MODULE 5 CHEMICAL AND PHYSICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

UNIT 1 CHEMICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

1.0 INTRODUCTION

The methods of "wet chemistry" such as titrimetric analysis and gravimetry still have an important role in modern analytical and environmental chemistry. There are many areas in which titrimetric and gravimetric procedures are quite invaluable. The advantages of titrimetric procedures include:

- The precision (0.1percent) is better than most instrumental methods.
- Methods are usually superior to instrumental techniques for major component analysis.
- When the sample throughout is small e.g. for one-off analysis, simple titrations are often preferable.
- Unlike instrumental methods, the instrument does not require constant recalibration.
- Methods are relatively inexpensive with low unit costs per determination.
- They are often used to calibrate and/or validate routine analysis using instruments.
- The methods can be automated.

The most significant disadvantage of titrimetric procedures is that, they are normally less, sensitive and frequently less selective than instrumental methods. Also, when a large number of similar determinations are required, instrumental methods are usually much quicker and often cheaper than the more labour intensive titrimetric methods.

Like titrimetric analysis, the advantages offered by gravimetric procedure are many including the following:

- It is accurate and precise when using modern analytical balances.
- Possible sources of error are readily checked, since filtration can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.
- It involves direct measurement without any form of calibration being required.
- Determinations can be carried out with relatively inexpensive apparatus; the most expensive items are a muffle finance and sometimes platinum crucibles.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- list some applications of titrimetric and gravimetric analysis involving “wet chemistry”
- explain how to carry out the analysis of such species as Cl^-, F^-, SO_4^{2-}, PO_4^{3-} e.t.c. in an environmental sample
- state some precautionary measures needed to achieve both accuracy and precision in the use of titrimetric and gravimetric analyses in the determination of a given chemical species.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Examples of "Wet Chemistry" Analysis.

4.2 Determination of Chloride (Cl^-)

4.2.1 Mohr Method (Argentometric Procedure)

The Mohr method employs 0.I M solution of silver nitrate, $AgNO_3$, for titration. In the titration the chloride ion is precipitated as white silver chloride, AgCl.

$$Ag^+ + Cl^- \rightleftharpoons AgCl(s) \qquad (K_{sp} = 3 \times 10^{-10}).$$

The end point cannot be detected visually unless an indicator capable of demonstrating the presence of excess Ag^+ is present. The indicator normally used is **potassium chromate**, which supplies chromate ion, CrO_4^{2-}. As the concentration of Cl^- ions approaches extinction, the Ag^+ concentration increases to a level at which the solubility product of silver chromate is exceeded and it begins to form a reddish-brown precipitate.

$$2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4(s) \quad (K_{sp} = 5 \times 10^{-12}).$$

This is taken as an evidence that all the chloride has been precipitated. Several **precautions** are to be observed in this determination if accurate results are to be obtained.

1. A uniform sample size, preferably 100 mL, must be used to that ionic concentrations needed to indicate the end point will be constant.

2. The pH must be in the range of 7 to 8 because Ag^+ is precipitated as AgOH(s) at high pH levels and the CrO_4^{2-} is converted to $Cr_2O_7^{2-}$ at low pH levels.
3. A definite amount of indicator must be used to provide a certain concentration of CrO_4^{2}; otherwise $Ag_2CrO_4(s)$ may form too soon or not soon enough.

The calculation for chloride may be simplified as

$$Cl^- \text{ (in mg/L)} = \frac{(mL AgNO_3\text{-blank}) \times 0.1 \times 35.45 \times 1000}{mL \text{ sample}}$$

4.2.2 Mercuric Nitrate Method

The mercuric nitrate method is less subjected to interferences than the Mohr method because the titration is performed on a sample whose pH is adjusted to a value of about 2.5. Under these conditions, Hg^{2+} ion combines with Cl^- to form the $HgCl_2$ complex which is soluble, therefore making end-point detection easier than with the Mohr procedure. As the Cl^- concentration approaches zero, the Hg^{2+} concentration increases to a level where it becomes significant as the mercuric nitrate is added.

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2(aq) \quad (\beta_2 = 1.7 \times 10^{13}).$$

Diphenylcarbazone is the indicator used to show the presence of excess Hg^{2+} ions. It combines with them to form a distinct purple colour. A blank correction is needed. Nitric acid is added to the indicator to reduce the sample pH to 2.5, a value that must be maintained uniformly in unknown samples, standards and blanks. A pH indicator, xylene cyanol FF, which is blue-green at pH 2.5 is also included and improves the end point by masking the pale colour developed by diphenylcarbazone during the titration. Using 0.1M $Hg(NO_3)_2$ solution makes the calculation similar to that of Mohr's method.

4.2.3 Ferricyanide Method

This is an automated colourimetric procedure. Mercuric ion contained in the mercuric thiocyanate titrant forms a soluble complex with chloride. This releases the thiocyanate to react with ferric ion, which is also added, to form intensely red ferric thiocyanate, the intensity of which is proportional to the chloride concentration.

4.3 Determination of Sulphate, SO_4^{2-}.

4.3.1 Gravimetric Method

The gravimetric method yields accurate results. The quantitative aspects of this method depend on the fact that barium ion combines with sulphate ion to form poorly soluble barium sulphate as follows:

$$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4(s), \quad Ksp = 1 \times 10^{-10}$$

The precipitate is normally accomplished by adding $BaCl_2$ solution in slight excess to samples of water acidified with HCl acid and kept near the boiling point. The samples are acidified to eliminate the possibility of precipitation of $BaCO_3$, which might occur in highly alkaline waters maintained near the boiling temperature. Excess $BaCl_2$ solution is used to produce sufficient common ion to precipitate sulphate ion as completely as possible.

Because of the great insolubility of $BaSO_4$, there is a considerable tendency for much of the precipitate to form in a colloidal condition that cannot be removed by ordinary filtration process. Digestion of the samples at temperatures near the boiling point for a few hours usually results in a transfer of the colloidal to crystalline forms. Filtration can then be accomplished. The crystals of $BaSO_4$ are quite small. Hence, a special grade of filter paper suitable for sulphate determinations should be used.

Having transferred all the sulphate crystals quantitatively to the filter paper, washing with distilled water must be sufficiently done to remove all excess $BaCl_2$ and other salts. Weigh the sulphate precipitate formed by subjecting the filter paper to a complete combustion or by drying the filter paper and the sulphate to a constant weight and then subtracting the weight of the filter paper (previously weighed) from the total to give the weight of the sulphate precipitate.

4.3.2 Turbidimetric Procedure

The turbidimetric method of measuring sulphate is based upon the fact that $BaSO_4$ formed following $BaCl_2$ solution addition to a sample tends to precipitate in a colloidal form. This tendency is enhanced in the presence of an acidic buffer solution containing magnesium chloride, potassium nitrate, sodium acetate and acetic acid.

By standardising the procedure used to produce the colloidal suspension of $BaSO_4$, it is possible to obtain quantitative and acceptable results. Sample with sulphate concentrations greater than 10 mg/L can be analysed by taking smaller portions and diluting them to the

recommended 50 mL sample size. At least, one standard sample of sulphate should be included in each set of samples to verify that conditions used in the test are comparable to those used in establishing the calibration curve.

4.3.3 Automated Methylthymol Blue Method

Here, a continuous-flow analytical instrument is used in which chemicals are automatically added to and mixed with samples in a flowing stream. After a standard time passes to allow for chemical reaction to occur, the sample enters a cell where measurement of colour or turbidity is made for quantification.

In the automated procedure for sulphate, $BaCl_2$ is first automatically added to the samples of low pH to form a $BaSO_4$ precipitate; the sample pH is then adjusted to about 10. Methylthymol blue reagent is then added and combines with the excess barium added to form a blue chelate. The uncompleted methylthymol blue remaining forms a grey colour which is automatically measured.

The amount of sulphate in the original sample is based on the instrument response that is obtained. The instrument must be calibrated with standard sulphate solution, the addition of chemicals must be precise and interferences must be absent. The method of automated approach helps to accomplish all these.

4.4 Determination of Fluoride (F^-)

The concentration of fluoride in drinking or wastewater may be determined indirectly by its ability to form a complex with Zirconium. In the presence of the dye SPADNS, solutions of Zirconium form a reddish coloured compound, called a "lake", that absorbs at 570 nm. When fluoride is added, the formation of the stable ZrF_6^{2-} complex causes a portion of the lake to dissociate, decreasing the absorbance.

$$(\text{Zr-SPADNS}) + 6F^- \rightarrow \text{SPADNS} + ZrF_6^{2-}$$

Thus, the Beer's law is satisfied in an inverse manner. A plot of absorbance versus the concentration of fluoride, therefore, has a negative slope. When photometric methods are used, care must be exercised to keep contact time and temperature the same as employed in developing the calibration curve. Good practice demands that at least one standard be included with samples each time photometric measurements are made.

4.5 Determination of Phosphate (PO_4^{3-})

4.5.1 Orthophosphate

Phosphorus occurring as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) can be measured quantitatively by gravimetric, volumetric or colourimetric methods. The gravimetric method is applicable where large amounts of phosphate are present, but such situation does not occur in ordinary practice. The volumetric method is applicable when phosphate concentrations exceed 50 mg/L, but such concentrations are seldom encountered except in boiler waters and anaerobic digester supernatant liquors. Colourimetric methods are the standard procedures usually adopted for water and wastewater, possibly at some sacrifice of accuracy.

In colourimetric methods, phosphate ion combines with ammonium molybdate under acid conditions to form a molybdophosphate complex.

$$PO_4^{3-} + 12(NH_4)_2\,MoO_4 + 12H^+ \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^+ + 12H_2O.$$

When large amounts of phosphate are present, the molybdophosphate forms a yellow precipitate that can be filtered and used for volumetric determination. At concentrations under 30 mg/L (the usual range in water analysis) the yellow colour of the colloidal sol is not discernible.

Using stannous chloride, $SnCl_2$, (or ascorbic acid), the molybdenum contained in ammonium phosphomolybdate is readily reduced to produce a blue-coloured sol, molybdenum blue, that is proportional to the amount of phosphate present. Excess ammonium molybdate is not reduced and therefore does not interfere.

$$(NH_4)_3PO_4.12MoO_3 + Sn^{2+} \longrightarrow \text{Molybdenum blue} + Sn^{4+}$$

The phosphomolybdate is first extracted from the sample into a benzene-isobutarnol solution prior to addition of the stannous chloride. This extraction is necessary to enhance increased sensitivity and to obtain accurate results when excessive interferences are present in the sample.

4.5.2 Polyphosphates

The orthophosphate present is first determined, and them, the polyphosphate is converted to orthophosphate by boiling samples that have been acidified with sulphuric acid for 90 minutes or more. The excess acid added must first be neutralised before proceeding with the addition of the ammonium molybdate solution. The orthophosphate

formed from the polyphosphate is measured in the presence of orthophosphate originally present in the sample by the method earlier described. The amount of polyphosphates is obtained as follows:

Total inorganic phosphate – orthophosphate = polyphosphate

4.5.3 Organic phosphorus

The organic matter (industrial wastes or sludges) is subjected to wet acid digestion using nitric acid first followed by perchloric acid. The excess acid remaining is neutralised. The phosphorus released can be measured using the method described for orthophosphate.
Total phosphorus – inorganic phosphorus = organic phosphorus

4.6 Determining Iron by Phenanthroline Method

The phenanthroline method is a reliable standard "wet chemistry" method for the measurement of Fe in water particularly when phosphate or heavy metal interference is absent. The method depends on the fact that 1, 10 - phenanthroline combines with Fe^{2+} to form a complex ion that is orange-red in colour. The colour produced conforms to Beer's law and is readily measured by visual or photometric comparison. It is necessary to make sure that all the iron is in a soluble condition. This is achieved by treating a portion of the sample with HCl acid to dissolve the ferric hydroxide:

$$Fe(OH)_3(s) + 3H^+_{(aq)} \longrightarrow Fe^{3+} + 3H_2O$$

Since 1,10 – phenanthroline will specifically measure Fe^{2+}, all iron in the Fe^{3+} form must be reduced to the ferrous (Fe^{2+}) form. This is readily accomplished by using hydroxylamine as the reducing agent.

$$4Fe^{3+} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + H_2O + 4H^+$$

Three molecules of 1, 10 – phenanthroline are required to sequester or form a complex ion with each Fe^{2+}. When interfering materials are present, satisfactory results can be obtained by the use of HCl to acidify the sample before the iron content is extracted into diisopropyl-ether prior to the addition of the phananthroline solution.

4.7 Persulphate Method for Manganese Determinations

This method is suited for routine determinations of manganese because pre-treatment of samples is not needed to overcome chloride interference. Ammonium persulphate is commonly used as the oxidising agent. It is subjected to deterioration during prolonged storage; hence, it

is good to always include a standard sample with each set of samples to verify the potency of the persulphate used.

Chloride interference is overcome by adding Hg^{2+} to form the neutral $HgCl_2$ complex. Since the Ksp of $HgCl_2$ is about $1.7x\ 10^{-13}$, the concentration of Cl^- is decreased to such a low level that it cannot reduce the permanganate ions formed. The oxidation of Mn in lower oxidation states to permanganate by persulphate requires the presence of Ag^+ as a catalyst.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow Ag^+ \quad 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

The colour produced by the permanganate ion is stable for several hours, provided a good quality distilled water is used for dilution purposes and reasonable care is taken to protect the sample from contamination by dust of the atmosphere.

4.8 EDTA Titrations

Ethylenediamine tetraacetic acid (EDTA) titrations are a type of complexometric titrations widely used in the quantitative determination of several elements in environmental waters generally. The success of EDTA titration depends on its ability to account for complexes with many metals and the fact that masking/demasking processes are possible thus aiding selective titration of given metals. Also, suitable metal ion indicators are available which helps to determine a precise end point for each titration.

For example, when Ca^{2+} and Mg^{2+} occur simultaneously in a sample of hard water, the concentration of each ion can be determined successfully using EDTA titration. To determine Ca^{2+}, 2 mL of 0.1M NaOH solution is added to 50 mL of the water sample and titrated with standard EDTA using murexide indicator. To now determine Mg^{2+} in the same sample, destroy murexide colour with (1) mL of concentrated HCl, add 3 mL of NH_3-NH_4Cl buffer and titrate with EDTA using Eriochrome black T.

5.0 ACTIVITY

i. Explain why a blank correction must be applied to the titration values in both the Mohr and mercuric nitrate methods of chloride determination.
ii. Would the analytical results by the Mohr method for chloride be higher, lower or the same as the true value of an excess if indicator were accidentally added to the sample? Why?
iii. What purpose is served by the nitric acid added to the indicator in the mercuric nitrate method of chloride determination?

iv. In the gravimetric determination of sulphate concentration in a 400mL wastewater sample, 0.0460g $BaSO_4$ was obtained. How many mg/L of sulphate was in the sample?
v. In the photometric analysis of fluoride in a sample of water supply, Beer's law is obeyed in an inverse manner. Why?
vi. Would you expect the analytical results for orthophosphate to be higher than, lower than or the same as the original value in a sample of domestic wastewater that had been acidified to prevent bacterial action and stored for several days prior to analysis? Why?

6.0 SUMMARY

In this unit, you have learnt that:

- wet chemistry predominates the field of chemical instrumentation in environmental sciences
- mercuric nitrate method is more reliable than argentometric procedure in the analysis of Cl^- since mercuric method is less subject to interferences.
- gravimetric methods are particularly suitable for species that can form stable precipitates of known molecular formula.
- visual or photometric methods are suitable where colour development of a given species is possible.
- certain metals e.g. Fe and Mn can be determined using visual or photometric methods.
- complexometric titration (using EDTA particularly) can be used to routinely determine the levels of many metals in water for example.

7.0 ASSIGNMENT

1. (a) List four precautions that must be observed to ensure an accurate gravimetric determination of sulphate concentration in a water sample.
   (b) In the determination of sulphate concentration by gravimetric procedure, a 100mL sample yielded 0.0140g of $BaSO_4$. How many mg/L of sulphate was in the sample?

8.0 REFERENCES

Sawyer, C., McCarty, P. & Parkin, G. (2006). *Chemistry for Environmental Engineering and Science.* 5th ed. New Delhi: Tata McGraw-Hill Put. Coy. Ltd.

Peavy, H., Rowe, D., & Tchobanoglous G. (1985). *Environmental Engineering*. New York: McGraw-Hill Int. Editions.

Ademoroti, C. (1996). *Standard Methods for Water and Effluents Analysis*. Ibadan: Foludex Press Ltd.

Mendham, J., Denney, R., Barnes, J. & Thomas, M. (2004) *VOGEL'S Textbook of Quantitative Chemical Analysis*. 6th ed. Delhi, India: Pearson Education Ltd.

UNIT 2 PHYSICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

CONTENTS

1.0 INTRODUCTION

In environmental sciences, all the pollutants of interest can readily be classified as organic or inorganic. These ones are of greater concern because they occur more often than any other ones we may think of.

Inorganic pollution arises from mining and smelting of metals, fossil fuel combustion and chemical production coupled with widespread applications in engineering, electronics, industrial and agricultural practices. These activities have led to the presence of heavy metals and other trace inorganic chemicals in the atmosphere, rainfall, rivers, groundwater, soil, sediments and the biota. Organic pollution was first manifested following the growth in the use of pesticides in the years immediately after the Second World War and through the 1950s. The first organochlorine pesticides were DDT, Lindane and Dieldrin. Overuse and misuse of these compounds led to the death of wildlife, especially species at the apex of food chains including raptorial birds, foxes and badgers.

Public concern requires that pollutants in the environment are detected and controlled. Current methods popularly used in profiling heavy metal levels in an environmental matrix include Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption

Spectrometry (GFAAS), Inductively Coupled Plasma-Mass Spectrophotometry (ICP-MS) and Energy Dispersive X-Ray Fluorescence (EDXRF) to mention a few. Chromatography is the dominant analytical technique for the identification and quantification of organic pollutants.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- list mostly used instrumental techniques for the analysis of heavy metals and organic compounds in an environmental sample
- state the principle of operation of each instrumental technique studied
- state the advantages of one technique over the other.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Instrumental Techniques for Heavy Metals Analysis

Various, instrumental techniques are used by chemists and other environmental scientists for the purpose of detecting and determining the levels of heavy metals in a given environmental samples. For the sake of brevity, only two of the techniques (AAS and NAA) are discussed here.

4.1.1 Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry is a technique that involves the aspiration of the sample solution into a flame or an electrothermal device whose high temperature converts the analyte ions into atoms in

the vapour state. When an electromagnetic radiation characteristic of the electronic transitions of atoms of a particular element is passed through an atomic vapour of that element, the radiation at certain frequencies is attenuated. The absorbed radiation excites electrons from the ground state to various higher energy levels (excited states). The degree of absorption is a quantitative measure of the concentration of ground-state atoms in the vapour.

AAS is the most widely used techniques for the quantitative determination of metals at trace levels (0.1 to 100ppm) in a wide range of materials; its relative precision is 0.5 to 2percent.

The major disadvantages include: (i) samples must be in solution or at least volatile; (ii) individual source lamps are required for each element; (iii) the technique is not capable of simultaneous multi-elemental determination; and (iv) it is not suitable for qualitative analysis.
Some of the various modifications of AAS are Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption spectroscopy (GFAAS).

4.1.2 Flame Atomic Absorption Spectroscopy (FAAS)

FAAS consists of a sharp-line radiation source, produced by a hollow-cathode lamp, characteristic of the element of interest, a solution nebulizer and burner, a monochromator, photomultiplier and recording system. Although FAAS is simple to operate and cheap, the burner-nebuliser system is relatively an inefficient sampling device. Only a small fraction of the sample reaches the flame and the atomised sample passes quickly through the light path thereby leading to a low detection limits, usually at the sub μg/g or μg/mL levels. Its dynamic range is also limited.

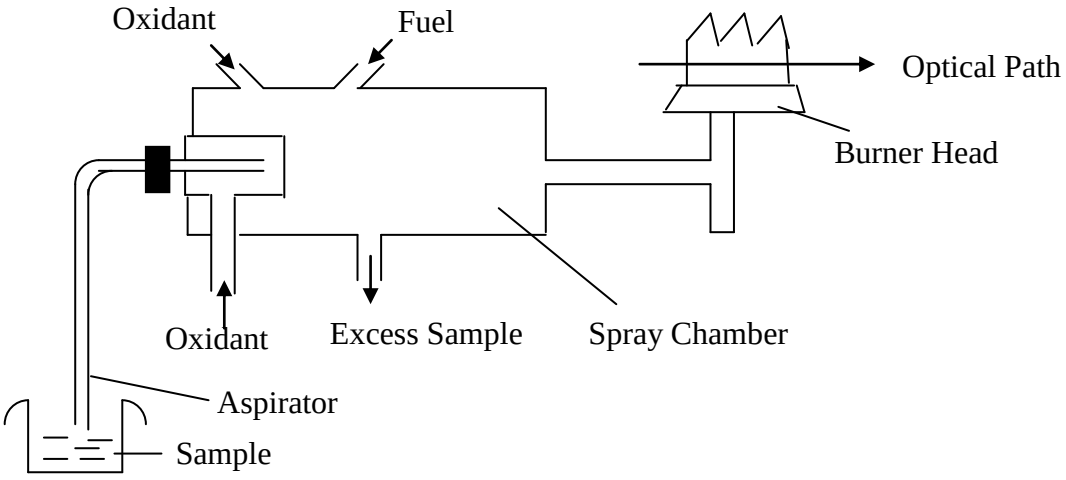

Fig. 6: The Premix Burner of a FAAS
Source: D. Harvey, 2000 (Modified)

4.1.3 Graphite Furnace Atomic Absorption spectroscopy (GFAAS)

One major instrumental difference between GFAAS and FAAS is that, graphite tube furnace (about 5 cm x 3 mm) is used in GFAAS in place of flame in the FAAS for the purpose of vapourisation and atomisation. The graphite tube furnace is flushed through with an inert gas, e.g. argon, before vapourising the sample so as to prevent the formation of refractory oxides and oxidation of the graphite tube. The axis of the furnace is aligned along the optical path of the radiation from the lamp. The sample (5 to 50 μL) is deposited on the platform at the bottom inner surface of the tube near the centre to enhance maximum sensitivity. The temperature is rapidly raised to about 2500 K by the passage of a heavy current for a period of 1 to 2 minutes. The heating cycle is controlled so as to allow solvents to evaporate or organic residues to be ashed before an atomic vapour of the metal under investigation is produced.

GFAAS has relatively low detection limits capability, which makes it particularly suited to the requirements of analyses of trace elements at low concentrations in a matrix. The main drawbacks of GFAAS are: (i) it is not multi-elemental; (ii) it has limited practical sample throughout; and (iii) the presence of high electrolyte species such as Na and Cl results in numerous non-specific absorption interferences.

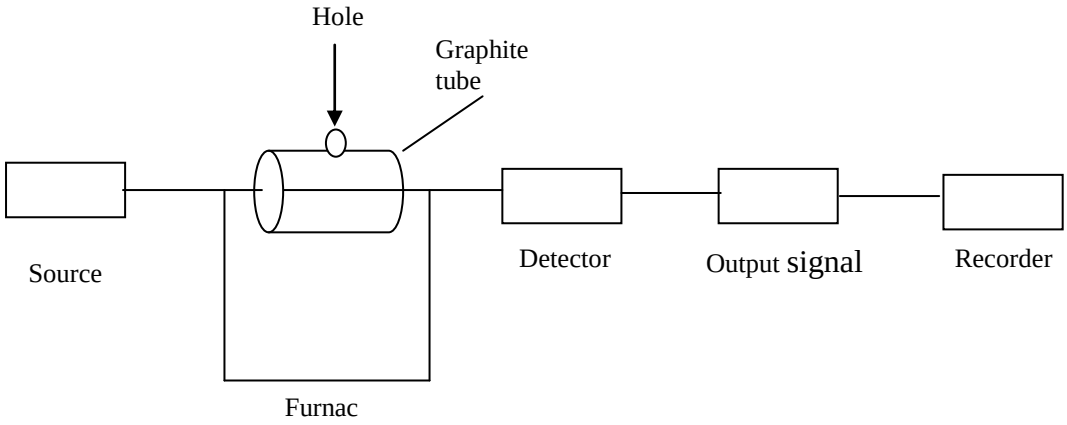

Fig. 7: A block diagram of GFAAS

4.2 Neutron Activation Analysis (NAA)

NAA is a non-destructive tool for routine trace element determination in many areas of innovative research. Apart from being able to determine many environmentally crucial trace elements such as Sb, Cd, Cr, Cu, Se,

Ni, Zn, etc. NAA is also capable of determining major elements such as Na, Cl, and K as well as rare earth elements.

The determination of the elemental concentrations is based on the measurement of induced radioactivity through the activation of the elements by neutrons. The radioactive decay of each element emits a characteristics X-ray spectrum. Hence, an individual nuclear "fingerprint" can be measured and quantified. The neutron sources used in NAA can be produced by a neutron reactor, a particle accelerator or artificial isotopes such as phitonium, and beryllium. The most common source is from a fission reactor due to its high neutron flux.

NAA is an extremely sensitive, selective and precise technique that provides both qualitative and quantitative information at ultra trace levels. These characteristics derive from a combination of factors: (i) Extremely sensitive instrumentation with a facility for spectrometric distinction between radionuclide is available; (ii) activation cross sections can be large and interise neutron fluxes are available; (iii) the reagent blank problem which is so common in trace element analysis is largely eliminated; (iv) when sample processing prior to measurement is needed, the problem of working with μg amounts of materials can be simplified by the addition of non-active "carrier' which does not affect the final activity measurement; and (v) very small sample size (flakes of paint, single hair strand, etc) can be analysed and identified by NAA.

Some of the disadvantages of NAA are; (i) liquid samples cannot be activated in a standard thermal neutron nuclear reactor; (ii) practical multi-elemental analysis is restricted due to the wide spectrum of short and long-lived nuclides; (iii) for short-lived nuclides measurement, the presence of major electrolyte species (Na, Cl, P, Br) on irradiation produces high background x-ray activities; (iv) the determination of many important elements like Be, B, Pb, P and Si is difficult due to poor nuclear cross-sections not activated by neutrons or, as in the case of P, not yielding a X-ray for analysis; and (v) it is an expensive and highly specialized instrumentation.

4.3 Instrumental Techniques for Organic Residues Analysis

In environmental chemistry, chromatography is the dominating technique with respect to organic matrix analysis. **Chromatography** is an instrumental analytical technique that combines separation and identification of components of a complex mixture into individual entities. The chromatographic methods have good speed, high resolution power and tendency to handle small amounts of material.

Every chromatographic system consists of moving or mobile phase in intimate contact with fixed or stationary phase. The latter is composed of the stationary or all non-moving portion of chromatographic column or bed. A sample component undergoes an equilibrium distribution between these two phases. This equilibrium in turn decides the velocity with which each component migrates on column. The band-broadening and dispersion of each component in the direction of migration also occurs. Thus differential migration and band-broadening decide the extent of separation of the sample.

The classes of chromatography are:

(i) **Adsorption chromatography**: This method is based on exploitation of the difference in adsorptivity of solute to the stationary support which is usually packed in a column e.g. various fatty acids can be separated by adsorption chromatography.

(ii) **Partition chromatography**: includes chromatographic techniques such as liquid-liquid chromatography (LLC), paper chromatography (PC) thin-layer chromatography (TLC), gas-liquid chromatography (GLC) and reversed – phase chromatography (RPC). Here, we explore the difference in the partition coefficient or distribution ratio of individual species in the mobile and stationary phase. Some partition chromatography techniques like PC and TLC use plates while others use columns.

(iii) **Ion exchange chromatography**: This method is based on differences in the exchange potential between various ion exchange resin packed in a column. Examples are CEC, AEC, IE and Liquid Exchanger (LE).

(iv) **Exclusion chromatography**: This is based fundamentally upon exploitation of the difference in size or molecular geometry of the components. In gel permeation, small constituents are retained in inter shell spaces or pores while large size components emerge first. Examples include gel permeation (GP), ion exclusion and molecular sieve chromatography.

(v) **Electro Chromatography**: Methods under this category are often classified as electrophoretic techniques. In such separations, the difference in mobility of different ions when an external potential is applied. Examples include zone electrophoresis, boundary layer electrophoresis, curtain chromatography and capillary electrophoresis of all the chromatographic techniques available, GC and HPLC are used more often for routine analysis of environmental samples.

5.3.1 The use of Gas Chromatography (GC) in Analysis

With GC, it is possible to separate a very complex mixture containing up to 200 or more related compounds, using either partition or adsorption, with very small sample sizes. It is similar to liquid-liquid chromatography except that the mobile liquid phase is replaced by a moving gas phase. The stationary phase may be solid or liquid.

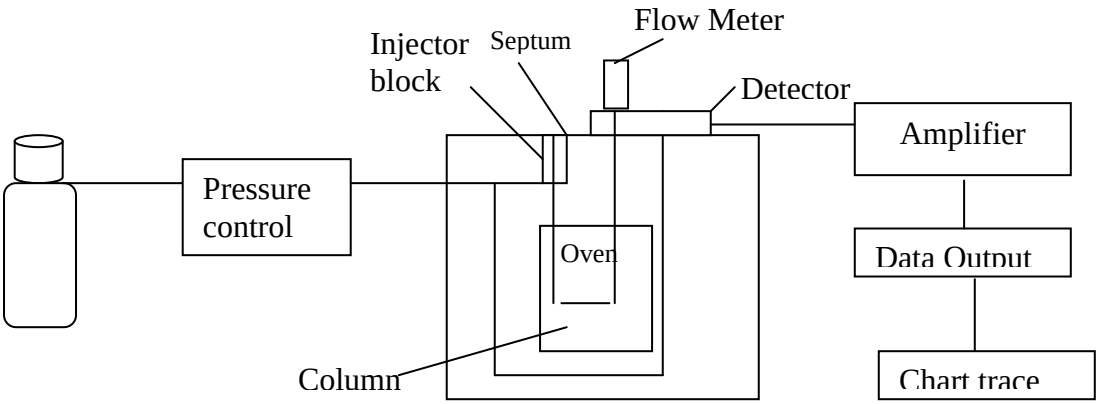

Fig. 8: Diagram of a Gas chromatograph
Source: D. Harvey, 2000 (Modified)

The sample for GC analysis must be able to exist in the gas phase, so it may be applied to volatile materials only. Thus, non-polar substances are easier to handle than polar materials; ionic materials cannot pass through a GC. For polar substances like alcohols, amines, free fatty acids and phenols, derivatization may be required.

$$\underset{\text{Phenol}}{Ph - OH} + \underset{\text{Trimethylsilyl chloride}}{Cl - SiMe_3} \longrightarrow \underset{\text{Phenyltrimethylsily ether}}{Ph - O - SiMe_z} + HCl$$

The carrier gas, from a high-pressure cylinder is helium, nitrogen, hydrogen or argon. The choice depends on factors such as availability, purity, consumption and type of detector.

Until recently, GC analysis was handled using packed columns in which the stationary phase is a liquid that has been coated on an inert granular solid called the **column packing** (held in a borosilicate glass tubing). More recently, however, the borosilicate glass tubing packed columns are being replaced by fused silica or quartz capillary columns. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven and detector is

maintained. Stationary phase material and concentration, column length and diameter, oven temperature, carrier gas flows and detector type are the control variables.

Sample solution is usually introduced using a microsyringe with hypodermic needle inserted through a self-sealing silicone rubber septum. The sample is smoothing injected into a heated metal block at the head of the column. Modes of placing samples onto the column can be by **split injection** or **splitless injection**. Manipulation of the syringe is an art developed with practice, and the aim is to introduce the sample in a reproducible manner. The temperature of the sample port should be such that the liquid is rapidly vaporised without either decomposing or fractionating the sample. A useful rule of the thumb is to set the sample port temperature approximately to the boiling point of the least volatile component. For greatest efficiency, the smallest possible sample size (1-10 μL) consistent with detector sensitivity should be used.

In GC sample analysis, interferences may arise from contamination of samples, chromatograph improper functioning and countermeasures that may manifest inform of septum bleed, column bleed and ghost peaks manifestation.

Gas Chromatograph Detectors

The function of a GC detector is to sense and measure the small amounts of the separated components present in the carrier gas leaving the column. The choice of a detector will depend on factors such as the concentration level to be measured, the nature of the separated components and the properties of the detector e.g. high sensitivity, good linearity, stability and response.

a) **Hot-wire detector (HWD)**: This is also known as the **thermal conductivity detector** (TCD) or **katherometer.** It is the oldest GC detector. Due to its inherently large volume, low sensitivity and contamination problems, it was long dismissed as unsuitable for capillary systems. It is universal in its applications.

b) **Electron capture detector (ECD)**: This usually used for the analysis of compounds that have high electron affinities such as chlorinated pesticides, drugs and their metabolites. This detector is somewhat selective in its response, being highly sensitive towards molecules containing electronegative groups: halogens, perozisdes, quinines and intro groups. It is insensitive towards such functional groups as amines, alcohols, and hydrocarbon

c) **Flame ionization detector (FID)**: This more or less universal detector is widely used because of its high sensitivity to organic carbon-containing compounds. It is perhaps the most widely used detector for GC. Its advantages include:

(i) it responds to virtually all organic compounds with high level of resolution;
(ii) it is resistant to common carrier gas impurities such as resistant to common carrier gas impurities such as water and carbon;
(iii) it has a large linear responds range and excellent baseline stability;
(iv) it is relatively insensitive to small column flow-rate fluctuations during temperature programming;
(v) it is highly reliable, rugged and easy to use; and
(vi) it has low detector dead-volume effects and fast response.

Its two major limitations are:
(i) it gives little or no response to non-combustible gases and all nobles gases; and
(ii) it is a destructive detector that changes both the physical and chemical properties of samples analyzed irreversibly.

d) **Photoionization detector (PID)**: Photoionization occurs when a molecular species dissociates into a parent ion and an electron upon interaction with UV light.

$$M \xrightarrow{uv} M^+ + e^-$$

The PID detects organic and some inorganic species in the effluent of a gas chromatograph with a detection limit as low as the pictogram range. The PID has a high sensitivity, low noise and an excellent linearity. It is non-destructive and can be used in series with a second detector for more selective detection. PID can be operated as a universal or selective detector by simply manipulating the photon energy of the ionization source.

e) **Mass spectrometer (MS)**: Mass spectrometers can serve as detectors when coupled to a GC. The MS combines the ability to detect a wide variety of compounds with the capability of deducing compound structures from fragmentation patterns or mass spectra. The computer (for recording) contains and can search a library of known mass spectra to identify tentatively an unknown compounds are used for confirmation after tentative identifications are made.

f) **Fourier Transform Infrared Spectrometers (FT-IR)**: Like the MS, FT-IR is also a
independent instrument which can be coupled to a GC to serve as a detector.

g) **Thermionic detector**: This particularly responds to compounds containing nitrogen or phosphorus

4.4 High-Performance Liquid Chromatography (HPLC)

Although GC is widely used, it is limited to samples that are thermally stable and easily volatilised. Non-volatile samples, such as peptides and carbohydrates, can be analysed by GC, but only after they have been made more volatile by a suitable chemical derivatisation. For this reason, the various techniques included within the general scope of liquid chromatography are among the most commonly used separation techniques.

In HPLC, a liquid sample, or a solid sample dissolved in a suitable solvent, is carried through a chromatographic column by a liquid mobile phase. Separation is determined by solute/stationary-phase interactions, including liquid-solid adsorption, liquid-liquid partitioning, ion exchange and size exclusion, and by solute/mobile-phase interactions. In each case, however, the basic instrumentation is essentially the same. An HPLC typically included two columns: the guard column and an analytical column. The guard column is an inexpensive column placed before the analytical column (a more expensive column), protecting it from contamination and damage, while the analytical column does the separation. In HPLC, the stationary phase is a liquid film coated on a packing material consisting of 3-10 μm porous silica particles.

Solvent proportioning valve

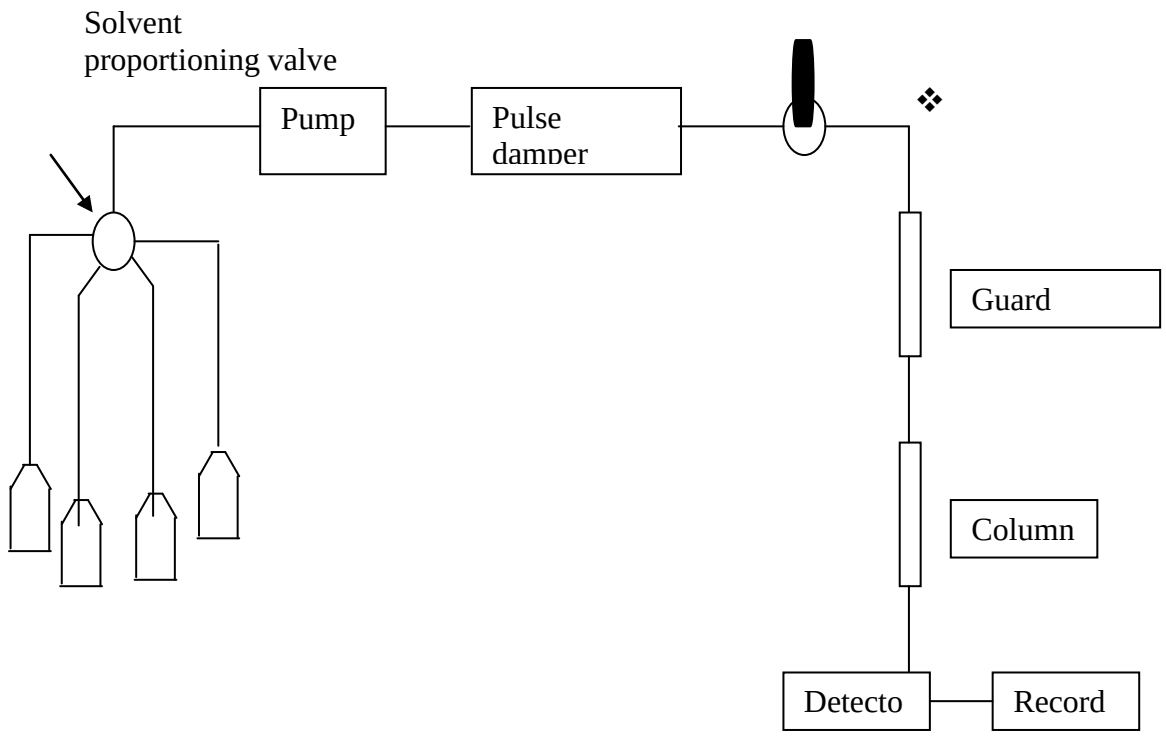

Fig. 9: Diagram of a high-performance liquid chromatograph
Source: D. Harvey, 2000 (modified)

The stationary phase may be partially soluble in the mobile phase, causing it to "bleed" from the column over time. To prevent this loss of stationary, it is covalently bonded to the silica particles by reacting the silica particles with an organochlorosilane ($Si(CH_3)_2$ RCl).

The elution order of solutes in HPLC is governed by polarity; the least polar solute spends less time in the polar stationary phase and is the first solute to elute from the column. Retention times in a normal-phase separation are controlled by selecting the mobile phase, with a less polar mobile phase leading to longer retention times. In a reverse-phase separation, however, the order of elution is reversed.

As with GC, numerous detectors have been developed for use in monitoring HPLC separations. To date, the most HPLC detectors are not unique to the method, but are either stand-alone instruments or modified versions of the same. The most popular ones are spectroscopic detectors (e.g. UV /visible absorption and fluorescence) and electrochemical detectors (such as amperometry, voltammetry, coulometry and conductivity based detectors). A refractive index detector is sometimes employed as a universal detector.

5.0 ACTIVITY

i. List some instrumental techniques suitable for the analysis of heavy/trace metals
ii. What are the advantages of (a) FAAS over GFAAS; (b) GFAAS over FAAS; (c) AAS over NAA; and (d) NAA over AAS?
iii. Explain the need of an inert gas to flush through the graphite furnace tube before vaporisation of an element is commenced in GFAAS analysis.
iv. List five detectors that are used in GC analysis.
v. With reasons, state the detectors you would adopt in carrying out (a) GC analysis of the following: Peptides, (b) Chlordane, (c) Gaseous hydrocarbons, (d) Mercaptans, (e) Carbohydrates.
vi. List three advantages and two disadvantages of flame ionization detector (FID) as a GC detector.

6.0 SUMMARY

In this unit, you have learnt that:

- Levels of heavy metals in a sample can be profiled by such instrumental techniques as AAS (FAAS and GFAAS), NAA, EDXRF and ICP-MS.
- Chromatographic techniques are well suited for the analysis of organic compounds in particular.

7.0 ASSIGNMENT

1. Briefly explain the following modes of sample injection in a GC analysis: (a) Split injection, (b) Split less injection.
2. With respect to interferences in GC analysis, explain the following: (a)Septum bleed, (b) Column bleed and (c) Ghost peaks.

8.0 REFERENCES

Mendham, J., Denney, R., Barnes, J. & Thomas, M. (2004) *VOGEL'S Textbook of Quantitative Chemical Analysis*, 6th ed. Delhi, India: Pearson Education Ltd.

Harris, D. (1999). *Quantitative Chemical Analysis*. 5th ed. New York: W.H. Freeman and Company.

Khopkar, S. (2008). *Basic Concepts of Analytical Chemistry*. New Delhi: New Age International Publishers.

Braun, R. (2000). *Introduction to Chemical Analysis.* London: McGraw-Hill Int. Editions.

Harvey, D. (2000). *Modern Analytical Chemistry*. USA: McGraw-Hill Companies Inc.