1.4.

The horizontal lines represent energy levels of an atom. The vertical arrows represent energy transitions. These energy transitions can be either radiations (i.e. absorption or emission of electromagnetic radiation) or thermal (energy transfer through collisions)

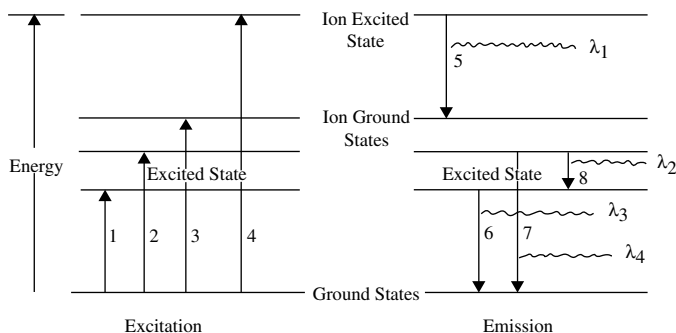


Figure 1.4 Energy level diagram depicting energy transition and the wavelength (λ) associated with each transition. The transitions 1,2 represent excitation; 3 is ionisation; 4 is ionisation/excitation; 5 is ion emission; and 6, 7 and 8 are atomic emission

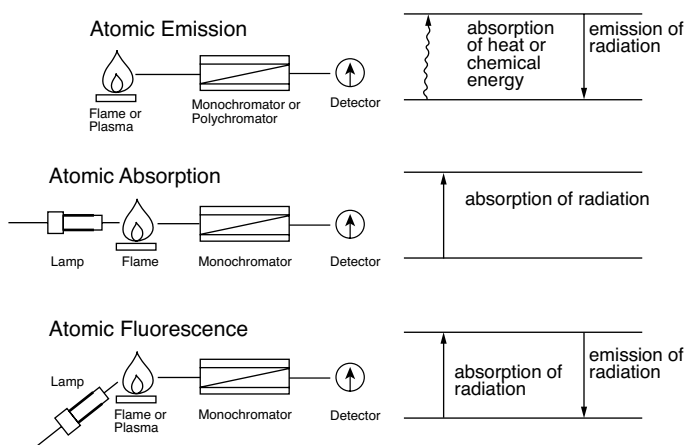


Figure 1.5 Three types of atomic spectroscopy techniques shown diagrammatically. (Reproduced by kind permission: copyright © 1999–2008, all rights reserved, PerkinElmer, Inc.)

with other atoms or particles). The difference in energy between the upper and lower levels of a radiation transition defines the wavelength of the radiation involved in that transition.

Atomic emission spectroscopy is applied to the measurement of light emitted by thermal energy caused by the thermal source from the chemical species present. Examples of emission, absorption and fluorescence spectroscopy can be shown schematically, as in Figure 1.5.

The colour of light obtained from excited atoms stems from the chromophore of the valence shell electrons emitting light as electromagnetic radiation. Photons are absorbed during the promotion of an electron between waves' mechanically allowed (i.e. quantised) energy levels. The ultraviolet (165–400 nm) and visible regions (400–800 nm) of the electromagnetic spectrum are the regions most commonly used for analytical atomic spectroscopy. Wavelengths from 700 nm upwards are in the infrared region and are inapplicable to atomic spectroscopy. The 165–700 nm region in the electromagnetic spectrum is generally referred to as 'light' although, technically, all electromagnetic radiation can be considered as light. Known wavelengths for elements can vary from 1 for Li to 5700 lines for Fe. Some lines are more sensitive than others and this fact is in itself useful because low levels would need very sensitive lines while less sensitive lines can be useful for higher concentrations of elements in samples.

1.3 Excitation Energy (Quantum Theory and Atomic Spectra) [7]

In 1900 Planck derived an empirical relationship for data from a 'black body radiation'; by introducing a concept of 'quantisation of energy' he was able to prove the relationship theoretically. It had been shown that at a specific temperature the spectrum of radiation from a 'black body' was unparalleled in its characteristics and the energy varied

throughout the spectrum and possessed a maximum value at one particular wavelength for one temperature of emission. Planck proposed that oscillations were emitting or absorbing energy as 'quanta'. Such 'quanta' had energy values dependent on the frequency of radiation and emitted as photons.

Balmer and Rydberg both described the spectrum of hydrogen through mathematical interpretations, which eventually included other elements such as the alkali and alkaline earth elements. Rydberg's equation explains that the wavenumber of a given spectrum line is constant for a given series of lines, leading to the quantum theory of atomic spectra in which discrete energy levels were described as coulomb forces between the valence state electrons and the positive atomic nucleus. Transition between the two states corresponds to the absorption or emission of energy in the form of electromagnetic radiation of frequency ' ν '. Niels Bohr (1885–1962) proposed the explanation of a spectrum of atomic hydrogen using Max Planck's theory that electrons in an atom could exist in a number of orbits and circulate about the nucleus without emitting radiation. He proposed that radiation was only emitted when an electron went from a higher orbital to a lower one. The magnitude of this energy is given by Planck's equation as follows:

$$\Delta E = E_o - E^* = h\nu = hc/\lambda \quad (1)$$

where h is Planck's constant (6.6×10^{-34} J s), ν is the frequency of the radiation and $E_o - E^*$ is the energy difference between the two energy levels in the atom. The frequency is related to wavelength by λ (m) = c (speed of light = 3×10^8 m s $^{-1}$)/ ν . To obtain energy in kJ mol $^{-1}$, we multiply the value of E by the Avogadro constant, $L = 6.02 \times 10^{23}$ mol $^{-1}$. Bohr also postulated that the further the electron is from the nucleus (i.e. greater orbital) the higher the energy level. When electrons of an atom are in orbit and close to the nucleus they are at the lowest energy levels sustained by the atom and in its preferred ground stable state. When thermal energy (other energies could be used) is added to the atom as the result of absorption of electromagnetic radiation or collision with other electrons, several events take place within the atom. One or all of these events cause excitation by absorbing energy causing electrons to move from the ground state orbital to an orbital further from the nucleus and to a higher energy level. This atom is said to be in an excited state and such an atom is less stable and will decay back to a less excited state losing energy in the process emitting this energy as photons (particles) of electromagnetic radiation. As a result the electron returns to an orbital closer to the nucleus.

In some cases if the energy absorbed by an atom is high enough, an electron may be completely lost from the atom leaving an ion with a net positive charge (see Figure 1.6). This energy is called ionisation, which is characteristic for each element in the periodic table. This form of energy has been assigned the *ionisation potential* for each element. Similar to atoms, ions can also have ground and excited states by being able to absorb and emit energy by the same process as a ground state atom.

Planck showed that a photon has particle properties and proved that the energy of a photon is proportional to its frequency. This shows that energy and wavelength are inversely related, i.e. as the energy increases, the wavelength decreases and vice versa.

In the ground state the electrons are at their lowest energy levels and by contacting the atoms with thermal or electrical excitation, the energy is transferred to the atoms causing the atoms to collide. These collisions cause the electrons in the atoms to change to higher

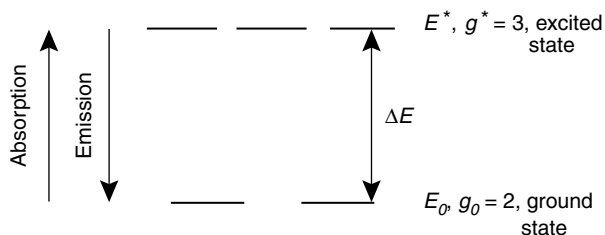


Figure 1.6 Energy levels at ground state and excited state of an atom showing degenerates

orbits. The quantity of energy transfer varies from atom to atom, sample matrices to sample matrices, resulting in a range of energy states. The result is radiation of a number of different species displaying a spectrum, which is highly complex. The proportion of excited and ground state atoms at a given temperature may be given by the Boltzmann distribution¹, which describes the temperature effect in atomic spectroscopy. It is well known that temperature determines the degree to which a sample breaks down to atoms and the extent to which a given atom is found in its ground, ionised or excited state. Consider a molecule with two possible energy levels, as shown in Figure 1.6.

The ΔE (positive number) is divided by the lower energy E_o and higher energy E^* . An atom may have several states at a given energy level. In Figure 1.6, there are three states at E^* and two at E_o . The number of states available at each energy level is called the degeneracy: denoted g^* and g_o . These are the statistical weights of. These the excited and ground state levels, respectively. The Boltzmann distribution describes the relative population of different states at thermal equilibrium.

1.4 Ionisation Energy and Number of Excited Atoms [7]

The intensity of atomic emission is dependent on temperature and is emphasised in the Boltzmann relationship. The relationship between the line intensity and temperature is derived from the energy transferred by collision of the argon ion with another atom or atoms. The ease with which an atom will form an ion depends on the magnitudes of its ionisation energy and its electron affinity. In the Bohr Theory of the hydrogen atom a certain amount of energy was required to completely remove the electron from its orbit to infinity. This energy is called the ionisation energy and the magnitude of ionisation potential depends on (i) the distance of the electron(s) from the nucleus, (ii) nuclear charge, less a correction for screening effect by inner shells and (iii) type of electron being removed i.e., s, p, d. In general, the further the electron is from the nucleus the less firmly it is held and the lower the ionisation potential. The approximate ionisation energy (in electron volts) of the argon ion is 15.9 eV and the ionisation energy of most elements detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) is in the order of

¹ Boltzmann is a distribution constant of a large number of particles among different energy states which could be discrete and quantified for particles under study. The Boltzmann constant is a constant per molecule and is given by $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

Table 1.1 Relationship between ionisation energy of selected elements and the degree of ionisation

Element	Ionisation energy (eV)	Degree of ionisation (%)
Li	5.4	99.0+
Na	5.1	99.0+
K	4.3	99.0+
Rb	4.2	99.0+
Be	9.3	74.0
Mg	7.7	96.0
Ca	6.1	97.0
Ba	5.2	91.0
Cr	6.8	96.0
Mn	7.4	95.0
Fe	7.9	96.0
Co	7.9	93.0
Cu	7.7	90.0
B	8.3	59.0
P	10.5	36.0
S	10.4	16.0
As	9.8	49.0
F	12.9	0.1
Cl	12.7	0.6

5 to 14 eV of which most are closer to 6 to 8 eV, hence sufficient energy is still available for several excitations of an ion. Therefore many transitions from ions are possible. The alkali elements usually have the lowest ionisation energies, metalloids are slightly more difficult to ionise and the non-metals are even more difficult. The ionisation energies would range from ~ 4.5 for alkali, ~ 8.5 for metalloid to ~ 12 eV for non-metals. Table 1.1 illustrates the relationship between ionisation energy and the degree of ionisation for Group 1 – alkali, Group 2 – alkaline, common transition elements and metalloids.

At equilibrium, the relative population of excited and ground state atoms at a given temperature can be considered using the Boltzmann relationship. N^* and N_o of any two states is given by:

$$\frac{N^*}{N_o} = \frac{g^*}{g_o} \exp[-E_1 - E_0/kT] \quad (2)$$

where N^* and N_o are the number of atoms in the excited and ground states, respectively, T is the temperature (K) and k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$). The terms E_1 and E_0 are energies at higher and lower states, respectively. This illustrates that ground state atoms can absorb light to be promoted to the excited state. Excited atoms, conversely, can emit light returning to the ground state. This equation holds for ionisation, and excitation of atoms and molecules provided that the energy levels considered are non-degenerate.

Table 1.2 shows the ratio of atoms in excited state for temperatures ranging from 2000 K to 8000 K as calculated using the Boltzmann equation above. The number of excited Na atoms at 2000 K is approximately 10^{-5} while at 8000 K it is in the order of 10^{-1} . The fraction of atoms excited increases with increasing temperature which is almost negligible at lower temperature but significant at higher temperatures. AAS measurements are less dependent on temperature because they are based on the number of unexcited atoms, however, in the case of inductively coupled plasma optical emission spectrometry (ICP-OES) the number of excited atoms at higher temperatures gives greater sensitivity. Table 1.2 shows the effect of temperature on the number of excited atoms.

1.5 Width of Atomic Lines [8]

Spectral lines have a very small but finite width (broadening), over a wide range of wavelengths giving a variety of breadth and shape, with a maximum at a certain wavelength. Some atomic lines are very thin and precise while others are not and it is an accepted analogy that their width is taken as the width at half the signal height ($\Delta\nu/2 \text{ cm}^{-1}$). Spectral interferences common are coincident line overlap, wing overlap from intense nearby lines of the same or another element and background shift. These signals lend themselves to several types of broadening, described below.

1.5.1 Natural Broadening

This type of broadening is the mean lifetime of an atom in an excited state when photons are absorbed in the atom. The absorption process is rapid and is in the order of 10^{-12} s while the excitation is longer and in the order of 10^{-8} s . This is short enough to support the Heisenberg Uncertainty Principle, which states that if we know the state of the atom, we must have uncertainty in the energy level, i.e the shorter the lifetime of the excited state, the more uncertain is its energy relative to the ground state. This uncertainty is expected at the level of the elementary particles, and yields a line broadening which is particularly noticeable at the base of the peak. This broadening is insignificant at 9000°C .

1.5.2 Doppler Broadening

The narrow natural line is broadened by motion of the atoms and ions in the plasma. This effect is due to the rapid motion in which atoms move and is based on the theory that if an excited atom in the process of emitting photons is moving towards a detector the resulting wavelength will appear to be shorter. If, on the other hand, the photon is moving away from the detector it will appear longer. This velocity observed in the line of sight will vary according to Maxwell distribution, for atoms moving in all directions relative to the observer.

1.5.3 Lorentzian Broadening or Pressure Broadening

This results from collision of atoms with atoms of other species. The energy level of both the ground and excited states of an atom will be influenced by interaction with

Table 1.2 *Effect of temperature on the number of excited atoms*

Element	Line (nm)	g_i/g_j	Excitation energy (eV)	2000 K	4000 K	6000 K	8000 K
Cs	852.10	2	2.340	4.21×10^{-4}	2.93×10^{-2}	1.21×10^{-1}	2.44×10^{-1}
Na	589.12	2	4.632	9.50×10^{-6}	4.37×10^{-3}	3.36×10^{-2}	9.41×10^{-2}
Ca	422.71	3	3.332	1.41×10^{-7}	6.47×10^{-4}	1.11×10^{-2}	4.33×10^{-2}
Mg	285.21	3	4.346	3.35×10^{-11}	7.65×10^{-6}	1.65×10^{-4}	5.55×10^{-2}
Co	338.29	1	3.664	5.85×10^{-10}	2.23×10^{-6}	6.73×10^{-5}	4.44×10^{-4}
Au	267.59	1	4.634	2.12×10^{-12}	7.88×10^{-7}	3.34×10^{-5}	6.61×10^{-4}
Fe	371.99	–	3.332	2.29×10^{-9}	5.43×10^{-5}	7.43×10^{-4}	3.12×10^{-3}
V	437.92	–	3.131	6.87×10^{-9}	7.34×10^{-5}	2.22×10^{-4}	5.89×10^{-3}
Zn	213.86	3	5.795	7.45×10^{-15}	1.94×10^{-7}	4.86×10^{-5}	7.75×10^{-4}

g_i/g_j = statistical weights of the corresponding levels, i.e. the atomic and molecular ground state degeneracies respectively.

surrounding particles. It is known that these collisions can shift, broaden and cause asymmetry in the line. Lorentzian broadening increases with pressure and temperature and is generally regarded as proportional to pressure and the square root of temperature. Therefore, $\Delta\nu$ increases with increasing temperature and pressure. It is accepted that Lorentzian broadening affects the wings of the signal profile. The Lorentzian half-width is of the same order of magnitude as the Doppler half-width (Table 1.3). The classical Lorentzian distribution predicts a symmetric line profile, but in practice there is an asymmetric profile and a red-shift of the maximum.

Table 1.3 Comparative list of approximate half-widths of selected elements for Doppler and Lorentzian broadening

Element	Wavelength	Doppler (4000 K)	Lorentz (4000 K)
Sodium	589.00	4.8	4.0
Calcium	422.70	2.9	1.3
Magnesium	285.21	2.8	—
Iron	371.99	1.9	1.7
Gold	267.59	0.8	—
Silver	328.07	1.5	1.4
Vanadium	437.92	2.6	—
Zinc	213.86	1.3	—
Cobalt	338.29	1.6	1.9

1.5.4 Holtzmark Broadening or Resonance Broadening

This is collision between atoms of the same element in the ground state and results in an intensity distribution similar to Lorentz broadening but without line asymmetry or shift. The effect depends on concentration and half-widths which are very small and negligible when compared with other collisions.

1.5.5 Field Broadening or Stark Broadening

This takes place in an electric or a magnetic field, where the emission line is split into several less intense lines. At electron densities above 10^{12} the field is relatively inhomogeneous, splitting varies for different atoms and the result is a single broadening line.

1.5.6 Self-Absorption and Self-Reversal Broadening

This is the sum of all factors considered so far because whilst the maximum absorption occurs at the centre of the line, proportionally more intensity is lost at the wings. As the concentration of atoms increases the intensity and profile change. High levels of self-absorption can cause self-reversal, i.e. a trough at the centre of the line. This is significant for emission lines in flames but is almost absent in ICP-AES which is a major advantage of this source.

1.6 Brief Summary of Atomic Spectroscopic Techniques Used for Elemental Analysis

With the development of electric spark or electric arc excitation, the spectra formed after a high voltage pulse are recorded using photographic plates, which form spectral lines characteristic of the element in the source. With the aid of a spectrograph, the spectra of the elements occur mostly in the ultraviolet region and the optical system used to disperse the radiation is generally made of quartz. The lines formed from an unknown sample are compared with calibration lines of known standard(s). Luckily these techniques have been replaced by atomic absorption, atomic emission and plasma emission spectroscopy, which have the ability to identify, measure and quantify up to 60–75 elements depending on the technique. There are three kinds of emission spectra: (i) continuous, (ii) band, and (iii) line. Incandescent solids for which sharply defined lines are absent and have little or no use in atomic spectroscopy emit continuous spectra. The band spectra consist of a group of lines that come nearer to each other until a limit is reached, and are caused by excited molecules. Line spectra, which have most use in emission spectroscopy, are definite lines and are characteristic of atoms or atomic ions, which have been excited to emit energy as light of constant wavelength.

Quantitative analysis by atomic spectroscopy is based on the measurement of radiant energy by free atoms in the gaseous state. The technique owes its selectivity to the fact that spectra of gaseous atomic species consist of defined narrow lines at wavelengths characteristic of the element of interest. The energy input into any of the techniques is converted to light energy by various atomic and electronic processes before being measured. The light energy is in the form of a spectrum, which consists of discrete wavelengths.

Regardless of the forms of energy the atom is subjected to, be it absorption, emission or fluorescence, they can all be used for analytical purposes. The following is a brief description of each of these thermal methods, commonly used to excite, isolate, identify and quantify metal concentrations in sample solutions.

1.6.1 The Atomic Absorption Spectrophotometer

This instrument is a very popular and versatile technique and finds use in many laboratories worldwide. However, limitation to certain elements in terms of poor sensitivity, detection and reproducibility means that some elements cannot be quantitatively determined by this technique. The type of samples that are difficult to measure at trace levels using AAS are refractory types, such as rocks, slags, lava, ceramic, cements, and ashes containing elements such as W, Mo, Si, P, B, Al, and Pb. The reason for this is that the use of the gas mixture acetylene/air to achieve temperatures of ~2100–2500°C or nitrous oxide/acetylene to achieve ~2500–3100°C are insufficient to fully excite these elements. However, this technique is very applicable to alkali, alkaline and first-row transition elements and can detect these elements with considerable ease. A further disadvantage of AAS is the limited linear range with which deviations from linearity occur for various reasons, such as unabsorbed radiation, stray light or disproportionate decomposition of molecules at high concentrations. It is desirable to work at the mid point of the generated linear straight line to achieve accurate results. A simple rule of

thumb is to prepare five to eight standards and note the linear range and obey the Beer-Lambert law of the relationship between concentration and absorbance. Modern AAS will also measure emission energy of selected elements.

AAS is relatively free from elemental interferences because it determines elements using absorption by specific lamps for the metal under test. However, it is prone to background interferences caused by:

- (a) absorbing molecular species of the sample, e.g. some absorptions by other species in the sample may occur at the same wavelength as the element under test;
- (b) absorbing atomic species from other elements in the sample, e.g. phosphorus in the presence of calcium;
- (c) particles from high salt concentration in the atom cell can cause light scattering.

Fortunately, methods for background correction are now a part of most modern AAS and the most commonly used background correctors are a deuterium source, the Zeeman effect and the Smith-Hieftje effect.

In atomic absorption most of the atoms in vapour phase are in the ground and unexcited state and therefore it might be expected that atomic absorption would be more sensitive than atomic emission. This is not true because the higher temperature achieved with plasma sources excites most of these atoms and it is easier to measure emission of small signals with good precision than a small difference between two large signals from the sample and reference beam in AAS. This ground state contains atoms that are capable of absorbing radiant energy of their own specific resonance wavelength, which is the wavelength of radiation that the atoms would emit if excited from the ground state. However, if light of resonance wavelength is passed through a flame containing atoms of similar wavelength the light will be absorbed. The absorption is proportional to the number of ground state atoms present in the flame. This is the principle of AAS.

1.6.2 Atomic Fluorescence Spectroscopy

These instruments analyse elements by observing the re-emission of absorbed energy by free atoms, and quantitative measurements are similarly monitored through fluorescence detection. This technique has not found favour in many laboratories but is used as a detector for liquid and gas chromatography for a limited number of elements such as Se, As, Cd, Sr, Ni, Ti, Sn, Pb, and Hg in their organo-metallic form, which are separated on columns for environmental samples. AFS detects resonance lines of the lowest frequency and its advantage is that it is easier to excite and is less affected by scatter when compared with resonance lines of higher frequency. The lack of instrument development because of the wide acceptance of AAS, which dominated the market since its inception, is unfortunate. If the market had responded with the same enthusiasm as that given to AAS, the commercial suppliers would certainly have responded with research, financial and development support.

1.6.3 Direct Current Plasma Optical Emission Spectrometry (DCP-OES)

This technique was first described in the 1920s having been thoroughly investigated since then as a source as an analytical tool. It was not until the late 1960s with the development

of suitable optics that it has improved to such an extent that it could compete with ASS and later to some extent with ICP-OES. The DCP jet source (which excites the atoms) consists of three electrodes arranged in an inverted 'Y' configuration consisting of two tungsten electrodes at the inverted base and a graphite electrode at the top (Figure 1.7). The argon plasma formed is caused by bringing the cathode momentarily into contact with the anodes where a high electrical charge ~ 15 A, initiates the argon to form the plasma.

The viewing region of the plasma can achieve a temperature of 5000–6000°C and is reasonably stable. The sample solution is aspirated into the core area between the two arms of the 'Y' where it is atomised, excited and viewed. This technique keeps with the atomic spectroscopy theory in that the measurements are obtained by emission from the valence electrons of the atoms that are excited, and the emitted radiation consists of short well-defined lines. All these lines fall in the UV or VIS region of the spectrum and identification of these lines permits qualitative/quantitative detection of elements.

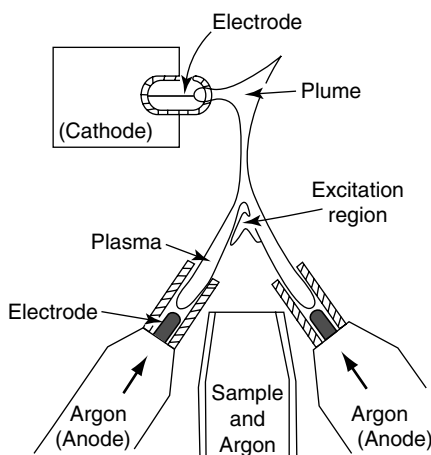


Figure 1.7 *Diagram of DCP-OES showing electrodes and plasma configuration*

The design of the DCP-OES allows the use of both aqueous and most non-aqueous solvents, providing standards and samples are prepared under similar conditions. It is more expensive to operate than AAS but cheaper than ICP-OES. The limitation of DCP-OES is the susceptibility to excitation interferences and increased signals from easily ionisable elements (EIEs). It has lower limits of detection and wider linear range for most elements but not as good as ICP-OES.

1.6.4 Microwave Induced Plasma (MIP)

This technique uses helium as the plasma gas which enables a higher temperature so that non-metals are excited. The MIP is hampered by matrix interferences, even water. Therefore it is used mainly for the analysis of gases, particularly in conjunction with gas chromatography.

1.6.5 Glow Discharge Optical Emission Spectrometry (GD-OES)

This technique is used mainly for surface analysis of electrically conductive materials provided that correction factors are applied if all components are known. The theory is based on the light emitted from a glowing discharge between a hollow cathode lamp and the sample (cathode) in an atmosphere of argon. Argon cations are formed which are accelerated in the direction of the negatively charged sample from which atoms are released, excited and quantified.

1.6.6 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

This instrument was developed by Stanley Greenfield 1964 [9] and is an analytical tool used for the determination of 75 elements and their states (oxidation, isotopic, etc.) in a wide range of sample matrices. Elements that are not determined are those already in the plasma from sources not in the sample, argon, carbon dioxide, hydrogen, oxygen, and nitrogen that are in the air surrounding conventional plasma, and elements that require very high energy, such as the halogens. Some elements not detected using ICP-OES may be detected with ICP-MS, which measures their mass to electron ratio (m/e). The inductively coupled plasmas are designed to reach temperatures higher than ordinary combustion flames. The argon gas used to generate this high temperature has many advantages in that it forms a stable and chemically inert environment, which eliminates many of the interferences encountered with combustion flames. Plasmas are used for emission because the temperature is high enough to excite most of these elements. Detection of elements at its wavelengths is usually by photomultiplier tube(s) (PMT) or by charge coupled device (CCD). More expensive ICPs are designed to direct individual emission lines from different elements in the plasma to individual detectors. Such instruments allow simultaneous multi-elemental analyses that are rapid and carry out considerably more analysis in a shorter analysis time. They are applicable where hundreds of samples need to be analysed per day. The disadvantage of this instrument is that they are confined to built in elements. Research carried out by Wendt and Fassel [10] showed that higher temperatures can be achieved by argon plasma created by a magnetic field using a radio frequency generator. The neutral atoms, ions and electrons collide under the influence of the magnetic field causing excitation and emission of wavelength energy in the UV-VIS region of the atomic spectrum. Therefore, this instrument offers a procedure to enable analysis of most elements in the periodic table including refractory type elements in the region of 160–700 nm with ease. The latest sophisticated optics developed for ICP-OES allows excellent resolution to cater for multiple elemental analyses and shows reduced interferences by other elements, for example, the determination of aluminium and phosphorus in the presence of a high concentration of calcium.

The basis of ICP-OES is a sample solution introduced into the core of a hot ($\sim 9000^{\circ}\text{C}$) argon gas, i.e. highly energetic ionised gas. At this temperature, all elements in the sample become thermally excited and emit light at their characteristic wavelengths. The light is collected by the spectrometer and passes through a diffraction grating that resolves the light into a spectrum of its constituent wavelengths. These wavelengths are amplified to a signal that can be measured and used for quantitative purposes by comparing with calibrated standards prepared under similar conditions. The interaction is based on thermal dissociation of the elements causing emission of the free atoms. This

technique is now prevalent in almost every field of chemical analysis, more so than any other technique in spectroscopy. Detection limits as low as 10^{-12} g can be achieved with reasonable accuracy and selectivity. Initially, these techniques were developed for aqueous and metallic samples but in latter years, with improvements in instrument design, elemental analysis of organic samples has also benefited. This instrument is now the most frequently used and most sensitive elemental analyser available and is adaptable to ancillary attachments to cater for difficult samples, to improved limits of detection and improved speed of analysis. The multi-element analysis feature offers considerable savings in analysis time and at the same time maintains excellent accuracy and reproducibility. Unfortunately, the technique is not without problems as it is very sensitive to trace analysis and extreme care must be applied in preparation of standards and samples in ensuring that the results obtained are true. The instrument parameters, such as gas flow, wavelengths, clean sample, tubing for transporting sample to the nebuliser must be correctly fitted and tested prior to use.

1.7 Summary: Applications of Atomic Spectroscopy

Flame atomic absorption and flame emission techniques were developed before inductively coupled plasma emission spectroscopy and are still used extensively for analysis of a wide variety of samples on a routine and non-routine basis. They are very useful techniques for elemental analysis of selected sample matrices; however, the lower temperature ($\sim 2800^{\circ}\text{C}$) of these techniques limits their sensitivity to a range of important samples. The development of plasma sources (1970s) capable of achieving temperatures of 9000°C has revived the use of emission instrumentations enabling improved sensitivity and multi-elemental analysis at major, minor and trace levels. The use of plasma as an excitation source has an added analytical advantage in its ability to use a wider linear dynamic range allowing little or no dilution and reducing chemical and physical interferences. The higher excitation temperature of plasmas compared with flames results in a more efficient atom excitation which leads to increased sensitivity especially for refractory elements such as B, P, W, Nb, Zr and U. The plasma source geometry and dynamics mean fewer sample atoms in the plasma and temperature profiles result in minimal line reversal and matrix interferences.

Both flame and plasma sources are sensitive and selective techniques measuring as little as 10^{-16} g of analyte solution in complex mixtures. However, understanding the techniques and the type of sample being analysed helps in deciding which technique is suited for a particular application.

Elements occur in natural and synthetic compounds at various levels and since the beginning of the development of atomic spectroscopy analytical instruments, more information about toxicity, benefits, etc., became known. Modern atomic spectroscopy instrumentation can determine from % levels to trace levels (ppm) and sub-trace low levels (sub-ppb) with a high degree of accuracy and precision. At whatever concentration, knowing the concentration of these elements plays a very important role in understanding more about products in terms of health issues, benefits, shelf life, stabilities, etc. Table 1.4 is a summary of elements of great importance that need to be monitored in order that any changes can be interpreted as part of behaviour that could be good or bad.

Table 1.4 List of some elements of importance requiring quantification using atomic spectroscopy techniques

Element	Area of importance
Mg, P, S, K, Si, V, Cr, Fe, Co, Ni Co, Zn, As, Sc, Mo, Sn and I	Biochemistry and medicine
Almost all elements in the periodic table	Environmental science
Contamination and wear metals e.g. Fe, Ni, Co, Mn, Cr, Mo, W, Na, K	Crude and virgin oil, and petroleum industries
Radioactive elements used for industrial and medicinal purposes	e.g. U^{238} , U^{235} , Cs^{132} , Pu^{239} , B, Si, Cd, etc.
Si, Al, As, Fe, Cu, Mo, Hg, Cr, Se, Ba, Sr, Sb, Au Bi, Nb, Zr and Pb	Electronics and semiconductor industries
Almost all earth and clay containing elements Cu, Pb, Al, P, S, Ca, Mg, Si, Hg, Cr, Co, etc.	Geological research Works of art, paint mixtures, etc.
Si, B, Cd, Pb, Fr, Cs, U Hg, As, Sn, Sr, Ni, Ge, Ga, etc.	Ceramic industries
All elements	Forensic support

The importance of major and trace elemental analysis is paramount in biological, biochemical, medicine, environmental, forensic, pharmaceutical compounds, geological and gas samples. In most cases quantifying the level of metal can play a vital role in obtaining information on whether samples contain toxic metals or metals that are beneficial, acting as a catalyst or retarding effect on compounds or formulations. In the early part of the 20th century trace metal determination was not possible, hence the effects of a wide range of elements were unknown. A colour method for the determination of iron in aqueous samples was developed in the 1940s and is an example of a non-spectroscopic method used for determining this metal at sub-trace levels. The procedure involved complexing the iron with thioglycolic acid using a series of operations and reactions. This colour test is extremely sensitive and prone to errors caused by impurities in reagents and some samples. It is also time-consuming, taking several hours for confirmation of presence, and can only be used for one element at a time. The same measurement can be carried out using an atomic spectrophotometer against standard iron prepared the same way as the sample eliminating impurities or correcting for them in the method of analysis. Measurement by atomic spectroscopy of the same sample and many more could be analysed in minutes. Nowadays, modern inductively coupled atomic spectroscopy methods can scan a sample for 75 elements in 60 s using a multi-elemental scanning ICP-OES.

Presence or absence of trace elements in living organisms is essential for health information. Analysis of such samples by atomic spectroscopic techniques can make a distinction between vital and non-vital elements. Deficiencies in element(s) lead to deficient syndromes and if supplemented, the element(s) may prevent or cure the syndrome. Therefore the correct dosages are extremely important. In some cases deficiency of certain elements can lead to a decrease in specific biochemical functions that could be fatal. However, a high intake of some elements through foods, drinks, and air particulates can also seriously damage health. Modern day scientists work closely

with health workers in sharing information and the detection of more elements at lower or higher concentrations is aiding in the better understanding of the behaviour of metals and determining their beneficial or non-beneficial effects.

To illustrate an example, monitoring the level of iron haemoglobin in blood, which acts as a binding agent for the oxygen molecule is an important test in terms of health control. Therefore, it would be assumed that the higher concentrations of iron in human blood would be beneficial. The pumping mechanism of the hearth transports blood containing the Fe-haemoglobin around the essential parts of the body. Monitoring the iron level can aid medical workers in diagnosing whether women have serious deficiencies of this metal due to monthly menstruation. Supplementing such deficiencies with the correct dosages established from analysis can assist the medical workers to correct this. Iron deficiencies can lead to anaemia, fatigue, headache and sometimes anorexia. However, on the other hand, consuming high dosages of iron can injure the alimentary canal, cause hepatitis, haemochromatosis and lead to cirrhosis that could be dangerous.

Elements such as oxygen, nitrogen and carbon which are available through normal chemical processes of the atmosphere and biochemical functions which are determined by these atomic spectrometric techniques are also as vital, as are Mg, S, P, Cl, Na, K, Ca, I, F, Si, Co, Ni, Cu, Zn, Se, Mo, Sn Cr, Mn, etc.

This book will be devoted to the practical approach of quantitative metal analysis using ICP-OES. There is a lack of analytical information and methodologies available on the analysis of simple and difficult organic matrices. In this book, I hope to present a few ideas in terms of sample preparation, quantification, and comparison of techniques of actual work carried out by the author over several years.

The plasma source is, at present, the most important method of atomic excitation and is compatible with organic solvents. As previously stated a definite wavelength can be assigned to each radiation, corresponding to a fixed position in the spectrum. However, as the colours for calcium, strontium and lithium are similar and with the advanced optics design it is now possible to differentiate between them with certainty by observing their spectra in the presence of each other. Similar elemental differentiation/identifications are carried out for 75 elements in the periodic table. By extending and amplifying the principles inherent in the flame qualitative test, an analytical application of emission spectroscopy has been developed using ICP-OES. The developments in atomic spectroscopy using plasma sources, instrument control and data processing by computers for multi-elemental determinations in a wide variety of inorganic and organic matrices are truly indicative of the trends in analytical analysis.

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