



# The Islamia University of Bahawalpur

Department of Chemistry

## Course Material Bundle (CMB)

### Mode of Education:

The Islamia University of Bahawalpur uses a combination of video lectures, reading material, audio/video tutorials and on-line interaction for imparting knowledge. However, it follows a very formal assessment and evaluation system in the same fashion as used in any conventional higher education institutions (HEI)

- Course Overview
- Related Links
- Reference Books
- Further reading (support) material
- Lecture Videos
- Solved examples
- Course Assignments

CHEM-02831 Inorganic Chemistry-V (BS-VIII)

### COURSE INFORMATION:

Course Category: Chemistry

Course Level: BS

Credit Hours: 04

Pre-requisites: FSc (Chemistry, Math, Physics, Biology)

Objectives: Flame emission and absorption spectroscopy, Mass spectrometry, Potentiometry

Instructor: Dr. Muhammad Imran (PhD)

### COURSE CONTENTS (Major Topics):

- Introduction to FES and AAS
- Principle and theory of FES/AAS
- Nebulizers
- Burner systems
- Interferences
- Hollow Cathode Lamp
- Flame-less techniques
- Hydride generation and Cold vapor techniques
- Applications of AAS and FES
- Mass spectrometer and its principle
- Mass spectrum

## **Reference Books**

1. **Book Title** Vogel's Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis

**Authors :** Bassette J., Denney C. Jeffery G.H. And Mendham, J

**Edition:** Fifth Edidtion

**Publisher:** John Willy and Sons, New York

2. **Book Title.** "Introduction to Spectroscopy" "

**Authors :** Pavia D. L., Lampman G. M. and Kriz G. S

**Edition:** Third Edidtion

**Publisher:** Saunders College Publishing.

3. **Book Title.** "A Text Book of Micro and Semimicro Qualitative Inorganic Analysis"

**Autors:** Vogle,

**Publisher:** Longman Green & Co.

4. **Book Title.** "Spectrochemical Analysis by Atomic Absorption and Emission"

**Autors:** L.H.J Lajunen, University of Oulu, Finland

**Publisher:** Royal Society of Chemistry, Thomas Graham House, The Science Park, Cambridge

## FURTHER READING MATERIAL

### **Introduction to Flame Emission and Atomic Absorption Spectroscopy:**

**Note: Introduction to Flame Emission and Atomic Absorption Spectroscopy has been covered in initial lectures, students must consider that lectures**

Atomic absorption and atomic emission spectrometry were the first instrumental techniques to be established for elemental analysis. They are based on the pioneering work of Bunsen and Kirchhoff in the middle of the 19th century who discovered that elements which are brought into a hot flame emit light of a characteristic wavelength. On the other hand, this characteristic emission can be absorbed again by the vapor of the same element. These two discoveries formed the basis for atomic absorption and emission spectrometry and demonstrate the close interrelation and complementary nature of these two techniques. Atomic absorption and atomic emission spectrometry have many theoretical and practical considerations in common, and they can be described by the same formalism. The theory of AAS and AES will thus be treated together.

1. Atomic Emission Spectroscopy (Flame Photometry) FES
2. Atomic Absorption Spectroscopy (AAS)

Inductively coupled plasma atomic emission spectrometry is another method for determining the concentration of metals. It has a similar method with flame photometry but different materials. The principle comes from the fact that excited atoms emit radiation. However, to atomize the atoms, plasma formed from argon is used. As the plasma has a high energy, the atoms emit radiation. By using this emitted radiation, the concentration of metal ions can be determined. It is more effective method when compared to the flame photometer.

Flame photometry is the origin of analytical chemistry in determining the ion concentration of aqueous solutions. It has the very inaccurate results than any of the newly formed methods of spectrophotometry so it is important to see how accurate it functions

### **Desireable Characteristics of Flame for FES & AAS:**

A flame should meet several desirable characteristics for use in flame emission:

- It should provide sufficient energy for the sample to be atomized; for the metals determined presently by flame photometry, the propane-air flame is sufficient.
- The flame should be nonturbulent so that atom population shows the least spatiotemporal variation.
- By itself the flame should have minimum emission and absorption at the wavelengths of interest, and
- The flame should be able to operate at low gas velocities so the emitting atoms remain in the view volume as long as possible.
- In addition, the flame operation should be safe and inexpensive.+

### **Atomic Absorption Spectroscopy:**

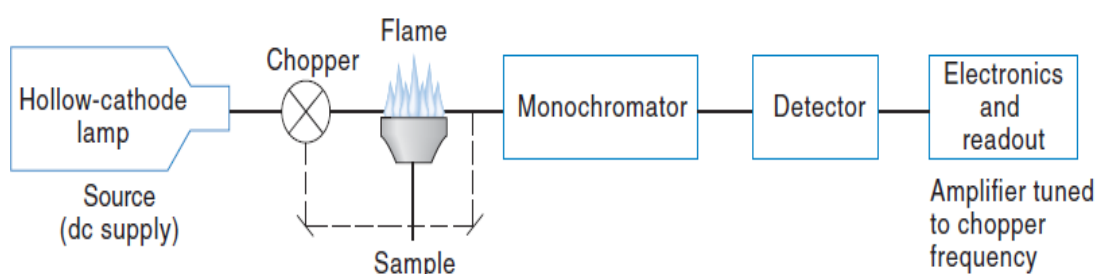
Since the number of atoms in the ground state far outweighs those in the excited state one would normally think that the study of absorption by atoms in a flame will parallel or even precede flame emission spectroscopy studies. This in fact has not been the case because in flame AAS we encounter a problem that has no parallel in molecular absorption spectrometry. This is that the flame itself emits some (often a lot) of

light at the wavelength(s) where we are trying to measure light absorption. Moreover, this background emission from the flame is not particularly constant over time; a simple subtraction of its contribution is not possible. Imagine a flashlight being aimed at a detector in an otherwise dark room. It is not difficult to tell when some of this light is

being absorbed by species present in the light path; this is the situation in molecular spectroscopy. On the other if the same experiment is conducted in a brightly sunlit room (and moreover, clouds are occasionally passing by, changing the background light intensity), it would not be easy for the detector to tell minor changes in the light it is receiving from the flashlight because of the presence of absorbing species.

### Principle of Atomic absorption spectroscopy:

A simplified functional diagram of the first commercial flame AAS instrument (Perkin Elmer Model 303) is shown below. The light source is a hollow cathode lamp that emits at the atomic absorption line of interest (more on this later). A mirror-equipped chopper alternately directs the beam through the flame and bypassing it, effectively providing a double-beam arrangement and compensating for any source drift. Modern AAS instruments mostly do not use such a double-beam arrangement, however. The drift of present-day light sources following a warm-up time is much smaller than drifts in the atomizer. Rather, the reference reading is often taken just before and after the sample is measured, thus effectively providing a double beam in time arrangement. The sample solution is aspirated into a flame as in flame emission spectrometry, and the analyte element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation emitted by the source that is deliberately composed of that element so its characteristic lines are emitted. Atomic absorption spectrophotometry is identical in principle to absorption spectrophotometry. The absorption follows Beer's law. That is, the *absorbance* is directly proportional to the pathlength in the flame and to the concentration of atomic vapor in the flame. Both of these variables are difficult to determine, but the pathlength is essentially held constant in a given burner and flame conditions and the concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution being aspirated. In practice, one calibrates the instrument response by aspirating samples of different concentration



**Schematic diagram of atomic absorption instrument**

### Types of AAS Instrumentation:

Broadly there are two types of AAS instrumentation in present use:

- (a) Line source AAS (LS-AAS) instruments, and
- (b) Continuum source AAS (CS-AAS) instruments

Either type can utilize flame or a graphite furnace (also called electrothermal) atom source. Walsh originally believed CS-AAS instruments would not be possible, not only because single-digit pm resolution is needed, but also because even if such resolution could be attained, there would not be enough light from a

continuum source through such a narrow bandwidth. Technology has advanced to the point, however, that such instruments have become commercially available since 2004, equipped with a very high-power water-cooled Xenon lamp operated in a “hot-spot” mode, a very high-resolution double monochromator, and a CCD-array detector. They have the advantage that very many different lamp sources are not needed for the analysis of

different elements. Bernhard Welz, perhaps the most ardent champion of AAS simply calls CS-AAS “The better way to do AAS”. As in molecular absorption spectrophotometry, the requirements for AAS include a light source, a beam path through the analyte (the flame or furnace), a monochromator, and a detector. As in molecular absorption spectroscopy with array detectors, the monochromator follows the sample. The various components of an atomic absorption spectrophotometer are described as follows.

### **Light Sources for AAS:**

The source emits the lines of the element to be measured. These possess the precise energies required for absorption by the analyte atoms.

#### **Hollow-cathode lamp (HCL):**

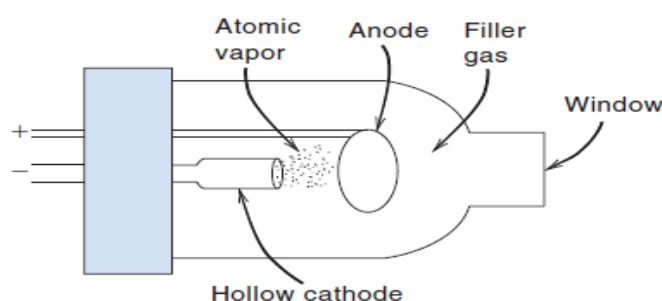
The basic construction of an HCL is illustrated in It consists of a cylindrical hollow cathode made of the element to be determined or an alloy of it, and an anode, usually of W or Zr. Alloying is used where an electrode cannot be made easily from the element (e.g., Na, As, etc.), in the case of precious elements where significant cost savings are possible without sacrificing performance, and where a superior long-term performance is observed from an alloy rather than the pure element (e.g., Cr, Cd, etc.). The alloying elements are carefully chosen not to interfere spectrally with the element of interest. The functioning cathode elements are typically pressed into a cathode cup, commonly made from steel but other metals may be used. The electrodes are enclosed in a borosilicate glass tube with the window material being borosilicate glass for wavelengths over 400 nm, special UV transparent glass for wavelengths between 240 (the exact low-end cut-off varies with the manufacturer) to 400 nm, and quartz for shorter wavelengths. The tube is under reduced pressure and filled with an inert gas, usually neon. Argon is used for those elements where interference from neon lines is possible. A high voltage is impressed across the electrodes, causing the gas atoms to be ionized at the anode. These positive ions are accelerated toward the negative cathode. When they bombard the cathode, they cause some of the metal to “sputter” and become vaporized. The vaporized metal is excited to higher electronic levels by continued collision with the high-energy gas. When the electrons return to the ground state, the characteristic lines of that metal are emitted. The filler gas lines are also emitted. “Boosted” HCLs are offered by some manufacturers. A secondary discharge, electrically isolated from the sputtering current, excites the already vaporized atoms. This provides a sharper and more intense line emission as a source for atomic fluorescence spectrometry. Single-element HCLs are available for some 70 elements. Elements whose emission lines do not interfere with each other can be combined to make multielement lamps. Lamps with two to as many as seven selected elements are available. In some cases, intensities comparable to single-element HCLs are attained, but in many cases significant intensity compromises have to be made to provide the convenience of a multielement source. They may also have shorter lifetimes than single-element HCLs due to selective volatilization (“distillation”) of one of the elements from the cathode with condensation on the walls. Most LS-AAS instruments come with a multi-lamp turret so that a different lamp can be brought online rapidly, whether in manual or automated fashion. The second type of line source is an **electrodeless discharge lamp (EDL)**.

#### **Electrodeless discharge lamp (EDL):**

An EDL contains a small quantity of the analyte as either the element or often as the iodide salt in a quartz bulb. The bulb is filled with an inert gas, typically Ar, at low pressure. The bulb is surrounded by a radio frequency coil. The second type of line source is an **electrodeless discharge lamp** (EDL). An EDL contains a small quantity of the analyte as either the element or often as the iodide salt in a quartz bulb (Figure 17.6). The bulb is filled with an inert gas, typically Ar, at low pressure. The bulb is surrounded by a radio frequency coil.

When the coil is powered to generate an intense electromagnetic field, an inductively coupled discharge occurs in the low-pressure lamp with characteristic line emission of the element. The EDL is a more intense source than an HCL and often has a narrower line width. EDLs require a different type of power supply. It is particularly for the more volatile elements that the EDL can be attractive: lamps are available for As, Bi, Cd, Cs, Ge, Hg, P, Pb, Rb, Sb, Se, Sn, Te, Tl, and Zn. Solid-state diode lasers can be tuned over a (limited) wavelength range and have been used in LS-AAS. Many advantages can be seen: The source is readily modulated at any desired frequency. With a properly designed reflective geometry, the coherent nature of a laser beam can allow multiple passes through the atom source, greatly increasing the sensitivity. Isotopic differences in an element make a small difference in the exact position of a transition line; the 670.8-nm line shifts by 0.015 nm from  $^6\text{Li}$  to  $^7\text{Li}$ , for example. The ability of a diode laser to be scanned over such ranges in a highly precise manner, thus provides the opportunity to perform isotopic analysis. Despite these advantages, until such lasers become readily available in the deep UV, they are unlikely to be of major importance in the general practice of AAS or AFS.

Especially since many laser sources will still be needed to cover the entire wavelength range of interest, the ability to use a single high-power continuum source as discussed below is likely to be increasingly attractive. For CS-AAS, the extremely high resolution needed also means that only a very small fraction of the total radiant power emitted by the continuum source will reach the detector.



**Fig. Hollow Cathode Lamp (HCL)**

## Analyte Atom Sources:

There are several ways to generate atomic vapor for AAS measurements, including various types of flames, electrothermal atomizers, and cold-vapor and hydride generation for atomization.

### 1. Flame Atomization:

The burners and nebulizers used in flame AAS are the same as those in FP but air-  $\text{C}_2\text{H}_2$  ( $2250^\circ\text{C}$ ) and  $\text{N}_2\text{O}$  –  $\text{C}_2\text{H}_2$  ( $2960^\circ\text{C}$ ) are essentially exclusively used. In flame AAS, there are additional criteria that the flame

should meet beyond those required in FP. The flame conditions/fuel-oxidant ratio should permit controlled variation to create either oxidizing or reducing conditions in the flame. Different elements exhibit optimum sensitivity under different flame conditions; both of the above flame types permit such variation and permit low gas velocities (maximum velocity  $\sim 160$  cm/s) so the residence time of atoms in the flame can be prolonged. Note that under a given flame condition, the best sensitivity for a given element may be at different observational heights in the flame. Air-propane flames are not hot enough for general use in AAS because most elements are not efficiently atomized. However, note that although the  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame is much hotter than the air-  $\text{C}_2\text{H}_2$  flame, it is not necessarily better for all elements because if the temperature is too high, some elements begin to significantly ionize. Indeed, this is the reason that in FP the elements that are measured are measured with a flame no hotter than propane-air. Air-  $\text{C}_2\text{H}_2$  is the preferred flame in AAS for the majority of elements except for about 30 elements that tend to form heat-stable most popular for AAS. The nitrous oxide-acetylene flame is best for refractory elements.(refractory) oxides. For these, the  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame is preferred. The burner must be suitable for supporting the very high temperature  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame. A special, thick, stainless steel burner head is used. The length of the flame is equivalent to the cell path length in molecular spectroscopy. The Boling design provides such a long path.

## **2. Getting a Little More from the Atoms:**

The reason that we are interested in low-flame velocities is that once atoms are formed, they stay around in the observation zone longer than at high-flame velocities; a longer time to observe the signal improves the signal-to-noise ratio. One way to prolong the residence time of the atoms with an oxygen-acetylene flame is to use a slotted quartz tube atop the flame. Such a tube is readily put in, but the gain in S/N is modest (only 2–3 times).

Before GFAA became widely used, the use of a tantalum/nickel boat/cup with a handle was popular; this was often used in conjunction with the quartz tube shown above. A desired volume of the sample (e.g., blood, to measure lead in blood) was put in the boat and the sample was then evaporated to dryness. The boat with the sample residue was then put in the flame, and the atoms formed travel into the quartz tube placed above and were measured. Obviously, the boat/cup cannot reach a temperature any greater than that of the flame; the technique was useful only for the relatively easily atomized elements, but many of these elements are of particular interest in biosamples, e.g., Cd, Pb, Hg, Zn, Se, etc.

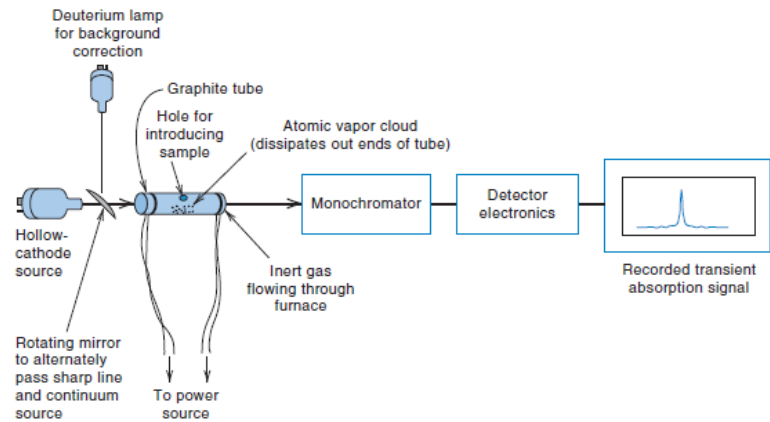
## **3. Electrothermal Atomization:**

Although aspiration into a flame is the most convenient and reproducible means of obtaining atomic vapor, it is not a particularly efficient means of converting all the analyte into atomic vapor and have it present in the optical path for a long enough time to measure the absorption. From the dissolved molecular/ionic entities in solution, as little as 0.1% of the aspirated analyte may actually be atomized and measured. The volume of solution required for flame atomization is minimally of the order of a milliliter or more. Electrothermal atomization uses some type of a mini-furnace (typically less than 1 cm<sup>3</sup> in volume) in which an aliquot of the sample is put in and dried. The furnace is made of an electrically conductive material. While tantalum and other substances have had utility in specific applications (e.g., for elements that form refractory carbides), presently graphite furnaces are nearly exclusively used. The furnace is then rapidly electrically heated (currents in excess of 100 amperes

and heating rates in excess of 1000°C/s are common) to a very high temperature to produce an atomic vapor cloud. Electrothermal atomizers have conversion efficiencies approaching 100%, so absolute detection limits are often 100 to 1000 times improved over those of flame aspiration methods. Our discussion will center on resistively heated atomizers (graphite furnace). Although these are not generally useful for



emission measurements, they are well suited for atomic absorption measurements. A schematic of a typical electrothermal atomizer is shown as follows



Photograph of a transversely heated graphite tube with an integrated platform. The light beam passes from left to right; electrical contact is between the front and back. The sample is introduced through the hole at the top directly onto the platform. (Courtesy PerkinElmer Inc.)

In a typical electrothermal atomization assay, a few microliters of sample are placed inside the graphite tube. Ordinary graphite is porous and leads to problems; to address this, the furnace is made of or coated with nonporous pyrolytic graphite. Original furnaces were simply a cylindrical tube (often referred to as the Massmanfurnace after Hans Massman) but much better results are obtained when the sample is put on a platform (often called the L’vov platform) resting within the tube. The furnace is heated resistively by passing electrical current through it. The furnace can be heated axially (i.e., the contact electrodes are placed on two sides of the long axis of the tube along which the light beam passes) or transversely, at right angles to the beam path. The latter arrangement leads to a more uniform axial temperature distribution; this is used in the high-end instruments. The sample is first dried at a low temperature for a few seconds (~ 100 to 200°C), followed by pyrolysis at 500 to 1400°C to destroy organic matter that produces smoke and scatters the source light during measurement; the smoke from pyrolysis is flushed out by flowing argon gas. Finally, the sample is rapidly thermally atomized at a high temperature, up to 3000°C. The light path passes over the atomizer (or through the tube). A sharp peak of absorbance versus time is recorded as the atomic cloud forms through the light path. Most commonly, the area of the observed peak, rather than its height, is used for quantitation. The heating, of course, is done in an inert atmosphere (e.g., argon) to prevent combustion of the graphite; refractory metal oxides can also form

if oxygen is present. Electrothermal atomization can be nearly 100% efficient and typically only a few microliters of sample are required. Inter-element effects are generally more pronounced in electrothermal AAS than in flame AAS. The inter-element effects are typically addressed by using a standard addition method in which the sample is remeasured after a known amount of a standard

is added to the sample. Electrothermal methods are complementary to flame methods. The latter are better suited when the analyte element is at a sufficiently high concentration to measure and adequate solution volume is available. They provide excellent reproducibility, and interferences are usually easier to deal with. On the other hand, electrothermal atomization excels when either the concentrations or available sample amounts are very small. Additionally, in many cases it is possible to analyze solid samples directly by electrothermal AAS. Method development and calibration of electrothermal methods require more care, however.

**4. Cold Vapor and Hydride Generation for Atomization:**

The best-known example in this class is that of mercury. Mercury is easily reduced to the element by reducing agents such as SnCl<sub>2</sub>. When a suitable reductant is added to a sample solution containing mercury, it is reduced to Hg(0); simultaneous purging of the solution (typically with argon) flushes the liberated



mercury into an AAS measurement cell. Sodium borohydride ( $\text{NaBH}_4$ ) is a much more powerful reducing agent, and it can reduce organically bound Hg to  $\text{Hg}(0)$ . The use of  $\text{SnCl}_2$  and  $\text{NaBH}_4$  as respective reducing agents allows the measurement of inorganic and total Hg, respectively. Although the vapor pressure of cadmium is very low at room temperature, Cd can also be successfully generated as  $\text{Cd}(0)$  vapor from solution by  $\text{NaBH}_4$ .  $\text{NaBH}_4$  also generates the hydrides of As, Bi, Ge, Pb, Sb, S, Se, Sn, Te, In, and Tl as the gases—these are easily decomposed to the element by introducing the generated gas into a flame, a hot quartz measurement cell, or even a graphite furnace. The great advantage of cold vapor and hydride generation is **matrix isolation**, meaning that the analyte of interest is totally isolated as a vapor from the original sample matrix. There are reports that while many other metals such as Au, Ag, Co, Cr, Cu, Fe, Ir, Mn, Ni, Os, Pd, Pt, Rh, Ru, and Zn do not form hydrides, they do form nanometer-size elemental aerosols, which can be then readily atomized.

## INTERFERENCES IN AAS

These fall under three classes, spectral, chemical, and physical. We will discuss these briefly and point out their relative effects in emission and absorption measurements

### 1. Spectral Interferences:

Atomic absorption lines are very narrow and absorption lines from different elements almost never overlap; a much more common problem is molecular absorption. Such absorption can be caused by flame gases/combustion products, undissociated sample-derived molecules and also scattering by particles that may be generated from the sample, especially in electrothermal atomization or in flame AAS when the aspirated sample has much dissolved solids, making it difficult to atomize all of the sample. Unless corrected for, this erroneously measured high absorbance can lead to a gross overestimation of the analyte concentration. The effects of such **background absorption** can be corrected for by making sequential measurements of the absorbance due to the background and that due to the analyte + background and determining that due to the analyte by difference. The most common way of doing this is to use an additional light source, a continuum source such as a D2 lamp, . Such a **continuum source background correction method** takes advantage of the fact that the background absorption is broad across the entire wavelength span that passes through the slit-monochromator combination. When a mirror switches the light source from the HCL to

the D2 lamp, the average absorbance is measured across the wavelength region. The atomic absorption line is so narrow compared to this passband that the absorbance due to the analyte atoms is considered essentially negligible. On the other hand, when the absorbance is measured with the HCL, it measures the absorbance due to the analyte atoms as well as the background absorbance at that wavelength. Typically a rotating mirror automatically switches between the two light sources and the difference signal is electronically generated; separate manual measurement or correction is not necessary. A D2 lamp does not provide enough energy above 330 nm, and a quartz halogen lamp needs to be used; low-end instruments do not often provide the ability to use another switchable lamp. The continuum source correction method is far from perfect; mismatches in the correction beam geometry with that of the HCL and lack of uniformity in its spatial and spectral energy distribution and contribution of atomic absorption in the background measurement process, all cause difficulties in high-accuracy measurements. However, it is relatively inexpensive to implement and convenient to use.

### 2. AAS Ionization Interference:

An appreciable fraction of alkali and alkaline earth elements and several other elements may be ionized in very hot flames. Since we are measuring the un-ionized atoms, both emission and absorption signals can

be decreased. In the present practice of flame photometry, only flames of modest temperatures are used, so ionization interference is not a problem. Much hotter flames are used in flame AAS, however, and ionization of easily ionizable elements do occur. If a fixed fraction of the element of interest is ionized, this would largely bIonization can be suppressed by included in its calibration behavior, except that the sensitivity and the linear dynamic adding a solution of a more easily ionized element, for example, potassium or cesium. range may suffer some. The main problem comes from the effects of one ionizable element upon another. Consider that we wish to measure calcium by flame AAS and a calibration curve was constructed with pure calcium standards. There is some ionization of the calcium, but this is accounted for in the calibration. The samples, on the other hand, contain significant and variable amounts of sodium. The sodium ionizes easily, increasing the free electron density in the flame and in turn suppressing the ionization of calcium, thus increasing the calcium atom/ion ratio and causing a positive measurement error. Ionization interference can usually be overcome either by adding large amounts of the interfering, easily ionizable, element to both the samples and the standards, to make the enhancement constant and ionization minimal. Ionization can usually be detected by noting that the calibration curve has a positive deviation or curvature upward at higher concentrations because the free electron density in the flame increases sufficiently at high analyte concentrations so that a lesser fraction of the atoms are ionized compared to that at lower concentrations.

### **3. Refractory Compound Formation:**

The sample may contain constituents that form a refractory (heat-stable) compound with the analyte element of interest. For example, when determining calcium, the presence of phosphate in the sample can cause the formation of calcium pyrophosphate,  $\text{Ca}_2\text{P}_2\text{O}_7$  that is not easily broken down to the atoms at flame temperatures. The lack of complete atomization of calcium thus causes a negative error in its determination. The best way to handle such interference is chemical intervention; in the above example, a high concentration (ca. 1%) of strontium chloride or lanthanum nitrate can be added to the solution. Called a releasing agent, the strontium or lanthanum will preferentially combine with the phosphate and prevent its reaction with the calcium. Alternatively, a high concentration of EDTA can be added to the solution to form a chelate with the calcium; this prevents its reaction with phosphate. The calcium–EDTA chelate is decomposed in the flame to Refractory compound formation is give free calcium atoms. A hotter flame such as the  $\text{N}_2\text{O}$ – $\text{C}_2\text{H}_2$  flame also successfully avoided by addition of a chemical competitor or use of very high temperatures. atomizes many compounds that are not easily decomposed at lower temperatures. In flame AAS, some elements, e.g., Al, Ti, V, Mo, etc., react with flame species, notably O and OH, forming refractory oxides and hydroxides that can only be decomposed in a  $\text{N}_2\text{O}$ – $\text{C}_2\text{H}_2$  flame. The flame is usually operated in the reducing (fuel-rich) condition in which a large red feather-like secondary-reaction zone is observed; this zone arises from the presence of CN, NH, and other highly reducing radicals. These (or the lack of oxygen-containing species), combined with the high temperature of the flame, decompose and/or prevent the formation of refractory oxides. Electrothermal atomization of some elements can suffer from interferences as well. Chemical modifiers, for specific elements or specific types of samples, have been developed. Volatilization of NaCl from highly saline samples such as seawater is a problem, and addition of  $\text{NH}_4\text{NO}_3$  solves this by forming volatile  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_3$ , which are easily thermally decomposed. Specific recommended additives for the analysis of different elements have been widely tabulated, see, e.g., [http://www.chem.agilent.com/library/usermanuals/public/gta\\_analytical\\_methods\\_0848.pdf](http://www.chem.agilent.com/library/usermanuals/public/gta_analytical_methods_0848.pdf). The formation of refractory carbides can cause serious problems.

### **4. Physical Interferences:**

Most parameters that affect the rate of sample uptake in the burner and the atomization efficiency can be considered physical interferences. This includes such things as variations in the gas flow rates, variation in

sample viscosity due to temperature or solvent variation, high and variable solids content, and changes in the flame temperature. Sample surface tension changes can affect the size of the nebulized droplets. These can generally be accounted for by frequent calibration, use of internal standards, or standard addition

## Flame Emission Spectrometry:

In this technique, the source of excitation energy is a flame. The sample is introduced into the flame in the form of a solution. A flame is a low-energy source, and so the emission spectrum is simple and there are few emission lines. In practice, the technique is inexpensive and attractive for only a few elements. As a direct result of the work of Kirchhoff and Bunsen in the early 1860s, the analytical utility of measuring the characteristic radiation emitted by specific elements excited in flames was realized. The earliest such instrument was used for the measurement of sodium in plant ash using a Bunsen flame. The difficult part in such an instrument was how best to introduce the sample into the flame. It wasn't until 1929, when Lundegardh utilized a nebulizer to introduce a significant fraction of the sample reproducibly into the flame, that a breakthrough was made. Characteristic atomic emission lines were dispersed by a quartz prism spectrograph and recorded photographically. Use of optical filters and electrical photodetectors improved convenience and precision in later years, and such instruments became widely useful for measuring Na, K, Li, and Ca. Work on many other elements then became possible with the use of grating spectrometers equipped with more sensitive photomultiplier detectors. But the commercial development of the more broadly applicable AAS technique in the 1960s essentially restricted the scope of flame emission spectrometry and arrested its further development.

Most commercial instruments in use today are dedicated to the measurement of Li, Na, K, Ca, and Ba, using interference filters centered at 670, 589, 766, 622, and 515 nm, respectively, and thus they are commonly called **flame photometers**. Calcium is actually measured by the emission of molecular CaOH, as this emission at 622 nm is more intense than the emission by atomic Ca at 423 nm. A propane-air flame (temperature 1900–2000°C) is commonly used. Butane-air or natural gas-air flames can also be used; these flames are not as hot and the measurement is less sensitive. With a propane-air flame, the best of current instruments claim LODs of 0.02 mg/L for Na and K to 10 mg/L for Ba. Most analyze one element at a time; the filter is manually changed to switch the target element, but some, such as the BWB Tech XP Flame Photometer, are capable of providing simultaneous multiple readouts using multiple detection channels. The formation of CaOH is much affected by the presence of Ba, however, and the two generally cannot be simultaneously determined. The atomic emission line of Ca at 423 nm is less susceptible to interference by Ba but is not commonly used because of lower sensitivity. Many such shortcomings of flame emission measurement can be overcome with higher temperature and more reducing flames such as air-acetylene and higher-resolution spectrometric detection. In many ways, flame emission as practiced today in the form of flame photometry (FP) is a step backward from the heights previously attained because incorporation of high temperature flames and high-resolution spectrometry is not cost competitive relative to the more broadly applicable flame AAS technique

## BURNERS USED FOR FLAME SPECTROMETRY AND DESIRABLE FLAME CHARACTERISTICS

In one type, the fuel (propane/acetylene) and the oxidant (air/oxygen/nitrous oxide) are premixed and the solution is nebulized by the flow of the premixed gas before the flame. This is the type of arrangement

pioneered by Lundegardh. Much of the liquid that is aspirated by the nebulizer actually tends to form large droplets and simply drains from the burner. In the second type of burner, often called a **total consumption burner**, the fuel and oxidant gases are not premixed. The design is basically that consisting of three concentric tubes that terminate in a nozzle. The outermost typically carries the fuel, the next one the oxidant, and the central tube, a capillary, was the sample inlet. The Venturi suction created by the fuel-oxidant flow aspirates the sample into the flame; the name derives from the fact that the entire aspirated sample enters the flame.

Notwithstanding the superiority the “total consumption” name may imply, the **premix burner**, sometimes called the **laminar flow burner**, ultimately produces better results. It is the only type of burner in present use. The primary reason for the difference is the sample droplet size generated. Whereas the direct sample injection process in the total consumption burner results in larger droplets of size  $\sim 7$  nL, the premix burner nebulizer produces droplets of size as small as 0.05 nL. The smaller droplets evaporate and eventually atomize much more easily. A three-slotted burner head, originally due to Boling, as shown in the figure, is the most common. It produces a wide flame, sufficient to accommodate the widest probe beam cross section. Atmospheric oxygen enters only the edges of the flame, permitting optimum reducing conditions in the central portion of the flame. The atom population is uniform with height over a significant portion of the flame, making adjustments simple. Three-slot burners have been shown to exhibit less noise and clog less easily with samples of significant dissolved solute content than most other designs. Past the nebulization point, most burner/nebulizer assemblies have baffles in their path that effectively remove the large droplets; these do not atomize as efficiently and result in local cooling of the flame.

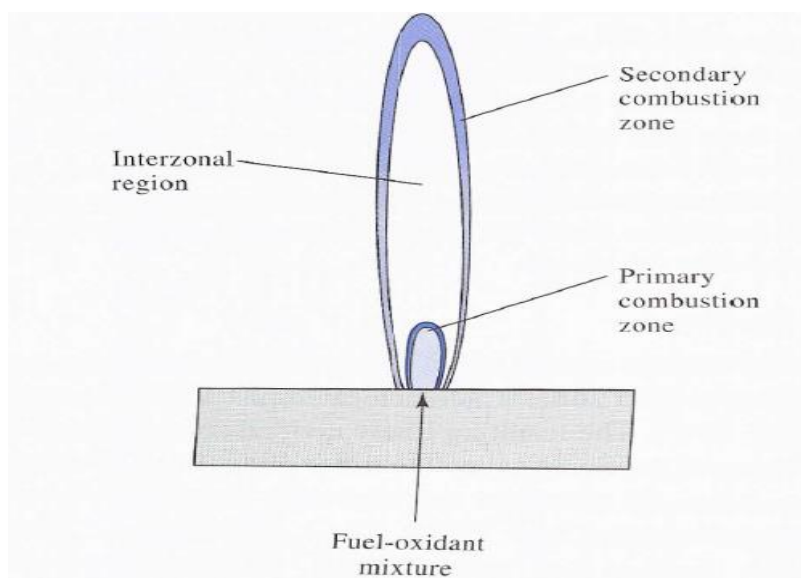
**A flame should meet several desirable characteristics for use in flame emission applications:**

(a) it should provide sufficient energy for the sample to be atomized; for the metals determined presently by flame photometry, the propane-air flame is sufficient, (b) the flame should be nonturbulent so that atom population shows the least spatiotemporal variation, (c) by itself the flame should have minimum emission and absorption at the wavelengths of interest, and (d) the flame should be able to operate at low gas velocities so the emitting atoms remain in the view volume as long as possible.

In addition, the flame operation should be safe and inexpensive.

## Properties of Flame:

When a nebulized *sample* is carried into a flame, desolvation of the droplets occurs in the **primary combustion zone**, which is located just above the tip of the burner, as shown in Figure 28-12. The resulting finely divided solid particles are carried to a region in the center of the *flame* called the **inner cone**. Here, in *this* hottest part of the flame, the *particles* are vaporized and converted to gaseous atoms, elementary ions, and molecular species. *Excitation* of *atomic* emission spectra also takes place in *this* region. Finally, the atoms, molecules, and ions are carried to the outer edge, or **outer cone**, where oxidation may occur before the atomization products disperse into the atmosphere. Because the velocity of the fuel/oxidant mixture through the flame is high, only a fraction of the sample undergoes all these processes; indeed, a flame is not a very efficient atomizer.



### Types of Flames Used in Atomic Spectroscopies:

The common fuels and oxidants employed in flame spectroscopy and the approximate range of temperatures realized with each of these mixtures is given in the table. Note that temperatures of 1700°C to 2400°C are obtained with the various fuels when air serves as the oxidant. At these temperatures, only easily excitable species such as the alkali and alkaline earth metals produce usable emission spectra heavy metal species, which are less readily excited, oxygen or nitrous oxide must be employed as the oxidant.

Flames Used in Atomic Spectroscopy	
Fuel and Oxidant	Temperature, °C
*Gas/Air	1700–1900
*Gas/O <sub>2</sub>	2700–2800
H <sub>2</sub> /air	2000–2100
H <sub>2</sub> /O <sub>2</sub>	2500–2700
†C <sub>2</sub> H <sub>2</sub> /air	2100–2400
†C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub>	3050–3150
†C <sub>2</sub> H <sub>2</sub> /N <sub>2</sub> O	2600–2800

### Effects of Flame Temperature on absorption and emission:

Both emission and absorption spectra are affected in a complex way by variations in flame temperature. In both cases, higher temperatures increase the total atom population of the flame and thus the sensitivity. With certain elements, such as the alkali metals, however, this increase in atom population is more than offset by the loss of atoms by ionization. To a large extent, flame temperature determines the efficiency of atomization that is, the fraction of the analyte that is desolvated, vaporized, and converted to free atoms or ions, or both. The flame temperature also determines the relative number of excited and unexcited atoms in a flame. In an air/acetylene flame, for example, the ratio of excited to unexcited magnesium atoms can be computed to be about 10<sup>-8</sup>, whereas in an oxygen/acetylene flame, which is about 7000° hotter, this ratio is about 10<sup>-6</sup>. Hence, from an excitation standpoint, control of temperature is very important in flame emission methods. For example, with a 2500° flame, a temperature increase of 100° causes the number of sodium atoms in the excited 3p state to increase by about 3%. In contrast, the corresponding decrease in the much larger number of ground-state atoms is only about 0.002%. Therefore, at first glance,



emission methods, based as they are on the population of *excited atoms*, require much closer control of flame temperature than do absorption procedures, in which the analytical signal depends on the number of *unexcited atoms*. In practice, however, because of the temperature dependence of the atomization step, both methods show similar dependencies. The number of unexcited atoms in a typical flame exceeds the number of excited atoms by a factor of  $10^3$  to  $10^{10}$  or more. This suggests that absorption methods should show lower detection limits than emission methods. In fact, however, several other variables also influence detection limits, and the two methods tend to complement each other in this regard.

### **Absorption and Emission Spectra in Flames:**

Both atomic and molecular emission and absorption can be measured when a sample is atomized in a flame.. Atomic emissions in this spectrum are made up of narrow lines, such as that for sodium at about 330 nm, potassium at approximately 404 nm, and calcium at 423 nm. Atomic spectra are thus called line spectra. Also present are emission bands that result from excitation of molecular species such as MgOH, MgO and OH. Here, vibrational transitions superimposed on electronic transitions.

### **Ionization in Flames:**

All elements ionize to some degree in a flame, which leads to a mixture of atoms, ions, and electrons in the hot medium. For example, when a sample containing barium is atomized, the equilibrium is established in the inner cone of the flame. The position of this equilibrium depends on the temperature of the flame and the total concentration of barium as well as on the concentration of the electrons produced from the ionization of *all elements* present in the sample. At the temperatures of the hottest flames ( $>3000$  K), nearly half of the barium is present in ionic form. The emission and absorption spectra of Ba and Ba<sup>+</sup> are, however, totally different from one another. Thus, in a high-temperature flame, two spectra for barium appear: one for the atom and one for its ion. Flame temperature again plays an important role in determining the fraction of the analyte ionized.

## **FLAME PROCESSES OCCURRING IN TYPICAL FLAME PHOTOMETRY**

When a sample solution is aspirated into the flame. The solvent evaporates from the fine droplets, leaving the dehydrated salt. The salt is dissociated into free gaseous atoms in the ground state. A certain fraction of these atoms can absorb energy from the flame and be raised to an excited electronic state. The excited levels have a short lifetime (1–10 ns) and drop back to the ground state, emitting photons of characteristic wavelengths, with energy equal to  $h\nu$ . Only electronic transitions are involved and very narrow emission lines are observed. Some of the atoms also ionize by thermal excitation; a fraction of them is excited by thermal energy to form excited ions. In the case of measuring calcium by flame photometry, side reactions in the relatively low-temperature propane-air flame result in largely CaOH formed in the flame, which is excited and the emission from this excited molecule (much broader than atomic emission lines) is measured in typical filter flame photometers. For all the other metals, the emission from the excited atom is measured. As indicated in the figure, side reactions in the flame may decrease the population of the desired emitting species and hence the emission signal. The intensity of emission is linearly proportional to the concentration



of the analyte in the solution being aspirated only at the low end of the calibration curve. For a number of reasons (including the fact that there is a much greater population of the atoms in the ground state that can reabsorb the emitted radiation) the signal at higher analyte concentrations is less than

In this technique, the source of excitation energy is a flame. The sample is introduced into the flame in the form of a solution. A flame is a low-energy source, and so the emission spectrum is simple and there are few emission lines. In practice, the technique is inexpensive and attractive for only a few elements. As a direct result of the work of Kirchhoff and Bunsen in the early 1860s, the analytical utility of measuring the characteristic radiation emitted by specific elements excited in flames was realized. The earliest such instrument was used for the measurement of sodium in plant ash using a Bunsen flame. The difficult part in such an instrument was how best to introduce the sample into the flame. It wasn't until 1929, when Lundegardh utilized a nebulizer to introduce a significant fraction of the sample reproducibly into the flame, that a breakthrough was made. Characteristic atomic emission lines were dispersed by a quartz prism spectrograph and recorded photographically. Use of optical filters and electrical photodetectors improved convenience and precision in later years, and such instruments became widely useful for measuring Na, K, Li, and Ca. Work on many other elements then became possible with the use of grating spectrometers equipped with more sensitive photomultiplier detectors. But the commercial development of the more broadly applicable AAS technique in the 1960s essentially restricted the scope of flame emission spectrometry and arrested its further development. Most commercial instruments in use today are dedicated to the measurement of Li, Na, K, Ca, and Ba, using interference filters centered at 670, 589, 766, 622, and 515 nm, respectively, and thus they are commonly called **flame photometers**. Calcium is actually measured by the emission of molecular CaOH, as this emission at 622 nm is more intense than the emission by atomic Ca at 423 nm. A propane-air flame (temperature 1900–2000°C) is commonly used. Butane-air or natural gas-air flames can also be used; these flames are not as hot and the measurement is less sensitive. With a propane-air flame, the best of current instruments claim LODs of 0.02 mg/L for Na and K to 10 mg/L for Ba. Flame Photometer, are capable of providing simultaneous multiple readouts using multiple detection channels. The formation of CaOH is much affected by the presence of Ba, however, and the two generally cannot be simultaneously determined. The atomic emission line of Ca at 423 nm is less susceptible to interference by Ba but is not commonly used because of lower sensitivity. Many such shortcomings of flame emission measurement can be overcome with higher temperature and more reducing flames such as air-acetylene and higher-resolution spectrometric detection. In many ways, flame emission as practiced today in the form of flame photometry (FP) is a step backward from the heights previously attained because incorporation of high temperature flames and high-resolution spectrometry is not cost competitive relative to the more broadly applicable flame AAS technique.

If a solution containing a metallic salt (or some other metallic compound) is aspirated into a flame (e.g. of acetylene burning in air), a vapour which contains atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to an energy level which is sufficiently high to permit the emission of radiation characteristic of the metal, e.g. the characteristic yellow colour imparted to flames by compounds of sodium. This is the basis of **flame emission spectroscopy** (FES) which was formerly referred to as **flame photometry**. However, a much larger number of the gaseous metal atoms will normally remain in an unexcited state or, in other words, in the ground state. These ground-state atoms are capable of absorbing radiant energy of their own specific resonance wavelength, which in general is the wavelength of the radiation that the atoms would emit if excited from the ground state. Hence if light of the resonance wavelength is passed through a flame containing the atoms in question, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground-state atoms present in the flame. This is the underlying principle of **atomic absorption spectroscopy** (AAS). **Atomic fluorescence spectroscopy** (AFS) is based on the re-emission of absorbed energy by free atoms.

The procedure by which gaseous metal atoms are produced in the flame may be summarised as follows. When a solution containing a suitable compound of the metal to be investigated is aspirated into a flame, the following events occur in rapid succession:

1. evaporation of solvent leaving a solid residue;
2. vaporisation of the solid with dissociation into its constituent atoms, which initially, will be in the ground state; and
3. some atoms may be excited by the thermal energy of the flame to higher energy levels, and attain a condition in which they radiate energy.

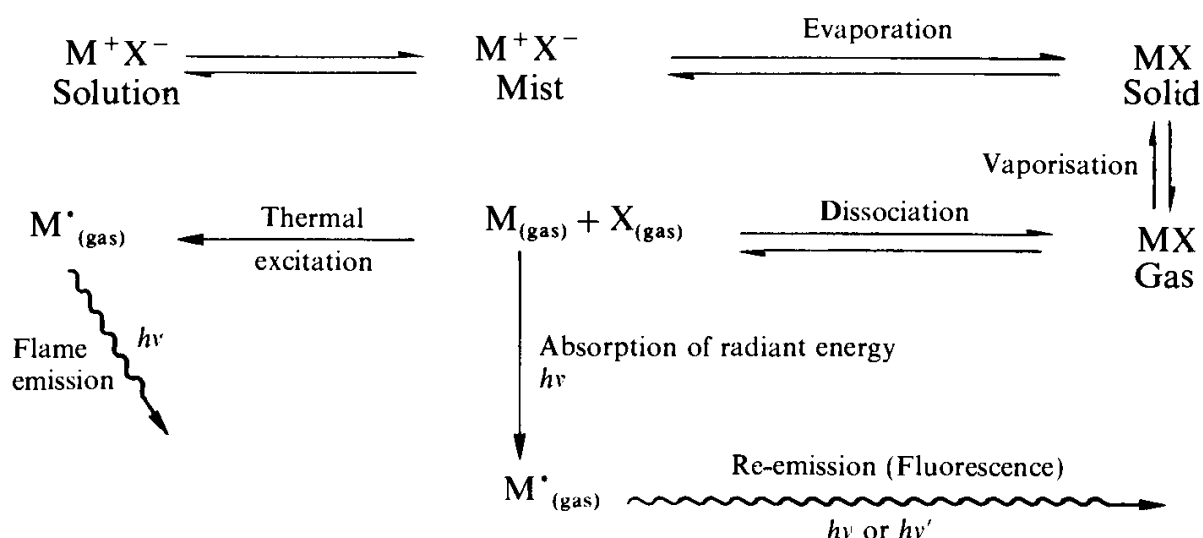


Fig. 21.1

## 21.1 ELEMENTARY THEORY

Consider the simplified energy-level diagram shown in Fig. 21.2, where  $E_0$  represents the ground state in which the electrons of a given atom are at their lowest energy level and  $E_1, E_2, E_3$ , etc., represent higher or excited energy levels.

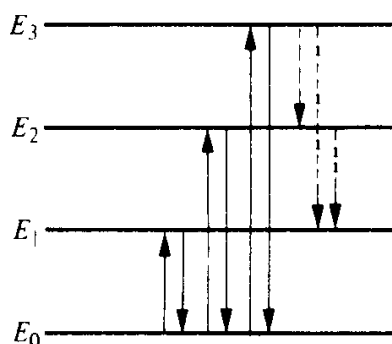


Fig. 21.2

Transitions between two quantised energy levels, say from  $E_0$  to  $E_t$ , correspond to the absorption of radiant energy, and the amount of energy absorbed ( $\Delta E$ ) is determined by Bohr's equation

$$\Delta E = E_t - E_0 = h\nu = hc/\lambda$$

where  $c$  is the velocity of light,  $h$  is Planck's constant, and  $\nu$  is the frequency and  $\lambda$  the wavelength of the radiation absorbed. Clearly, the transition from  $E_t$  to  $E_0$  corresponds to the *emission* of radiation of frequency  $\nu$ .

Since an atom of a given element gives rise to a definite, characteristic line spectrum, it follows that there are different excitation states associated with different elements. The consequent emission spectra involve not only transitions from excited states to the ground state, e.g.  $E_3$  to  $E_0$ ,  $E_2$  to  $E_0$  (indicated by the full lines in Fig. 21.2), but also transitions such as  $E_3$  to  $E_2$ ,  $E_3$  to  $E_1$ , etc. (indicated by the broken lines). Thus it follows that the emission spectrum of a given element may be quite complex. In theory it is also possible for absorption of radiation by already excited states to occur, e.g.  $E_1$  to  $E_2$ ,  $E_2$  to  $E_3$ , etc., but in practice the ratio of excited to ground state atoms is extremely small,

and thus the absorption spectrum of a given element is usually only associated with transitions from the ground state to higher energy states and is consequently much simpler in character than the emission spectrum.

The relationship between the ground-state and excited-state populations is given by the Boltzmann equation

$$N_t/N_0 = (g_t/g_0)e^{-\Delta E/kT}$$

where

- $N_t$  = number of atoms in the excited state,
- $N_0$  = number of ground state atoms,
- $g_t/g_0$  = ratio of statistical weights for ground and excited states,
- $\Delta E$  = energy of excitation =  $h\nu$ ,
- $k$  = the Boltzmann constant,
- $T$  = the temperature in Kelvin.

It can be seen from this equation that the ratio  $N_t/N_0$  is dependent upon both the excitation energy  $\Delta E$  and the temperature  $T$ . An increase in temperature and a decrease in  $\Delta E$  (i.e. when dealing with transitions which occur at longer wavelengths) will both result in a higher value for the ratio  $N_t/N_0$ .

Calculation shows that only a small fraction of the atoms are excited, even under the most favourable conditions, i.e. when the temperature is high and the excitation energy low. This is illustrated by the data in Table 21.1 for some typical resonance lines.

Table 21.1 Variation of atomic excitation with wavelength and with temperature

Element	Wavelength (nm)	$N_t/N_0$	
		2000K	4000K
Na	589.0	$9.86 \times 10^{-6}$	$4.44 \times 10^{-3}$
Ca	422.7	$1.21 \times 10^{-7}$	$6.03 \times 10^{-4}$
Zn	213.9	$7.31 \times 10^{-15}$	$1.48 \times 10^{-7}$

Since, as already explained, the absorption spectra of most elements are simple in character as compared with the emission spectra, it follows that atomic absorption spectroscopy is less prone to inter-element interferences than is flame emission spectroscopy. Further, in view of the high proportion of ground state to excited atoms, it would appear that atomic absorption spectroscopy should also be more sensitive than flame emission spectroscopy. However, in this respect the wavelength of the resonance line is a critical factor, and elements whose resonance lines are associated with relatively low energy values are more sensitive as far as flame emission spectroscopy is concerned than those whose resonance lines are associated with higher energy values. Thus sodium with an emission line of wavelength 589.0 nm shows great sensitivity in flame emission spectroscopy, whereas zinc (emission line wavelength 213.9 nm) is relatively insensitive.

The integrated absorption is given by the expression

$$Kdv = fN_0(\pi e^2/mc)$$

where

- $K$  is the absorption coefficient at frequency  $\nu$ ,
- $e$  is the electronic charge,
- $m$  the mass of an electron,
- $c$  the velocity of light,
- $f$  the oscillator strength of the absorbing line (this is inversely proportional to the lifetime of the excited state),
- $N_0$  is the number of metal atoms per mL capable of absorbing the radiation.

In this expression the only variable is  $N_0$  and it is this which governs the extent of absorption. Thus it follows that the integrated absorption coefficient is directly proportional to the concentration of the absorbing species.

It would appear that measurement of the integrated absorption coefficient should furnish an ideal method of quantitative analysis. In practice, however, the absolute measurement of the absorption coefficients of atomic spectral lines is extremely difficult. The natural line width of an atomic spectral line is about  $10^{-5}$  nm, but owing to the influence of Doppler and pressure effects, the line is broadened to about 0.002 nm at flame temperatures of 2000–3000 K. To measure the absorption coefficient of a line thus broadened would require a spectrometer with a resolving power of 500 000. This difficulty was overcome by Walsh,<sup>4t</sup> who used a source of sharp emission lines with a much smaller half width than the absorption line, and the radiation frequency of which is centred on the absorption frequency. In this way, the absorption coefficient at the centre of the line,  $K_{\max}$ , may be measured. If the profile of the absorption line is assumed to be due only to Doppler broadening, then there is a relationship between  $K_{\max}$  and  $N_0$ . Thus the only requirement of the spectrometer is that it shall be capable of isolating the required resonance line from all other lines emitted by the source.

It should be noted that in atomic absorption spectroscopy, as with molecular absorption, the absorbance  $A$  is given by the logarithmic ratio of the intensity of the incident light signal  $I_0$  to that of the transmitted light  $I_t$ , i.e.

$$A = \log I_0/I_t = KLN_0$$

where

- $N_0$  is the concentration of atoms in the flame (number of atoms per mL);
- $L$  is the path length through the flame (cm),
- $K$  is a constant related to the absorption coefficient.

For small values of the absorbance, this is a linear function.

With flame emission spectroscopy, the detector response  $E$  is given by the expression

$$E = k\alpha c,$$

where

- $k$  is related to a variety of factors including the efficiency of atomisation and of self-absorption,
- $\alpha$  is the efficiency of atomic excitation,
- $c$  is the concentration of the test solution.

It follows that any electrical method of increasing  $E$ , as for example improved amplification, will make the technique more sensitive.

The basic equation for atomic fluorescence is given by

$$F = QI_0kc$$

where

$Q$  is the quantum efficiency of the atomic fluorescence process,

$I_0$  is the intensity of the incident radiation,

$k$  is a constant which is governed by the efficiency of the atomisation process,

$c$  is the concentration of the element concerned in the test solution.

It follows that the more powerful the radiation source, the greater will be the sensitivity of the technique.

To summarise, in both atomic absorption spectroscopy and in atomic fluorescence spectroscopy, the factors which favour the production of gaseous atoms in the ground state determine the success of the techniques. In flame emission spectroscopy, there is an additional requirement, namely the production of excited atoms in the vapour state. It should be noted that the conversion of the original solid MX into gaseous metal atoms ( $M_{\text{gas}}$ ) will be governed by a variety of factors including the rate of vaporisation, flame composition and flame temperature, and further, if MX is replaced by a new solid, MY, then the formation of  $M_{\text{gas}}$  may proceed in a different manner, and with a different efficiency from that observed with MX.

## 21.3 INSTRUMENTATION

The three flame spectrophotometric procedures require the following essential apparatus.

- (a) For flame emission spectroscopy a **nebuliser-burner system** which produces gaseous metal atoms by using a suitable combustion flame involving a fuel gas-oxidant gas mixture is needed. Note however that with so-called non-flame cells, the burner is not required.
- (b) A **spectrophotometer system** which includes a suitable optical train, a photosensitive detector and appropriate display device for the output from the detector.
- (c) For both atomic absorption spectroscopy and atomic fluorescence spectroscopy, a **resonance line source** is required for each element to be determined, these line sources are usually modulated (see Section 21.9).

A schematic diagram showing the disposition of these essential components for the different techniques is given in Fig. 21.3. The components included within the frame drawn in broken lines represent the apparatus required for flame emission spectroscopy. For atomic absorption spectroscopy and for atomic fluorescence spectroscopy there is the additional requirement of a resonance line source, In atomic absorption spectroscopy this source is placed in line with the detector, but in atomic fluorescence spectroscopy it is placed in a position at right angles to the detector as shown in the diagram. The essential components of the apparatus required for flame spectrophotometric techniques will be considered in detail in the following sections.



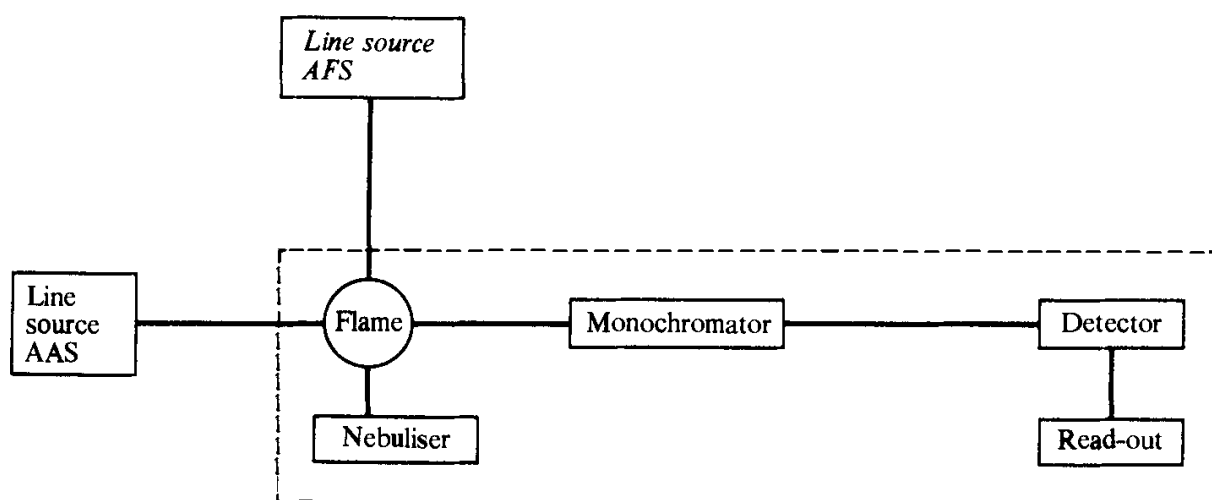


Fig. 21.3

## 21.4 FLAMES

For flame spectroscopy an essential requirement is that the flame used shall produce temperatures in excess of 2000 K. In most cases this requirement can only be met by burning the fuel gas in an oxidant gas which is usually air, nitrous oxide, or oxygen diluted with either nitrogen or argon. The flame temperatures attained by the common fuel gases burning in (1) air and (2) nitrous oxide are given in Table 21.2. The flow rates of both the fuel gas and the oxidant gas should be measured, for some flames are required to be rich in the fuel gas, whilst other flames should be lean in fuel gas: these requirements are discussed in Section 21.20. The concentration of gaseous atoms within the flame, both in the ground and in the excited states, may be influenced by (a) the flame composition, and (b) the position considered within the flame.

**Table 21.2** Flame temperatures with various fuels

Fuel gas	Temperature (K)	
	Air	Nitrous oxide
Acetylene	2400	3200
Hydrogen	2300	2900
Propane	2200	3000

As far as flame composition is concerned, it may be noted that an acetylene–air mixture is suitable for the determination of some 30 metals, but a propane–air flame is to be preferred for metals which are easily converted into an atomic vapour state. For metals such as aluminium and titanium which form refractory oxides, the higher temperature of the acetylene–nitrous oxide flame is essential, and the sensitivity is found to be enhanced if the flame is fuel-rich.

With regard to position within the flame, it can be shown that in certain cases the concentration of atoms may vary widely if the flame is moved either vertically or laterally relative to the light path from the resonance line source. Rann and Hambly<sup>42</sup> have shown that with certain metals (e.g. calcium and

molybdenum), the region of maximum absorption is restricted to specific areas of the flame, whereas the absorption of silver atoms does not alter appreciably within the flame, and is unaffected by the fuel gas/oxidant gas ratio.

For the sake of brevity, the so-called ‘cool flame’ techniques based upon the use of an oxidant-lean flame such as hydrogen/nitrogen-air, have not been included.

## 21.5 THE NEBULISER–BURNER SYSTEM

The purpose of the nebuliser–burner system is to convert the test solution to gaseous atoms as indicated in Fig. 21.2, and the success of flame photometric methods is dependent upon the correct functioning of the nebuliser–burner system. It should, however, be noted that some flame photometers have a very simple burner system (see Section 21.13).

The function of the nebuliser is to produce a mist or aerosol of the test solution. The solution to be nebulised is drawn up a capillary tube by the Venturi action of a jet of air blowing across the top of the capillary; a gas flow at high pressure is necessary in order to produce a fine aerosol.

There are two main types of burner system: (a) the **pre-mix or laminar-flow burner**, and (b) the **total consumption or turbulent-flow burner**. In the pre-mix type of burner, the aerosol is produced in a vaporising chamber where the larger droplets of liquid fall out from the gas stream and are discharged to waste. The resulting fine mist is mixed with the fuel gas and the carrier (oxidant) gas, and the mixed gases then flow to the burner head. In atomic absorption spectroscopy the burner is a long horizontal tube with a narrow slit along its length. This produces a thin flame of long path length which can be turned into or away from the beam of radiant energy. The flame path of a burner using air–acetylene, air–propane or air–hydrogen mixtures is about 10–12 cm in length, but with a nitrous oxide–acetylene burner it is usually reduced to about 5 cm because of the higher burning velocity of this gas mixture. In addition to a long light path, this type of burner has the advantages of being quiet in action and with little danger of incrustation around the burner head since large droplets of solution have been eliminated from the stream of gas reaching the burner. Its disadvantages are (1) that with solutions made up in mixed solvents, the more volatile solvents are evaporated preferentially; (2) a potential explosion hazard exists since the burner uses relatively large volumes of gas, but in modern versions of this type of burner this hazard is minimised.

A typical burner of this type is shown in Fig. 21.4. In this particular burner (Perkin–Elmer Corporation), the mixing chamber is a steel casting lined with a plastic (‘Penton’) which is extremely resistant to corrosion. The burner head is manufactured from titanium, thus avoiding the occasional high readings which are encountered when solutions containing iron and copper in presence of acid are examined with burners having a stainless-steel head. The nebuliser is capable of adjustment so that it can handle sample uptake rates of from 1–5 mL min<sup>-1</sup>. The burner can be adjusted in three directions, and horizontal and vertical scales are provided so that its position can be recorded. The head may be turned through an angle of 90° with respect to the light beam, and so the path length of the flame traversed by the resonance line radiation may be varied considerably: by choosing a small path length it becomes possible to analyse solutions of relatively high concentration without the need for prior dilution.

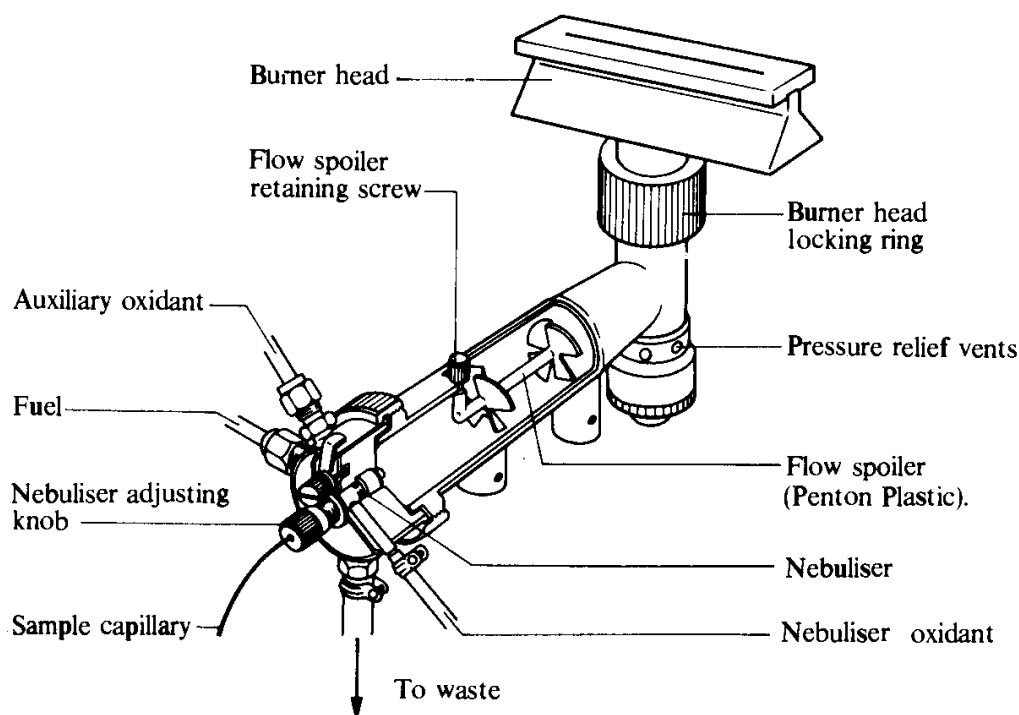


Fig. 21.4

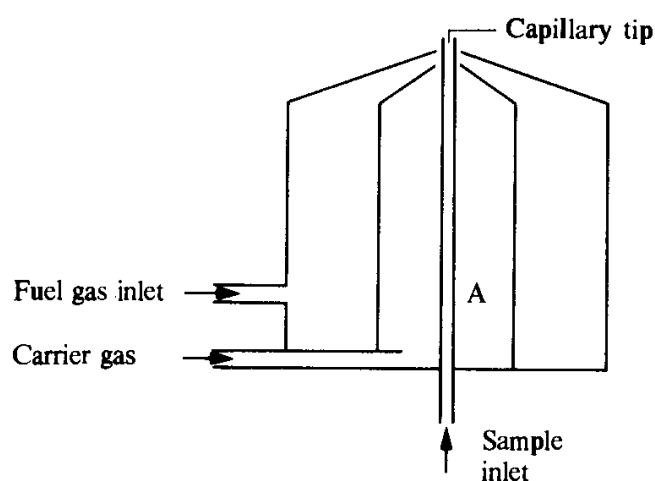


Fig. 21.5

The **total consumption type** of burner consists of three concentric tubes as shown in Fig. 21.5. The sample solution is carried by a fine capillary tube A directly into the flame. The fuel gas and the oxidant gas are carried along separate tubes so that they only mix at the tip of the burner. Since all the liquid sample which is aspirated by the capillary tube reaches the flame, it would appear that this type of burner should be more efficient than the pre-mix type of burner. However, the total consumption burner gives a flame of relatively short path length, and hence such burners are predominantly used for flame emission studies. This type of burner has the advantages that (1) it is simple to manufacture, (2) it allows a totally representative sample to reach the flame, and (3) it is free from explosion hazards arising from unburnt gas mixtures. Its disadvantages are that (1) the aspiration rate varies with different solvents, and (2) there is a tendency for incrustations to form at the tip of the burner which can lead to variations in the signal recorded.

In general terms, Thomerson and Thompson<sup>43</sup> have cited the following disadvantages of flame atomisation procedures:

1. Only 5–15 per cent of the nebulised sample reaches the flame (in the case of the pre-mix type of burner) and it is then further diluted by the fuel and oxidant gases so that the concentration of the test material in the flame may be extremely minute.
2. A minimum sample volume of between 0.5 and 1.0 mL is needed to give a reliable reading by aspiration into a flame system.
3. Samples which are viscous (e.g. oils, blood, blood serum) require dilution with a solvent, or alternatively must be 'wet ashed' before the sample can be nebulised.

## 21.6 NON-FLAME TECHNIQUES

Instead of employing the high temperature of a flame to bring about the production of atoms from the sample, it is possible in some cases to make use of either (a) non-flame methods involving the use of electrically heated graphite tubes or rods, or (b) vapour techniques. Procedures (a) and (b) both find applications in atomic absorption spectroscopy and in atomic fluorescence spectroscopy.

### (a) Electrothermal atomisers

(1) *The graphite tube furnace.* A diagram of a graphite tube furnace is shown in Fig. 21.6. It consists of a hollow graphite cylinder about 50 mm in length and about 9 mm internal diameter and so situated that the radiation beam passes along the axis of the tube. The graphite tube is surrounded by a metal jacket through which water is circulated and which is separated from the graphite tube by a gas space. An inert gas, usually argon, is circulated in the gas space, and enters the graphite tube through openings in the cylinder wall.

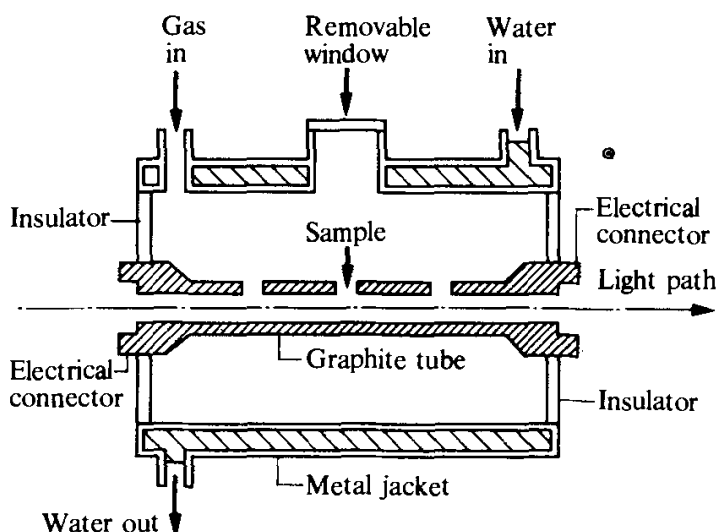


Fig. 21.6

The solution of the sample to be analysed (1–100  $\mu\text{L}$ ) is introduced by inserting the tip of a micropipette through a port in the outer (water) jacket, and into the gas inlet orifice in the centre of the graphite tube. The graphite cylinder is then heated by the passage of an electric current to a temperature

which is high enough to evaporate the solvent from the solution. The current is then increased so that firstly the sample is ashed, and then ultimately it is vaporised so that metal atoms are produced, typically at a temperature of about 3000 K. For reproducibility, the temperatures and the timing of the drying, ashing and atomisation processes must be carefully selected according to the metal which is to be determined. The absorption signals produced by this method may last for several seconds and can be recorded on a chart recorder. Each graphite tube can be used for 100–200 analyses depending upon the nature of the material to be determined.

(2) **The graphite rod.** A graphite rod of 2 mm diameter was introduced by West and Williams<sup>44</sup> as a means of producing atoms from the sample. The sample is placed upon the rod which is heated, typically by a current of 100 A from a low-voltage (5 V) supply. The rod is placed just below the path of the beam from the radiation source so that vapour from the sample can move upwards into the beam and its absorbance be measured. The whole assembly is contained in a chamber fitted with quartz windows which is purged with argon.

In some circumstances it is found advantageous to coat graphite rods (or tubes) with a layer of pyrolytic graphite: this leads to improved sensitivity with elements such as vanadium and titanium which are prone to carbide formation.

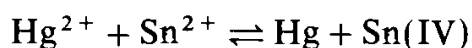
The main advantages of electrothermal atomisers are that (a) very small samples (as low as 0.5  $\mu\text{L}$ ) can be analysed; (b) often very little or no sample preparation is needed, in fact certain solid samples can be analysed without prior dissolution; (c) there is enhanced sensitivity, particularly with elements with a short-wavelength resonance line; in practice there is an improvement of between  $10^2$ - and  $10^3$ -fold in the detection limits for furnace AAS compared with flame AAS.

There are, however, disadvantages in the electrothermal atomisation technique compared with flame atomic absorption. Background absorption effects (see Section 21.11) are usually far more serious. There is also a danger of the loss of analyte during the ashing stage. This can be a serious effect when dealing with volatile salts, e.g. the chlorides of cadmium and mercury. On some occasions the sample may not be completely volatilised during the atomisation stage, which can result in 'memory effects' within the graphite furnace. Generally speaking, the precision of furnace AAS (typically 5 per cent when the sample is injected manually) is much poorer than that obtained by flame AAS (often 1 per cent). However, the recent introduction of furnace auto-samplers has considerably enhanced the precision of furnace AAS.

Amongst other devices used to produce the required atoms in the vapour state are the **Delves cup** which enables the determination of lead in blood samples; the sample is placed in a small nickel cup which is inserted directly into an acetylene–air flame. The tantalum boat is a similar device to the Delves cup; in this case the sample is placed into a small tantalum dish which is then inserted into an acetylene–air flame. The use of these devices, especially for small sample volumes, has now been largely superseded by the graphite furnace.

(b) **Cold vapour technique.** This procedure is strictly confined to the determination of mercury,<sup>45</sup> which in the elemental state has an appreciable vapour pressure at room temperature so that gaseous atoms exist without the need for any special treatment. As a method for determining mercury compounds the procedure consists in the reduction of a mercury(II) compound with either

sodium borohydride or (more usually) tin(II) chloride to form elemental mercury.



A diagram of a suitable apparatus is shown in Fig. 21.7. The mercury vapour is flushed out of the reaction vessel by bubbling argon through the solution, into the absorption tube.

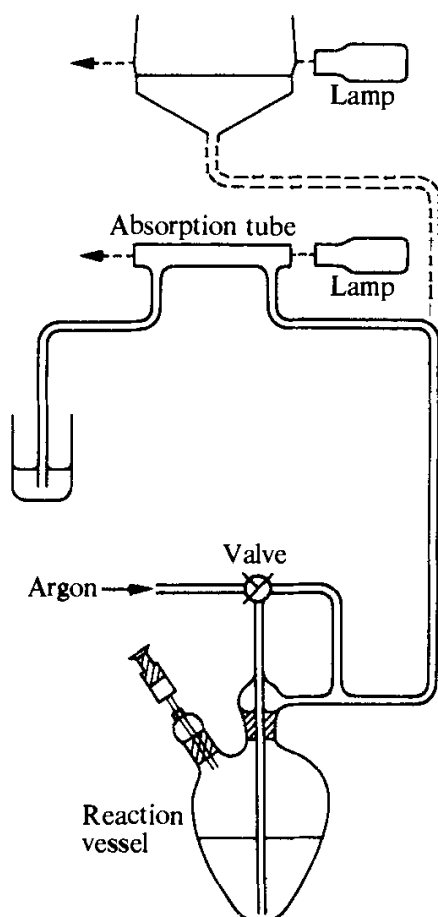
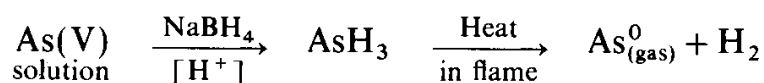


Fig. 21.7

This apparatus may also be adapted for what are termed '**hydride generation methods**' (which are strictly speaking flame-assisted methods). Elements such as arsenic, antimony, and selenium are difficult to analyse by flame AAS because it is difficult to reduce compounds of these elements (especially those in the higher oxidation states) to the gaseous atomic state.

Although electrothermal atomisation methods can be applied to the determination of arsenic, antimony, and selenium, the alternative approach of hydride generation is often preferred. Compounds of the above three elements may be converted to their volatile hydrides by the use of sodium borohydride as reducing agent. The hydride can then be dissociated into an atomic vapour by the relatively moderate temperatures of an argon–hydrogen flame.

The reaction sequence, in the case of arsenic, may be represented as follows:





**Interferences:**

Various factors may affect the flame emission of a given element and lead to interference with the determination of the concentration of a given element.

Various factors may affect the flame emission of a given element and lead to interference with the determination of the concentration of a given element.

These factors may be broadly classified as (a) **spectral interferences** and (b) **chemical interferences**.

Spectral interferences in AAS arise mainly from overlap between the frequencies of a selected resonance line with lines emitted by some other element; this arises because in practice a chosen line has in fact a finite ‘bandwidth’. Since in fact the line width of an absorption line is about 0.005 nm, only a few cases of spectral overlap between the emitted lines of a hollow cathode lamp and the absorption lines of metal atoms in flames have been reported. Table 21.3 includes some typical examples of spectral interferences which have been observed.<sup>47-50</sup> However, most of these data relate to relatively minor resonance lines and the only interferences which occur with preferred resonance lines are with copper where europium at a concentration of about 150 mg L<sup>-1</sup> would interfere, and mercury where concentrations of cobalt higher than 200 mg L<sup>-1</sup> would cause interference.

**Table 21.3** Some typical spectral interferences

Resonance source	Wavelength, $\lambda$ (nm)	Analyte	Wavelength, $\lambda$ (nm)
Aluminium	308.216	Vanadium	308.211
Antimony	231.147	Nickel	231.095
Copper	324.754	Europium	324.755
Gallium	403.307	Manganese	403.307
Iron	271.903	Platinum	271.904
Mercury	253.652	Cobalt	253.649

With flame emission spectroscopy, there is greater likelihood of spectral interferences when the line emission of the element to be determined and those due to interfering substances are of similar wavelength, than with atomic absorption spectroscopy. Obviously some of such interferences may be eliminated by improved resolution of the instrument, e.g. by use of a prism rather than a filter, but in certain cases it may be necessary to select other, non-interfering, lines for the determination. In some cases it may even be necessary to separate the element to be determined from interfering elements by a separation process such as ion exchange or solvent extraction (see Chapters 6, 7).

Apart from the interferences which may arise from other elements present in the substance to be analysed, some interference may arise from the emission band spectra produced by molecules or molecular fragments present in the flame gases: in particular, band spectra due to hydroxyl and cyanogen radicals arise in many flames. Although in AAS these flame signals are modulated (Section 21.9), in practice care should be taken to select an absorption line which does not correspond with the wavelengths due to any molecular bands because of the excessive ‘noise’ produced by the latter: this leads to decreased sensitivity and to poor precision of analysis.

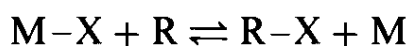
## Chemical Interferences

The production of ground-state gaseous atoms which is the basis of flame spectroscopy may be inhibited by two main forms of chemical interference: (*a*) by stable compound formation, or (*b*) by ionisation.

**Stable compound formation.** This leads to incomplete dissociation of the

substance to be analysed when placed in the flame, or it may arise from the formation within the flame of refractory compounds which fail to dissociate into the constituent atoms. Examples of these types of behaviour are shown by (1) the determination of calcium in the presence of sulphate or phosphate, and (2) the formation of stable refractory oxides of titanium, vanadium, and aluminium. Chemical interferences can usually be overcome in one of the following ways.

1. Increase in flame temperature often leads to the formation of free gaseous atoms, and for example aluminium oxide is more readily dissociated in an acetylene–nitrous oxide flame than it is in an acetylene–air flame. A calcium–aluminium interference arising from the formation of calcium aluminate can also be overcome by working at the higher temperature of an acetylene–nitrous oxide flame.
2. By the use of ‘releasing agents’. If we consider the reaction



then it is clear that an excess of the releasing agent (R) will lead to an enhanced concentration of the required gaseous metal atoms M: this will be especially true if the product R–X is a stable compound. Thus in the determination of calcium in the presence of phosphate, the addition of an excess of lanthanum chloride or of strontium chloride to the test solution will lead to formation of lanthanum (or strontium) phosphate, and the calcium can then be determined in an acetylene–air flame without any interference due to phosphate. The addition of EDTA to a calcium solution before analysis may increase the sensitivity of the subsequent flame spectrophotometric determination: this is possibly due to the formation of an EDTA complex of calcium which is readily dissociated in the flame.

3. Extraction of the analyte or of the interfering element(s) is an obvious method of overcoming the effect of ‘interferences’. It is frequently sufficient to perform a simple solvent extraction to remove the major portion of an interfering substance so that, at the concentration at which it then exists in the solution, the interference becomes negligible. If necessary, repeated solvent extraction will reduce the effect of the interference even further and, equally, a quantitative solvent extraction procedure may be carried out so as to isolate the substance to be determined from interfering substances.

**Ionisation.** Ionisation of the ground-state gaseous atoms within a flame



will reduce the intensity of the emission of the atomic spectra lines in flame emission spectroscopy, or will reduce the extent of absorption in atomic absorption spectroscopy. It is therefore clearly necessary to reduce to a minimum the possibility of ionisation occurring, and an obvious precaution to take is to use a flame operating at the lowest possible temperature which is satisfactory for the element to be determined. Thus, the high temperature of an acetylene–air or of an acetylene–nitrous oxide flame may result in the appreciable ionisation of elements such as the alkali metals and of calcium, strontium, and barium. The ionisation of the element to be determined may also be reduced by the addition of an excess of an **ionisation suppressant**; this is usually a solution containing a cation having a lower ionisation potential than that of the analyte.

Thus, for example a solution containing potassium ions at a concentration of  $2000 \text{ mg L}^{-1}$  added to a solution containing calcium, barium, or strontium ions creates an excess of electrons when the resulting solution is nebulised into the flame, and this has the result that the ionisation of the metal to be determined is virtually completely suppressed.

**Other effects.** In addition to the compound formation and ionisation effects which have been considered, it is also necessary to take account of so-called **matrix effects**. These are predominantly physical factors which will influence the amount of sample reaching the flame, and are related in particular to factors such as the viscosity, the density, the surface tension and the volatility of the solvent used to prepare the test solution. If we wish to compare a series of solutions, e.g. a series of standards to be compared with a test solution, it is clearly essential that the same solvent be used for each, and the solutions should not differ too widely in their bulk composition. This procedure is commonly termed **matrix matching**.

In some circumstances interference may result from **molecular absorption**. Thus, for example, in an acetylene–air flame a high concentration of sodium chloride will absorb radiation at wavelengths in the neighbourhood of  $213.9 \text{ nm}$ , which is the wavelength of the major zinc resonance line: hence sodium chloride would represent an interference in the determination of zinc under these conditions. Such interferences can usually be avoided by choosing a different resonance line, or alternatively by using a hotter flame resulting in an increase in the operating temperature, thus leading to dissociation of the interfering molecules. The interference referred to as **background absorption** which arises from the presence in the flame of gaseous molecules, molecular fragments and in some instances, where organic solvents are used, of smoke, are dealt with instrumentally by the incorporation of a **background correction** facility. In addition, background effects can be caused by light scatter. The degree of scatter is inversely proportional to the fourth power of the radiation wavelength. Hence, background effects due to scatter are a particularly important interference at high-energy wavelengths in the UV (between  $185$  and  $230 \text{ nm}$ ).

Background effects especially due to the generation of particulate material to form a smoke are a major problem in furnace AAS.

It should be stressed that background correction methods should always be used in furnace AAS. The background effect in this case may be as high as 85 per cent of the total absorption signal.

To summarise, it may be stated that almost all interferences encountered in atomic absorption spectroscopy can be reduced, if not completely eliminated, by the following procedures.

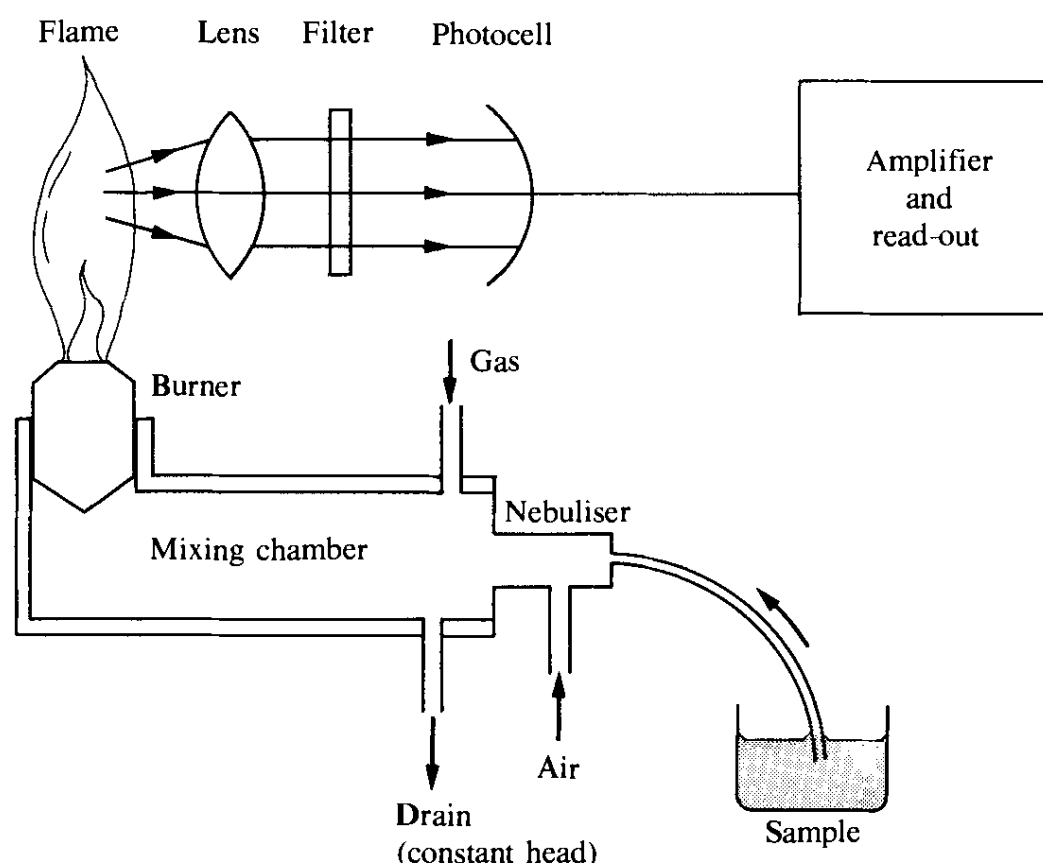
1. Ensure if possible that standard and sample solutions are of similar bulk composition to eliminate matrix effects (matrix matching).
2. Alteration of flame composition or of flame temperature can be used to reduce the likelihood of stable compound formation within the flame.
3. Selection of an alternative resonance line will overcome spectral interferences from other atoms or molecules and from molecular fragments.
4. Occasionally, separation, e.g. by solvent extraction or by an ion exchange process, may be necessary to remove an interfering element; such separations are most frequently necessary when dealing with flame emission spectroscopy.
5. Use an appropriate background correction facility (see Section 21.12).

## 21.13 FLAME EMISSION SPECTROSCOPY

There are now two main methods used for flame emission spectroscopy. The original method, known as flame photometry, is now used mainly for the analysis of alkali metals.

At present, however, the usual flame emission method is obtained by simply operating a flame atomic absorption spectrometer in the emission mode (see Fig. 21.3).

**Flame photometers.** A flame photometer can be compared with a photoelectric absorptiometer and the intensity of the filtered radiation from the flame is measured with a photoelectric detector. The filter, interposed between the flame and the detector, transmits only a strong line of the element. The simplest and least expensive detector is a barrier-layer cell (Section 17.6): if sufficient energy reaches the cell no amplification or external power supply is necessary, and only a sensitive galvanometer is required. The barrier-layer cell has a high temperature coefficient: it must, therefore, be placed at a cool part of the photometer. In some cases the precision is improved by the use of an internal standard and two filters and, in general, two photocells (one for the standard and one for the unknown) are utilised; the electronic circuit can be devised to give a direct reading of the ratio of line intensities. Flame photometers are intended primarily for analysis of sodium and potassium and also for calcium and lithium, i.e. elements which have an easily excited flame spectrum of sufficient intensity for detection by a photocell. The layout of a simple flame photometer is shown in Fig. 21.13. Air at a given pressure is passed into an atomiser and the suction this produces draws a solution of the sample into the atomiser, where it joins



the air stream as a fine mist and passes into the burner. Here, in a small mixing chamber, the air meets the fuel gas supplied to the burner at a given pressure and the mixture is burnt. Radiation from the resulting flame passes through a lens, and finally through an optical filter which permits only the radiation characteristic of the element under investigation to pass through the photocell. The output from the photocell is measured on a suitable digital read-out system.

An example of a modern instrument of this type is the Corning Model 410 flame photometer. This model can incorporate a 'lineariser module' which provides a direct concentration read-out for a range of clinical specimens. Flame photometers are still widely used especially for the determination of alkali metals in body fluids, but are now being replaced in clinical laboratories by ion-selective electrode procedures (see Section 15.7).

## Evaluation Methods:

Before dealing with the experimental details of AAS or FES determinations it is necessary to consider the mode of treatment of the experimental data obtained. To convert the measured absorption values into the concentration of the substance being determined it is necessary either to make use of a calibration curve, or to carry out the 'standard addition' procedure.

**(a) Calibration curve procedure.** A calibration curve for use in atomic absorption or in flame emission measurements is plotted by aspirating into the flame samples of solutions containing known concentrations of the element to be determined, measuring the absorption (emission) of each solution, and then constructing a graph in which the measured absorption (emission) is plotted against the concentration of the solutions. If we are dealing with a test solution which contains a single component, then the standard solutions are prepared by dissolving a weighed quantity of a salt of the element to be determined in a known volume of distilled (de-ionised) water in a graduated flask. If, however, other substances are present in the test solution, then these should also be incorporated in the standard solutions and at a similar concentration to that existing in the test solution. At least four standard solutions should be used covering the optimum absorbance range of 0.1 to 0.4, and if the calibration curve is found to be non-linear (this often happens at high absorbance values), then measurements with additional standard solutions should be carried out. In common with all absorbance measurements, the readings must be taken after the instrument zero has been adjusted against a 'blank' which may be either distilled water, or a solution of similar composition to the test solution but minus the component to be determined. It is usual to examine the standard solutions in order of increasing concentration, and after making the measurements with one solution, distilled water is aspirated into the flame to remove all traces of solution before proceeding to the next solution. At least two, and preferably three, separate absorption readings should be made with each solution, and an average value taken.

If necessary, the test solution must be suitably diluted using a pipette and a graduated flask, so that it too gives absorbance readings in the range 0.1–0.4.



Using the calibration curve it is a simple matter to interpolate from the measured absorbance of the test solution the concentration of the relevant element in the solution. The working graph should be checked occasionally by making measurements with the standard solutions, and if necessary a new calibration curve must be drawn.

**Note.** Most instruments now include a microcomputer which stores the calibration curve and allows a direct read-out of concentration.

**(b) The standard addition technique.** When dealing with a test solution which is complex in character, or one whose exact composition is unknown, it may be very difficult and even impossible to prepare standard solutions having a similar composition to the sample. In such a case the method of standard addition can be employed. As described in Section 16.5, this involves the addition of known amounts of the ion to be determined to a number of aliquots of the sample solution; the solutions thus obtained should all be diluted to the same final volume. Naturally, if the absorbance of the test solution is too high, a quantitative dilution must be carried out, and the measurements made with this diluted solution. The absorbance of the test solution is first measured, and then each of the prepared solutions is examined in turn, leading up to the solution of highest concentration, and remembering to aspirate distilled water into the flame between each solution. The absorbance values are then plotted against the added concentration values; a straight-line plot should result and the straight line can be extrapolated to the concentration axis — the point where the axis is cut gives the concentration of the test solution. If the graph is non-linear, then extrapolation cannot be undertaken with any confidence. It is important to realise that an extrapolation procedure is never as reliable as interpolation, and the latter should, therefore, be chosen if at all possible.

### Preparation of Sample Solution:

For the application of flame spectroscopic methods the sample must be prepared in the form of a suitable solution unless it is already presented in this form: exceptionally, solid samples can be handled directly in some of the non-flame techniques (Section 21.6).

Aqueous solutions may sometimes be analysed directly without any pre-treatment, but it is a matter of chance that the given solution should contain the correct amount of material to give a satisfactory absorbance reading. If the existing concentration of the element to be determined is too high then the solution must be diluted quantitatively before commencing the absorption measurements. Conversely, if the concentration of the metal in the test solution is too low, then a concentration procedure must be carried out by one of the methods outlined at the end of this section.

Solutions in organic solvents may, with certain reservations, be used directly, provided that the viscosity of the solution is not very different from that of an aqueous solution. The important consideration is that the solvent should not lead to any disturbance of the flame; an extreme example of this is carbon tetrachloride, which may extinguish an air-acetylene flame. In many cases, suitable organic solvents [e.g. 4-methylpentan-2-one (methyl isobutyl ketone) and the hydrocarbon mixture sold as 'white spirit'] give enhanced production of ground-state gaseous atoms and lead to about three times the sensitivity

which is achieved with aqueous solutions. Due regard must of course be paid to the question of safety: see Section 21.19.

Inorganic solids such as metallic alloys, minerals, cements, etc., must be brought into solution by the usual standard techniques, the aim being to produce a clear solution with no loss of the element to be determined. Generally speaking, the final solution should not contain acid at a greater concentration than about 1 M since the aspiration of extremely corrosive solutions into the burner of the apparatus should be avoided as far as possible: the instruction manual supplied with the instrument will normally give guidance in this direction.

Organic solids which contain trace elements can sometimes be dissolved in a suitable organic solvent, or alternatively the organic material may be oxidised and the residue treated to give an aqueous solution of the element to be determined.

Separation techniques may have to be applied if the given sample contains substances which act as interferences (Section 21.10), or, as explained above, if the concentration of the element to be determined in the test solution is too low to give satisfactory absorbance readings. As already indicated (Section 21.10), the separation methods most commonly used in conjunction with flame spectrophotometric methods are solvent extraction (see Chapter 6) and ion exchange (Chapter 7). When a solvent extraction method is used, it may happen that the element to be determined is extracted into an organic solvent, and as discussed above it may be possible to use this solution directly for the flame photometric measurement.

### **Preparation of standard Solution:**

In flame spectrophotometric measurements we are concerned with solutions having very small concentrations of the element to be determined. It follows that the standard solutions which will be required for the analyses must also contain very small concentrations of the relevant elements, and it is rarely practicable to prepare the standard solutions by weighing out directly the required reference substance. The usual practice therefore is to prepare stock solutions which contain about  $1000 \mu\text{g mL}^{-1}$  of the required element, and then the working standard solutions are prepared by suitable dilution of the stock solutions. Solutions which contain less than  $10 \mu\text{g mL}^{-1}$  are often found to deteriorate on standing owing to adsorption of the solute on to the walls of glass vessels. Consequently, standard solutions in which the solute concentration is of this order should not be stored for more than 1 to 2 days.

The stock solutions are ideally prepared from the pure metal or from the pure metal oxide by dissolution in a suitable acid solution; the solids used must be of the highest purity, e.g. the Johnson Matthey 'Specpure' range, and the acids should ideally be of Aristar quality supplied by BDH Ltd, Poole, Dorset, UK.

A wide variety of SpectrosoL stock solutions ( $1000 \mu\text{g mL}^{-1}$ ) suitable for AAS can be obtained from BDH Ltd.

### **Concentration Units:**

SOLID SAMPLES

Mass and weight are really different. See Chapter 2. We deal with masses but will use mass and weight interchangeably.

Calculations for solid samples are based on weight.<sup>3</sup> The most common way of expressing the results of macro determinations is to give the weight of analyte as a **percent** of the weight of sample (weight/weight basis). The weight units of analyte and sample are the same. For example, a limestone sample weighing 1.267 g and containing 0.3684 g iron would contain

$$\frac{0.3684\text{ g}}{1.267\text{ g}} \times 100\% = 29.08\% \text{ Fe}$$

The general formula for calculating percent on a weight/weight basis, which is the same as parts per hundred, then is

$$\%(\text{wt/wt}) = \left[ \frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^2 \text{ (\%/g solute/g sample)}$$

(5.8)

It is important to note that in such calculations, grams of solute do *not* cancel with grams of sample solution; the fraction represents grams of solute per gram of sample. Multiplication of the above by 10<sup>2</sup> converts to grams of solute per 100 g of sample. Since the conversion factors for converting weight of solute and weight of sample (weights expressed in any units) to grams of solute and grams of sample are always the same, the conversion factors will always cancel. Thus, we can use any weight in the definition.

Trace concentrations are usually given in smaller units, such as **parts per thousand** (ppt, ‰), **parts per million** (ppm), or **parts per billion** (ppb). These are calculated in a manner similar to parts per hundred (%):

$$\text{ppt (wt/wt)} = \left[ \frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^3 \text{ (ppt/g solute/g sample)}$$

(5.9)

$$\text{ppm (wt/wt)} = \left[ \frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^6 \text{ (ppm/g solute/g sample)}$$

(5.10)

$$\text{ppb (wt/wt)} = \left[ \frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^9 \text{ (ppb/g solute/g sample)}$$

(5.11)

You can use any weight units in your calculations so long as both analyte and sample weights are in the same units. **Parts per trillion** (parts per 10<sup>12</sup> parts) is also abbreviated ppt, so be careful to define which one you mean. Some authors like to use ppth to denote parts per thousand and pptr to denote parts per trillion. In the above example, we have 29.08 parts per hundred of iron in the sample, or 290.8 parts per thousand and 290,800 parts per million (290,800 g of iron per 1 million grams of sample, 290,800 lb of iron per 1 million pounds of sample, etc.). Working backward, 1 ppm corresponds to 0.0001 part per hundred, or 10<sup>-4</sup>%. Table 5.2 summarizes the concentration relationships for ppm and ppb. Note that ppm is simply mg/kg or μg/g and that ppb is μg/kg, or ng/g.

Trace gas concentrations are also expressed in ppb, ppm, and so forth. In this case the ratio refers not to mass ratios, but to volume ratios (which for gases is the same as mole ratios). Thus, present atmospheric CO<sub>2</sub> concentration of 390 ppm means that each liter of air (this is a million microliters) contains 390 microliters of CO<sub>2</sub>.

1 ppt (thousand) = 1000 ppm = 1,000,000 ppb; 1 ppm = 1000 ppb = 1,000,000 ppt (trillion).  
Usually ppt refers to parts per trillion, but in some cases it could be used as parts per thousand. Take note of the units when you see this!

ppt = mg/g = g/kg  
ppm = μg/g = mg/kg  
ppb = ng/g = μg/kg

# FLAME EMISSION EXPERIMENTS

## 21.25 DETERMINATION OF ALKALI METALS BY FLAME PHOTOMETRY

Although flame emission measurements can be made by using an atomic absorption spectrometer in the emission mode, the following account refers to the use of a simple flame photometer (the Corning Model 410 flame photometer). Before attempting to use the instrument read the instruction manual supplied by the manufacturers.

**Preparation of standard solutions for calibration curves.** The following concentrations are suitable:

- (a) *Sodium.* Dissolve 2.542 g sodium chloride in 1 L de-ionised water in a graduated flask. This solution contains the equivalent of 1.000 mg Na per mL (i.e. 1000 ppm). Dilute this stock solution to give four solutions containing 10, 5, 2.5, and 1 ppm of sodium ions.
- (b) *Potassium.* Dissolve 1.909 g potassium chloride in 1 L de-ionised water. This solution contains the equivalent of 1.000 mg K per mL (i.e. 1000 ppm). Dilute this stock solution to give four solutions containing 20, 10, 5, and 2 ppm of potassium ions.
- (c) *Calcium.* Dissolve 2.497 g calcium carbonate in a little dilute hydrochloric acid, and dilute to 1 L with de-ionised water. This stock solution contains the equivalent of 1.000 mg Ca per mL. Dilute this solution to give solutions containing 100, 50, 25, and 10 ppm of calcium ions.
- (d) *Lithium.* Dissolve 5.324 g pure lithium carbonate in a little dilute hydrochloric acid and dilute to 1 L with de-ionised water. This solution contains 1.000 mg Li per mL (i.e. 1000 ppm). Dilute the stock solution to give solutions containing 20, 10, 5, and 2 ppm, of lithium ions.

Prepare calibration curves for each of the above four elements. With the aid of these calibration curves, carry out the following simple determinations.

- 1. *Potassium in potassium sulphate.* Weigh out accurately about 0.20 g potassium sulphate and dissolve it in 1 L de-ionised water. Dilute 10.0 mL of this solution to 100 mL, and determine the potassium with the flame photometer using the potassium filter.
- 2. *Potassium and sodium in a mixture.* Mix suitable volumes of the above stock solutions so that the resulting solution contains, say, 4–10 ppm Na and 10–15 ppm K. Determine the Na and K with the aid of the appropriate filters. Compare the results obtained with the true values.
- 3. *Sodium, potassium, and calcium in a mixture.* Mix appropriate volumes of the above stock solutions so that the test solution contains, say, 5 ppm Na, 10 ppm K, and 40 ppm Ca. Determine the Na, K, and Ca with the aid of the appropriate filters. Compare the results obtained with the true values.
- 4. *Calcium in calcium carbonate.* Determine the calcium in an analysed sample of dolomite. Dissolve about 0.38 g, accurately weighed in 1:1 hydrochloric acid, warm gently, filter through a quantitative filter paper, wash, dilute the combined filtrate and washings to 1 L. Measure the calcium content of the resulting solution: use a calcium filter. Compare the value for Ca thus obtained with the known Ca content.

**Table 5.2**  
Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million (1 ppm = 10 <sup>−4</sup> %)	ppm	mg/kg μg/g	mg/L μg/mL	μL/L nL/mL
Parts per billion (1 ppb = 10 <sup>−7</sup> % = 10 <sup>−3</sup> ppm)	ppb	μg/kg ng/g	μg/L ng/mL	nL/L pL/mL <sup>a</sup>
Milligram percent	mg%	mg/100 g	mg/100 mL	

<sup>a</sup>pL = picoliter = 10<sup>−12</sup> L.

Sometimes for this reason, these concentrations are written as ppmv or ppbv, and so on, indicating “by volume”.

### Example 5.14

A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μg zinc. What is the concentration of zinc in the plant in ppm? In ppb?

**Solution**

$$\frac{3.6\ \mu\text{g}}{2.6\ \text{g}} = 1.4\ \mu\text{g/g} \equiv 1.4\ \text{ppm}$$

$$\frac{3.6 \times 10^3\ \text{ng}}{2.6\ \text{g}} = 1.4 \times 10^3\ \text{ng/g} \equiv 1400\ \text{ppb}$$

One ppm is equal to 1000 ppb. One ppb is equal to 10<sup>−7</sup>%.

Clinical chemists sometimes prefer to use the unit **milligram percent** (mg%) rather than ppm for small concentrations. This is defined as milligrams of analyte per 100 g of sample. The sample in Example 5.14 would then contain (3.6 × 10<sup>−3</sup> mg/2.6 g) × 100 mg% = 0.14 mg% zinc.

## Further material on Hydride generation methods and Cold vapor Techniques

Eight elements including germanium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium form volatile, covalent hydrides. Hydride generation can be employed both to separate these elements from the main sample matrix before their introduction into the light path of the instrument, and to convert them into an atomic vapour once they are there. Hydride generation methods involve three or four successive steps depending on the technique used: (i) The hydride is generated by chemical reduction of the sample; (ii) The formed hydride may be collected in the

batch type methods; (iii) The hydride is entrained in a gas stream into the atomizer; (iv) The hydride is decomposed in the atomizer to form the atomic vapour, and the absorption signal is measured. A number of methods in use are based on this principle, but they differ in the means of reduction, atomization, and sample introduction. Reduction Methods. Early methods used a zinc-hydrochloric acid reduction (Gutzeit method), together with some kind of collecting device for the hydrides formed:

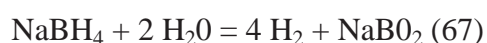


M is the analyte and m may be equal to or not (for example, As<sup>III</sup> and As<sup>V</sup> are both reduced to AsH<sub>3</sub>). Hydrides were collected in U-tubes in a nitrogen trap or in rubber balloons. Titanium(III) chloride-hydrochloric acid and magnesium-zinc reductants were used to extend the hydride method to bismuth, antimony, and tellurium. For some elements, especially tin, lead, and tellurium, the hydride formation reaction is relatively slow and hence the collection vessel is necessary. In addition, arsenic(v) must be reduced to arsenic(III) by tin(II) chloride or potassium iodide before the actual hydride generation when a metal-acid reduction is employed. Sodium borotetrahydride is now generally used as the reductant in various hydride generation methods. The reduction may be illustrated by the following reactions:



The hydride is generated by first adding the sample to a HCl solution (0.5-5.0 mol l<sup>-1</sup>) and then NaBH<sub>4</sub> (about 1% solution). The hydride formation by NaBH<sub>4</sub> is very fast and the hydride vapour may be flushed immediately or after reaction times of 10 to 100 seconds into a silica tube atom cell at carrier gas flow rates of 20 to 100 ml s<sup>-1</sup>.

Advantages of sodium borotetrahydride as the reductant are: (i) The reaction time is fast (varies from 10 to 30 seconds); (ii) NaBH<sub>4</sub> can be employed to produce all the eight volatile metal hydrides; (iii) NaBH<sub>4</sub> can be added in solution form. Sodium borotetrahydride hydrolyses in aqueous solutions in the following way.

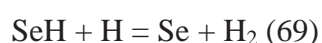


The hydrolysis may be prevented by addition of some potassium or sodium hydroxide. The 1% NaBH<sub>4</sub> solution may be stored for about 3 weeks. 6.2.2 Apparatus. Initially in the hydride generation methods, atomization was performed mainly in argon/hydrogen diffusion flames, and later these were replaced by graphite furnaces or heated quartz tubes. Nowadays, commercial hydride generation systems use almost exclusively either electrically heated or flame heated quartz tubes for atomization. The basic systems are represented in principle in Figure 89. In each case a standard atomic absorption spectrometer is used. A quartz absorption tube is either positioned above the burner (Figure 89A) or the burner assembly of the spectrometer is replaced with a quartz tube which is heated electrically by a coiled wire (Figure 89B). The

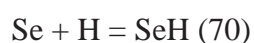


hydride vapour is atomized in the quartz tube and the resulting atoms are detected by the radiation beam from the hollow cathode lamp (or EDL) which passes down the axis of the tube. Non-specific background absorption is almost unknown with this technique when heated quartz tubes are used. Another widely used hydride generation system is represented in Figure 90. A small oxygen-hydrogen flame burns inside an unheated quartz tube. The hydride vapour is flushed by a stream of hydrogen into the tube where it is atomized in the hot oxygen-hydrogen flame. Excess hydrogen is burnt at the ends of the tube. The flow rate of hydrogen is about 1.5 lmin<sup>-1</sup> and that of oxygen about 6 ml min<sup>-1</sup>. In this technique oxygen-hydrogen and air-hydrogen flames cause background absorption which must be corrected. Two modes of operation can be applied for the hydride generation technique: (i) In the normal 'batch' system, the whole sample is reduced in a hydride generator and the hydride formed transported in a carrier gas stream to an absorption tube; (ii) In the flow injection (FIA) technique all stages of the hydride generation method take place in a fully automated closed system.

**6.2.3 Atomization Mechanisms.** The relatively easy atomization of the gaseous hydrides in heated quartz tubes and the increase in sensitivity with increasing atomizer temperature, led to a conclusion that atomization of the hydrides is a simple thermal dissociation. However, on the basis of a series of later observations it has been shown that thermal dissociation is not the only atomization mechanism of the hydrides. Dedina and Rubeska investigated the atomization of selenium hydride in a cool oxygen-hydrogen flame burning in an unheated quartz tube. They concluded that atomization is brought about by the free radicals (OH and H) that are produced in the primary reaction zone of the flame. The concentration of H radicals is several orders of magnitude higher than that of OH radicals. Thus, most probably atomization takes place via a two-step mechanism with the predominating H radicals:

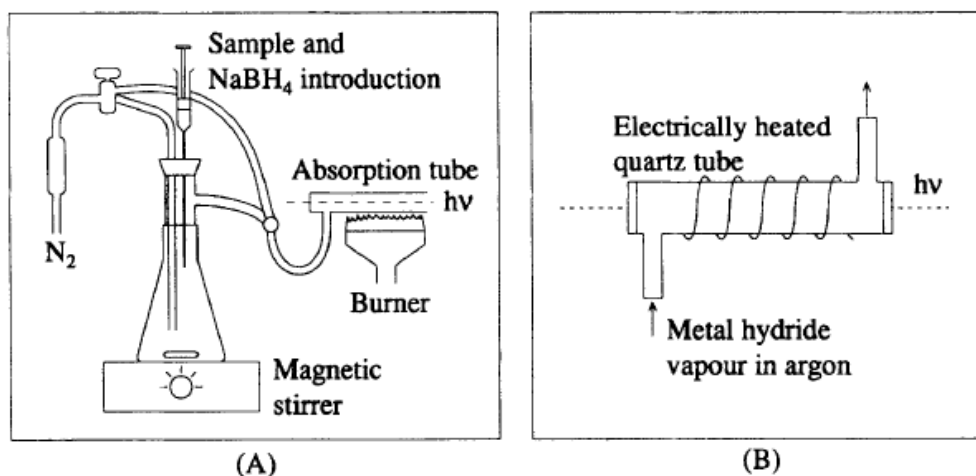


Correspondingly, reactions with OH radicals are also possible, but because of their low concentration these reactions are negligible. However, recombination must also be taken into account:

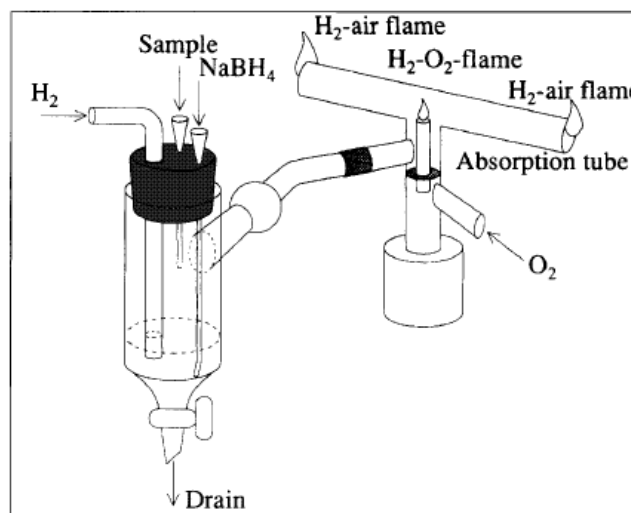


After a sufficiently large number of collisions with H radicals there is equilibrium between reactions (68), (69), and (70). The probability of the formation of free Se atoms from SeH<sub>2</sub> is proportional to the number of collisions with free H radicals and the efficiency of atomization should increase with increasing number of radicals. Analogous conclusions can be drawn for atomization of selenium hydride and other volatile hydrides in hydrogen diffusion flames. In heated quartz tubes oxygen plays an active role in the atomization of gaseous hydrides. If measurements are performed with the exclusion of air (oxygen), all other hydrogen forming elements except bismuth exhibit either no measurable signal or distinctly reduced sensitivity at 1000-1100 K. With increasing temperature, sensitivity of all elements increases. In contrast, in the presence of oxygen maximum sensitivity is obtained at 1000 K and further increases in temperature do not bring further signal increases. When there is adequate oxygen and hydrogen (from the reaction of NaBH<sub>4</sub> with the acidified sample solution) in the quartz tube, it is conceivable that similar reactions to those in a fuel rich hydrogen flame take place. Arsenic hydride (arsine) is not measurable when atomized in a pure argon atmosphere, even in a quartz tube heated up to 1300 K. The hydride is thermally decomposed, but its dissociation does not lead to free arsenic atoms. Probably the stable tetramer As<sub>4</sub> or dimer As<sub>2</sub> is formed. Atomization takes place as soon as hydrogen is mixed with the argon. Maximum sensitivity is attained at about 900 K when some oxygen is also introduced (argon with 1 % oxygen). Hydrogen is essential for the atomization of gaseous hydrides in a heated quartz tube and oxygen plays a supporting role at least at lower temperatures.





**Figure 89** The basic hydride generation technique systems with (A) flame heated and (B) electrically heated quartz tubes for atomization



**Figure 90** A widely used hydride generation system in which a small oxygen-hydrogen flame is burning inside an unheated quartz tube. (Adapted from: D. D. Siemer and L. Hagemann, *Anal. Lett.*, 1975, 8, 323)

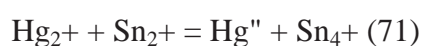
## Cold Vapor Techniques:

The determination of mercury is possible by the cold vapour technique, since it is based on the unique properties of this element. Mercury has an appreciable vapour pressure at ambient temperatures (0.16 Pa at 293 K) and the vapour is stable and monoatomic. Mercury can easily be reduced to metal from its compounds. By selective reductions of inorganic mercury( II) compounds and organomercury compounds, it is possible to determine successively the inorganic and organic mercury fraction in the same sample.

The mercury vapour may be entrained in a stream of an inert gas or in air and measured by the atomic absorption of the cold vapour without the need of either flame or flame atomizers.

## Dynamic Method:

In the simple dynamic method (Figure 92), air is circulated by a small pump through the reaction vessel, spray trap, and absorption tube with the longest path length and minimum volume possible. A length of 15 cm and a diameter of 0.75 cm would be suitable for many AAS instruments. The cuvette is usually made of glass with ultraviolet transmitting windows (quartz). After the determination, mercury is collected, for instance, in an active carbon trap. Mercury is usually reduced to metallic mercury by tin(II) chloride:



Hypophosphoric acid, hydrazine, or sodium borotetrahydride may also be used as reductants. The procedure is as follows: A clear sample solution, containing 0-300 mg of mercury, is transferred to the reaction vessel and the reductant is added. For example, 2 ml of 10% SnCl<sub>2</sub> solution. The bottle head is immediately inserted and the circulating pump switched on. Reduced mercury is liberated and swept through the absorption cuvette. The absorbance value rises to a plateau. When the constant absorbance value has been reached and recorded, mercury vapour is collected in a trap or allowed to escape through the extraction hood. When the absorbance returns to zero the next sample or standard can be inserted and reduced. The repeatability of the dynamic system depends on the constancy of the total volume of the circulating air. Thus, the flask and sample solution volumes should be exactly the same during a particular analysis run. The time required to liberate mercury increases with increasing sample volume and the increasing mercury content of the sample. In practice, a suitable sample volume is about 30-50 ml. For example, 50 pg of mercury may be liberated in 15 seconds from a sample volume of 30 ml, and 2 pg of mercury may be liberated in 10 seconds from a sample volume of 10 ml, whereas from 500 ml the time required is 4 minutes. When the circulating rates are too high the sample solution starts to foam, and when they are too small the liberation of mercury takes too long time. The inorganic and organic mercury fractions of a sample may be determined in the following way: Inorganic mercury, Hg<sup>II</sup> compounds, are reduced by 10% SnCl<sub>2</sub> solution. The liberated mercury vapour is circulated until the stable maximum absorbance value is reached. The vapour is then circulated through an active carbon trap until the absorbance returns to zero. After that a desired amount of a standard mercury solution is added to the reaction vessel and its absorbance reading recorded in the same way. In order to reduce organomercury compounds, SnCl<sub>2</sub>-CdCl<sub>2</sub> solution is added to the reaction vessel. The calibration for the organomercury fraction is carried out by a standard methyl mercury solution.

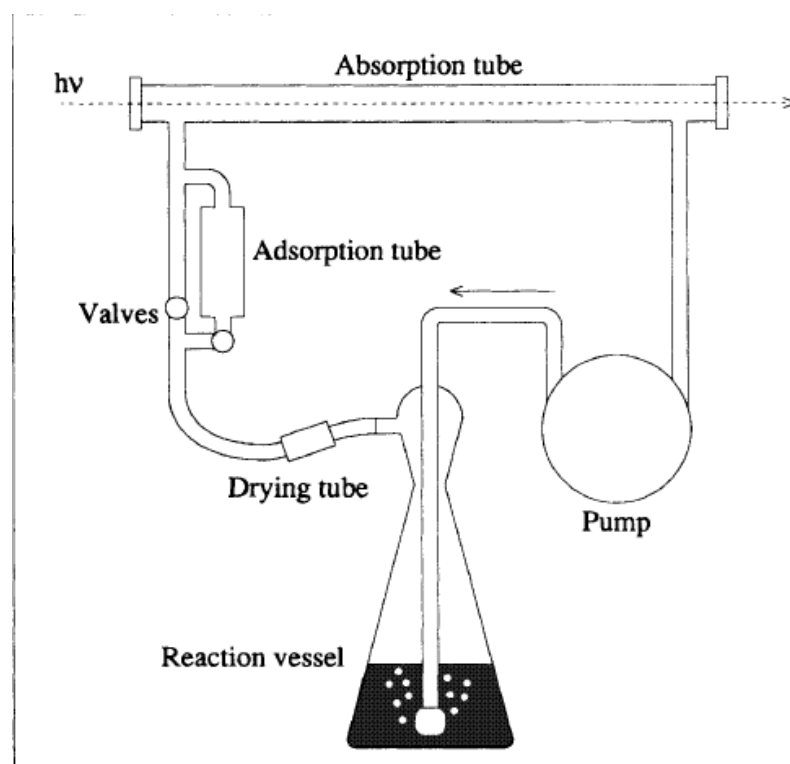


Fig: Principle dynamic cold vapor method

## Static Method:

In the static method, the reduction of mercury is performed as in the dynamic method. The mercury vapour is passed first through a vacuum flask, and then via a gas pipette to the absorption cuvette (Figure 93). In practice, the precision of the static method is better than that for the dynamic one since the mercury vapour

is not circulated through the absorption cuvette. Hence the circulating rate does not affect the results, and it is not necessary to measure standards so often.

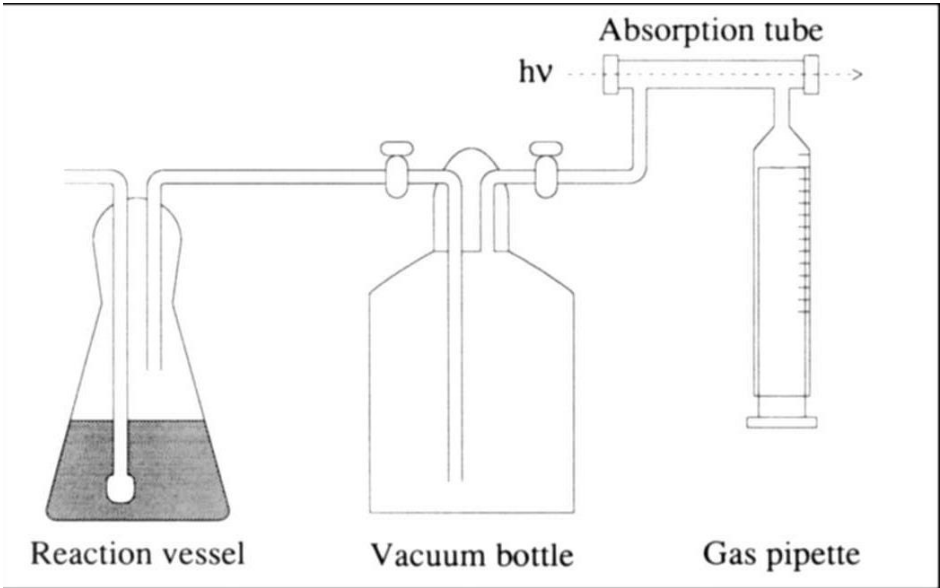


Fig: Principle of static cold vapor method

## Atomic Absorption Experiments

### 21.21 DETERMINATION OF MAGNESIUM AND CALCIUM IN TAP WATER

The determination of magnesium in potable water is very straightforward; very few interferences are encountered when using an acetylene–air flame. The determination of calcium is however more complicated; many chemical interferences are encountered in the acetylene–air flame and the use of ‘releasing agents’ such as strontium chloride, lanthanum chloride, or EDTA is necessary. Using the hotter acetylene–nitrous oxide flame the only significant interference arises from the ionisation of calcium, and under these conditions an ‘ionisation buffer’ such as potassium chloride is added to the test solutions.

**(a) Determination of magnesium. Preparation of the standard solutions.** A magnesium stock solution ( $1000 \text{ mg L}^{-1}$ ) is prepared by dissolving 1.000 g magnesium metal in 50 mL of 5M hydrochloric acid. After dissolution of the metal the solution is transferred to a 1 L graduated flask and made up to the

mark with distilled water. An intermediate stock solution containing  $50 \text{ mg L}^{-1}$  is prepared by pipetting 50 mL of the stock solution into a 1 L graduated flask and diluting to the mark. Dilute accurately four portions of this solution to give four standard solutions of magnesium with known magnesium concentrations lying within the optimum working range of the instrument to be used (typically  $0.1\text{--}0.4 \mu\text{g Mg}^{2+} \text{ mL}^{-1}$ ).

**Procedure.** Although the precise mode of operation may vary according to the particular instrument used, the following procedure may be regarded as typical. Place a magnesium hollow cathode lamp in the operating position, adjust the current to the recommended value (usually 2–3 mA), and select the magnesium line at 285.2 nm using the appropriate monochromator slit width.

Connect the appropriate gas supplies to the burner following the instructions detailed for the instrument, and adjust the operating conditions to give a fuel-lean acetylene–air flame.

Starting with the least concentrated solution, aspirate in turn the standard magnesium solutions into the flame, and for each take three readings of the absorbance; between each solution, remember to aspirate de-ionised water into the burner. Finally read the absorbance of the sample of tap water; this will usually require considerable dilution in order to give an absorbance reading lying within the range of values recorded for the standard solutions. Plot the calibration curve and use this to determine the magnesium concentration of the tap water.

If the magnesium content of the water is greater than  $5 \mu\text{g mL}^{-1}$  it might be considered preferable to work with the less sensitive magnesium line at wavelength 202.5 nm.

**(b) Determination of calcium.** Two procedures are described, (i) involving the use of releasing agents, and (ii) involving the use of an ‘ionisation buffer’: the latter is the preferred technique provided that an acetylene–nitrous oxide flame is available.

**Preparation of the standard solutions.** For procedure (i) it is necessary to incorporate a releasing agent in the standard solutions. Three different releasing agents may be used for calcium, (a) lanthanum chloride, (b) strontium chloride and (c) EDTA; of these (a) is the preferred reagent, but (b) or (c) make satisfactory alternatives.

- (a) Prepare a lanthanum stock solution ( $50\,000 \text{ mg L}^{-1}$ ) by dissolving 67 g of lanthanum chloride ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ) in 100 mL of 1 M nitric acid. Warm gently to dissolve the salt, then cool the solution and make up to 500 mL in a graduated flask.
- (b) A strontium stock solution is prepared by dissolving 76 g of strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) in 250 mL of de-ionised water and then making up to 500 mL in a graduated flask.
- (c) An EDTA stock solution is prepared by dissolving 75 g of EDTA disodium salt (analytical grade) in 800 mL of de-ionised water. Warm gently until the salt is dissolved, then cool and make up to 1 L in a graduated flask.

For procedure (ii) an ionisation buffer is required and this involves preparing a potassium stock solution ( $10\,000 \text{ mg L}^{-1}$ ). Dissolve 9.6 g of potassium chloride in de-ionised water and make up to 500 mL in a graduated flask.

Prepare a calcium stock solution ( $1000 \text{ mg L}^{-1}$ ) by dissolving 2.497 g of dried calcium carbonate in a minimum volume of 1 M hydrochloric acid: about 50 mL will be required. When dissolution is complete, transfer the solution to a 1 L graduated flask and make up to the mark with de-ionised water. An intermediate calcium stock solution is prepared by pipetting 50 cm of the stock solution into a 1 L flask and making up to the mark with de-ionised water.

The working standard solutions for procedure (i) contain between  $1 \mu\text{g Ca}^{2+} \text{ mL}^{-1}$  to  $5 \mu\text{g Ca}^{2+} \text{ mL}^{-1}$  and are prepared by mixing appropriate volumes of the intermediate stock solution (measured with a grade A pipette), with suitable volumes of the chosen releasing agent solution, and then making up to 50 mL in a graduated flask; the releasing agent solution is measured in a 25 mL measuring cylinder. Five standard solutions are prepared containing respectively 1.0, 2.0, 3.0, 4.0, and 5.0 mL of the intermediate stock solution and 10 mL of releasing agent (a) or 5 mL of either reagent (b) or (c). A blank solution is similarly prepared but without the addition of any of the intermediate calcium stock solution.

For procedure (ii) the working standard solutions are prepared as detailed for procedure (i) except that the releasing agent solution is replaced by 10 mL of the stock potassium solution.

The unknown calcium solution (the tap water) will normally require to be diluted in order that its absorbance reading shall lie on the calibration curve, and the same amount of releasing agent [procedure (i)], or of ionisation buffer [procedure (ii)], must be added as in the standard solutions. So, for example, if the tap water contains about  $100 \mu\text{g mL}^{-1}$  of calcium, 25 mL of it are pipetted into a 100 mL graduated flask and made up to the mark with de-ionised water. Then 5 mL of this solution is pipetted into a 50 mL graduated flask, and if procedure (i) is being followed, 10 mL of reagent (a) is added, or 5 mL of either reagent (b) or (c) and then the solution is made up to the mark. If procedure (ii) is being followed, then 10 mL of the stock potassium solution are used in place of the releasing agent. If any cloudiness should develop during the preparation of the final solution, add 1 mL of 1 M hydrochloric acid before making up to the mark.

**Procedure (i).** Set up a calcium hollow cathode lamp selecting the resonance line of wavelength 422.7 nm, and a fuel-lean acetylene–air flame following the details given in the instrument manual. The calibration procedure is similar to that described above for magnesium, but the aspiration of de-ionised water into the burner after taking the readings for each solution is even more important in this case owing to the relatively high concentrations of salts present as releasing agent; remember that de-ionised water should be aspirated into the burner for a few minutes at the conclusion of the series of readings.

**Procedure (ii).** Make certain that the instrument is fitted with the correct burner for an acetylene–nitrous oxide flame, then set the instrument up with the calcium hollow cathode lamp, select the resonance line of wavelength 422.7 nm, and adjust the gas controls as specified in the instrument manual to give a fuel-rich flame. Take measurements with the blank, and the standard solutions, and with the test solution, all of which contain the ‘ionisation buffer’; the need, mentioned under procedure (i), for adequate treatment with de-ionised water after each measurement applies with equal force in this case. Plot the calibration graph and ascertain the concentration of the unknown solution.

## Flame Emission Experiments:

### 21.25 DETERMINATION OF ALKALI METALS BY FLAME PHOTOMETRY

Although flame emission measurements can be made by using an atomic absorption spectrometer in the emission mode, the following account refers to the use of a simple flame photometer (the Corning Model 410 flame photometer). Before attempting to use the instrument read the instruction manual supplied by the manufacturers.

**Preparation of standard solutions for calibration curves.** The following concentrations are suitable:

- (a) *Sodium*. Dissolve 2.542 g sodium chloride in 1 L de-ionised water in a graduated flask. This solution contains the equivalent of 1.000 mg Na per mL (i.e. 1000 ppm). Dilute this stock solution to give four solutions containing 10, 5, 2.5, and 1 ppm of sodium ions.
- (b) *Potassium*. Dissolve 1.909 g potassium chloride in 1 L de-ionised water. This solution contains the equivalent of 1.000 mg K per mL (i.e. 1000 ppm). Dilute this stock solution to give four solutions containing 20, 10, 5, and 2 ppm of potassium ions.
- (c) *Calcium*. Dissolve 2.497 g calcium carbonate in a little dilute hydrochloric acid, and dilute to 1 L with de-ionised water. This stock solution contains the equivalent of 1.000 mg Ca per mL. Dilute this solution to give solutions containing 100, 50, 25, and 10 ppm of calcium ions.
- (d) *Lithium*. Dissolve 5.324 g pure lithium carbonate in a little dilute hydrochloric acid and dilute to 1 L with de-ionised water. This solution contains 1.000 mg Li per mL (i.e. 1000 ppm). Dilute the stock solution to give solutions containing 20, 10, 5, and 2 ppm, of lithium ions.

Prepare calibration curves for each of the above four elements. With the aid of these calibration curves, carry out the following simple determinations.

1. *Potassium in potassium sulphate*. Weigh out accurately about 0.20 g potassium sulphate and dissolve it in 1 L de-ionised water. Dilute 10.0 mL of this solution to 100 mL, and determine the potassium with the flame photometer using the potassium filter.
2. *Potassium and sodium in a mixture*. Mix suitable volumes of the above stock solutions so that the resulting solution contains, say, 4–10 ppm Na and 10–15 ppm K. Determine the Na and K with the aid of the appropriate filters. Compare the results obtained with the true values.
3. *Sodium, potassium, and calcium in a mixture*. Mix appropriate volumes of the above stock solutions so that the test solution contains, say, 5 ppm Na, 10 ppm K, and 40 ppm Ca. Determine the Na, K, and Ca with the aid of the appropriate filters. Compare the results obtained with the true values.
4. *Calcium in calcium carbonate*. Determine the calcium in an analysed sample of dolomite. Dissolve about 0.38 g, accurately weighed in 1:1 hydrochloric acid, warm gently, filter through a quantitative filter paper, wash, dilute the combined filtrate and washings to 1 L. Measure the calcium content of the resulting solution: use a calcium filter. Compare the value for Ca thus obtained with the known Ca content.

Prepare a calibration curve for each element (see Section 21.16) and use this to evaluate the concentration of any unknown sample (see Note).

**Note.** The unknown solution may require dilution to give a reading on the calibration curve.



# Mass Spectrometry

## MASS SPECTROMETRY

The principles that underlie mass spectrometry predate all of the other instrumental techniques described in this book. The fundamental principles date to 1898. In 1911, J. J. Thomson used a mass spectrum to demonstrate the existence of neon-22 in a sample of neon-20, thereby establishing that elements could have isotopes. The earliest mass spectrometer, as we know it today, was built in 1918. However, the method of mass spectrometry did not come into common use until quite recently, when reasonably inexpensive and reliable instruments became available. With the advent of commercial instruments that can be maintained fairly easily, are priced within reason for many industrial and academic laboratories, and provide high resolution, the technique has become quite important in structure elucidation studies.

### 1 THE MASS SPECTROMETER

In its simplest form, the mass spectrometer performs three essential functions. First, it subjects molecules to bombardment by a stream of high-energy electrons, converting some of the molecules to ions, which are accelerated in an electric field. Second, the accelerated ions are separated according to their mass-to-charge ratios in a magnetic or electric field. Finally, the ions that have a particular mass-to-charge ratio are detected by a device which can count the number of ions striking it. The detector's output is amplified and fed to a recorder. The trace from the recorder is a **mass spectrum**—a graph of the number of particles detected as a function of mass-to-charge ratio.

When we examine each function in detail, we see that the mass spectrometer is actually somewhat more complex than just described. Before the ions can be formed, a stream of molecules must be introduced into the **ionization chamber** where the ionization takes place. A **sample inlet system** provides this stream of molecules.

A sample studied by mass spectrometry may be a gas, a liquid, or a solid. Enough of the sample must be converted to the vapor state to obtain the stream of molecules that must flow into the ionization chamber. With gases, of course, the substance is already vaporized, so a simple inlet system can be used. This inlet system is only partially evacuated so that the ionization chamber itself is at a lower pressure than the sample inlet system. The sample is introduced into a larger reservoir, from which the molecules of vapor can be drawn into the ionization chamber, which is at low pressure. To ensure that a steady stream of molecules is passing into the ionization chamber, the vapor travels through a small pinhole, called a **molecular leak**, before entering the chamber. The same system can be used for volatile liquids or solids. For less volatile materials, the system can be designed to fit within an oven, which can heat the sample to provide a greater vapor pressure. Care must be taken not to heat any sample to a temperature at which it might decompose.

With rather nonvolatile solids, a direct-probe method of introducing the sample may be used. The sample is placed on the tip of the probe, which is then inserted through a vacuum lock into the ionization chamber. The sample is placed very close to the ionizing beam of electrons. The probe can be heated, thus causing vapor from the sample to be evolved in proximity to the beam of electrons. A system such as this can be used to study samples of molecules with vapor pressures lower than  $10^{-9}$  mm Hg at room temperature.

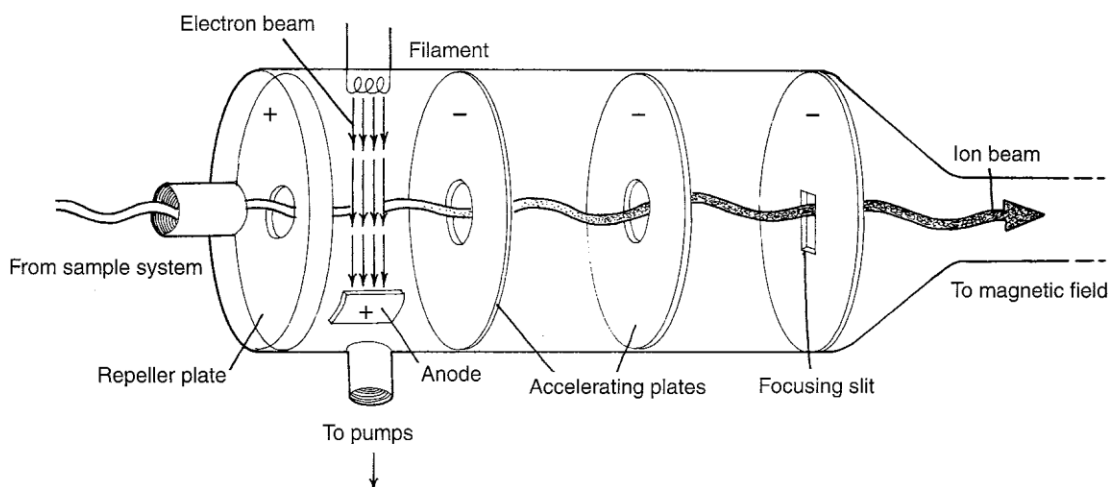


FIGURE 8.1 Ionization chamber.

Once the stream of sample molecules has entered the ionization chamber, a beam of high-energy electrons bombards it. This process converts the molecules to ions. The ions are then accelerated in an electric field. Figure 8.1 is a diagram of a typical ionization chamber.

In the ionization chamber, the beam of high-energy electrons is emitted from a **filament** that is heated to several thousand degrees Celsius. In normal operation, the emitted electrons have an energy of about 70 electron volts (eV). These high-energy electrons strike the stream of molecules that has been admitted from the sample system and ionize the molecules in the stream by removing electrons from them; the molecules are thus converted to positive ions. A **repeller plate**, which carries a positive electrical potential, directs the newly created ions toward a series of **accelerating plates**. A large potential difference, ranging from 1 to 10 kilovolts (kV), applied across these accelerating plates produces a beam of rapidly traveling positive ions. One or more **focusing slits** direct the ions into a uniform beam.

Most of the sample molecules are not ionized at all but are continuously drawn off by vacuum pumps that are connected to the ionization chamber. Some of the molecules are converted to negative ions through the absorption of electrons. The repeller plate absorbs these negative ions. A small proportion of the positive ions that are formed may have a charge greater than one (a loss of more than one electron). These are accelerated in the same way as the singly charged positive ions.

The energy required to remove an electron from an atom or molecule is its **ionization potential**. Most organic compounds have ionization potentials ranging between 8 and 15 eV. However, a beam of electrons does not create ions with high efficiency until it strikes the stream of molecules with a potential of 50 to 70 eV. To produce reproducible spectra, electrons of this energy range are generally used to ionize the sample.

From the ionization chamber, the beam of ions passes through a short field-free region. From there it enters the **mass analyzer**, the region where the ions are separated according to their mass-to-charge ratios.

The kinetic energy of an accelerated ion is equal to

$$\frac{1}{2}mv^2 = eV$$

where  $m$  is the mass of the ion,  $v$  is the velocity of the ion,  $e$  is the charge on the ion, and  $V$  is the potential difference of the ion-accelerating plates. In the presence of a magnetic field, a charged particle describes a curved flight path. The equation which yields the radius of curvature of this path is

$$r = \frac{mV}{eH}$$

where  $r$  is the radius of curvature of the path and  $H$  is the strength of the magnetic field. If these two equations are combined to eliminate the velocity term, the result is

$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

Equation 8.1

This is the important equation that governs the behavior of an ion in the mass-analyzer portion of the mass spectrometer.

As can be seen from Equation 8.1, the greater the value of  $m/e$ , the larger the radius of the curved path. The analyzer tube of the instrument is constructed to have a fixed radius of curvature. A particle with the correct  $m/e$  ratio can negotiate the curved analyzer tube and reach the detector. Particles with  $m/e$  ratios that are either too large or too small strike the sides of the analyzer tube and do not reach the detector. The method would not be very interesting if ions of only one mass could be detected. Therefore, either the accelerating voltage or the magnetic field strength is continuously varied in order that all of the ions produced in the ionization chamber can be detected. The record produced from the detector system is in the form of a plot of the numbers of ions versus their values of  $m/e$ .

An important consideration in mass spectrometry is **resolution**, defined according to the relationship

$$R = \frac{M}{\Delta M}$$
Equation 8.2

where  $R$  is the resolution,  $M$  is the mass of the particle, and  $\Delta M$  is the difference in mass between a particle of mass  $M$  and the particle of next higher mass that can be resolved by the instrument. Low-resolution instruments have  $R$  values ranging as high as 2000. For some applications, resolutions 5 to 10 times that amount are required.

To obtain higher resolutions, modifications of this basic instrument design are used. Since the particles leaving the ionization chamber do not all have precisely the same velocity, a **double-focusing mass spectrometer** may be used. In such an instrument, the beam of ions passes through an electric field region before entering the magnetic field. The particles describe a curved path in each of these regions. In the presence of an electric field, the particles all travel at the same velocity, so the resolution of the magnetic field region improves.

The **detector** of a typical instrument consists of a counter that produces a current that is proportional to the number of ions that strike it. Through the use of electron multiplier circuits, this current can be measured so accurately that the current caused by just one ion striking the detector can be measured. The signal from the detector is fed to a **recorder**, which produces the mass spectrum. In modern instruments, the output of the detector is fed through an interface to a computer. The computer can store the data, provide the output in both tabular and graphic forms, and compare the data to standard spectra, which are contained in spectra libraries that are also stored in the computer. In some older instruments, the electron current from the detector is fed to a series of five galvanometers of varying sensitivity. The galvanometers frequently have sensitivities in the ratios 1, 1/3, 1/10, 1/30, and 1/100. Each is capable of recording a spectrum with five simultaneous traces at different sensitivities. By using the five traces, it is possible to record the weakest peaks while still keeping the strongest peaks on scale.

## 8.2 GAS CHROMATOGRAPHY–MASS SPECTROMETRY

A very useful innovation in sample introduction systems is the use of a gas chromatograph coupled to a mass spectrometer. In effect, the mass spectrometer acts in the role of detector. In this technique, known as **gas chromatography–mass spectrometry (GC-MS)**, the gas stream emerging from the gas chromatograph is admitted through a valve into a tube, where it passes over a molecular leak. Some of the gas stream is thus admitted into the ionization chamber of the mass spectrometer. In this way it is possible to obtain the mass spectrum of every component in a mixture being injected into the gas chromatograph.

A drawback of this method involves the need for rapid scanning by the mass spectrometer. The instrument must determine the mass spectrum of each component in the mixture before the next component exits from the gas chromatography column, in order that one substance is not contaminated by the next fraction before its spectrum has been obtained.

Since high-efficiency capillary columns are used in the gas chromatograph, in most cases compounds are completely separated before the gas stream is analyzed. The instrument must have the capability of obtaining at least one scan per second in the range of 10 to 300 amu. Even more scans are necessary if a narrower range of masses is to be analyzed.

The effluent from the gas-chromatograph part of the instrument can also be directed into an FT-IR instrument so that infrared spectra rather than mass spectra can be obtained. In that case, the infrared spectrophotometer acts as the detector for the gas chromatograph.

The mass spectrometer which is coupled to the gas chromatograph should be relatively compact and capable of high resolution. In many instruments, a highly useful modification has been to replace the magnetic field region with a quadrupole system. In a **quadrupole mass spectrometer** (Fig. 8.2), a set of four solid rods is arranged parallel to the direction of the ion beam. The rods should be hyperbolic in cross section, although cylindrical rods may be used. A direct-current voltage and a radiofrequency are applied to the rods, generating an oscillating electrostatic field in the region between the rods. Depending upon the ratio of the radiofrequency amplitude to the direct-current voltage, ions acquire an oscillation in this electrostatic field. Ions of an incorrect mass-to-charge ratio (too small or too large) undergo an unstable oscillation. The amplitude of the oscillation continues to increase until the particle strikes one of the rods. Ions of the correct mass-to-charge ratio undergo a stable oscillation of constant amplitude. These ions do not strike the rods but pass through the analyzer to reach the detector. The resolution of the system can be adjusted by varying the ratio of radiofrequency amplitude to DC voltage. Resolutions as high as 10,000 may be obtained with this type of mass analyzer.

With a GC-MS system, one can also analyze a mixture and conduct a library search on each component of the mixture. If the components are known compounds, they can be identified tentatively by

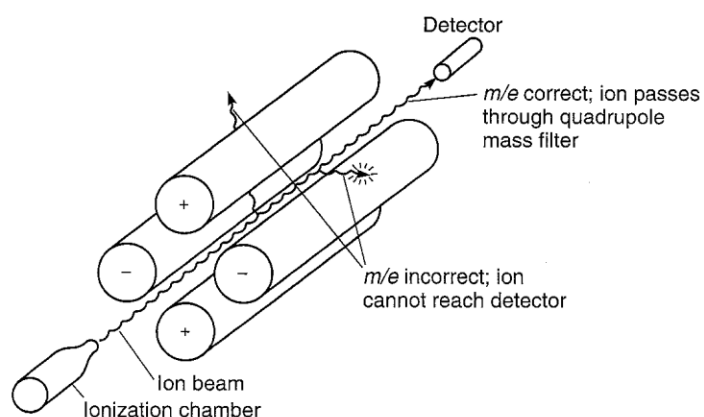


FIGURE 8.2 Quadrupole mass analyzer.

comparisons with compounds found in the computer library. In this way, a “hit list” can be generated which reports on the probability that the compound in the library matches the known substance (see Section 8.8).

A new technique that resembles the GC-MS technique described here is **high-performance liquid chromatography–mass spectrometry (HPLC-MS)**. An HPLC instrument is coupled through a special interface to a mass spectrometer. The substances that elute from the HPLC column are detected by the mass spectrometer, and their mass spectra can be displayed, analyzed, and compared with standard spectra found in the computer library built into the instrument.

### 8.3 THE MASS SPECTRUM

The mass spectrum is a plot of ion abundance versus  $m/e$  ratio. Figure 8.3 is a portion of a typical mass spectrum—that of dopamine, a substance that acts as a neurotransmitter in the central nervous system. The upper part of Figure 8.3 shows the five traces that are obtained with a multiple-galvanometer detection system. Because a spectrum of this sort is difficult to use, usually this information is converted to the form of a bar graph. Such a graph appears beneath the spectrum in Figure 8.3. With a modern instrument, in which the signal from the detector is digitized and stored in the instrument's computer, it is possible to obtain a direct plot of the data in a form essentially identical to the bar graph in Figure 8.3. Commonly, mass spectral results may also be presented in tabular form, as in Table 8.1.

The most abundant ion formed in the ionization chamber gives rise to the tallest peak in the mass spectrum, called the **base peak**. In the mass spectrum of dopamine, the base peak is indicated at an  $m/e$  value of 124. The relative abundances of all the other peaks in the spectrum are reported as percentages of the abundance of the base peak.

As we mentioned earlier, the beam of electrons in the ionization chamber converts some of the sample molecules to positive ions. Some of these types of ions are of sufficient importance to warrant further examination. The simple removal of an electron from a molecule yields an ion whose weight is the actual molecular weight of the original molecule. This ion is the **molecular ion**, which is frequently symbolized by  $M^+$ . The value of  $m/e$  at which the molecular ion appears on the mass spectrum, assuming that the ion has only one electron missing, gives the molecular weight of the original molecule. If you can identify the molecular ion peak in the mass spectrum, you will be able to use the spectrum to determine the molecular weight of an unknown substance. Ignoring heavy isotopes for the moment, the molecular ion peak is the heaviest peak in the mass spectrum; it is indicated in the graphic presentation in Figure 8.3 ( $m/e = 153$ ). Strictly speaking, the molecular ion is a **radical-cation** since it contains an unpaired electron as well as a positive charge.

Molecules in nature do not occur as isotopically pure species. Virtually all atoms have heavier isotopes that occur in characteristic natural abundances. Hydrogen occurs largely as  $^1\text{H}$ , but about 0.02% of hydrogen atoms are the isotope  $^2\text{H}$ . Carbon normally occurs as  $^{12}\text{C}$ , but about 1.1% of carbon atoms are the heavier isotope  $^{13}\text{C}$ . With the possible exception of fluorine and a few additional elements, most other elements have a certain percentage of naturally occurring heavier isotopes. Peaks caused by ions bearing those heavier isotopes also appear in mass spectra. The relative abundances of such isotopic peaks are proportional to the abundances of the isotopes in nature. Most often, the isotopes occur one or two mass units above the mass of the “normal” atom. Therefore, besides looking for the molecular ion ( $M^+$ ) peak, one would also attempt to locate the  $M + 1$  and  $M + 2$  peaks. As Section 8.5 will demonstrate, the relative abundances of the  $M + 1$  and  $M + 2$  peaks can be used to determine the molecular formula of the substance being studied. In Figure 8.3, the isotopic peaks are the low-intensity peaks at  $m/e$  values higher (154 and 155) than that of the molecular ion peak.

We have seen that the beam of electrons in the ionization chamber can produce the molecular ion. This beam is also sufficiently powerful to break some of the bonds in the molecule, producing a series of molecular fragments. The positively charged fragments are also accelerated in the ionization

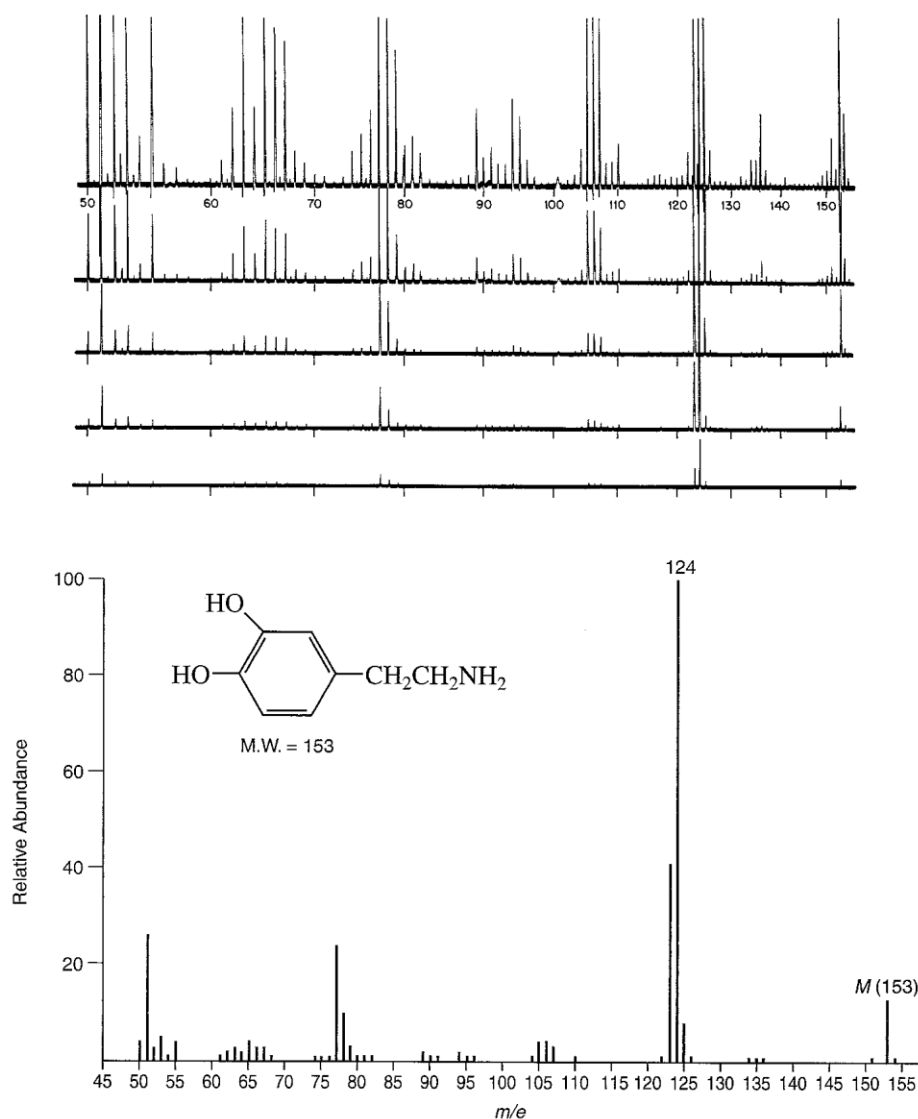


FIGURE 8.3 Partial mass spectrum of dopamine.

chamber, sent through the analyzer, detected, and recorded on the mass spectrum. These **fragment ions** appear at  $m/e$  values corresponding to their individual masses. Very often a fragment ion, rather than the parent ion, is the most abundant ion produced in the mass spectrum. A second means of producing fragment ions exists if the molecular ion, once it is formed, is so unstable that it disintegrates before it can pass into the accelerating region of the ionization chamber. Lifetimes less than  $10^{-6}$  sec are typical in this type of fragmentation. The fragments that are charged then appear as fragment ions in the mass spectrum. A great deal of structural information about a substance can be determined from an examination of the fragmentation pattern in the mass spectrum. Section 8.6 will examine some fragmentation patterns for common classes of compounds.

Ions with lifetimes on the order of  $10^{-6}$  sec are accelerated in the ionization chamber before they have an opportunity to disintegrate. These ions may disintegrate into fragments while they are passing into the analyzer region of the mass spectrometer. The fragment ions formed at that point have considerably lower energy than normal ions, since the uncharged portion of the original ion carries away