CHAPTER 1

INTRODUCTION

1.1 Flow Injection Analysis (FIA)

1.1.1 General and Principles

There are two general types of continuous-flow analysis (CFA) , segmented and unsegmented. Segmented-flow analysis (SFA) was first described by Skeggs in 1957 [1]. The sample is injected into a flowing reagent stream and air bubbles are used to break-up sample-reagent mixture into separate compartments, and time is allowed for equilibrium to be reached in each compartment. The air bubbles are usually removed before they reach the detector cell.

Unsegmented-flow analysis techniques, reported for the first time by Ruzicka and Hansen in 1975 [2], are now referred to as flow injection analysis (FIA) and differ from segmented-flow analysis in that the flow is not segmented by air bubbles. The sample is injected as a plug into the reagent stream in a reproducible manner, then the sample zone disperses and reacts with the components of the reagent stream. The reaction product is sensed by a flow-through detector (such as pH, conductivity, absorbance, fluorescence, luminescence, electrode potential) and recorded. Although reaction is not necessary to reach equilibrium, the extent of reaction is the same for both samples and standards. The simplest flow injection analysis is shown in Figure 1.1. A typical recorded output has the form of peak, the height H, width W, or area A of which is related to the concentration of the analyte.

So FIA is based on a combination of three principles : (1) sample injection (2) reproducible timing of its movement from the injection point toward and into the detector and (3) controlled dispersion of the injection sample zone.

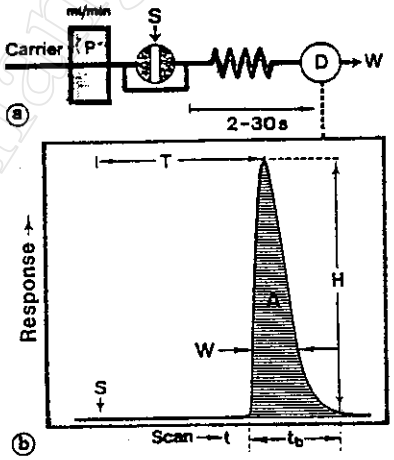

Figure 1.1 (a) The simplest single-line FIA manifold utilizing a carrier stream of reagent ; S : the injection port, D : the flow cell and W : waste. (b) The analog output has the form of a peak, the recording starting at S (time of injection to); H : the peak height, W : the peak width at a selected level, A : the peak area, T : the residence time corresponding to the peak height measurement, and t_b : the peak width at the baseline. [4]

In FIA, the sample zone is subjected to some degree of mixing or dilution with the carrier, and this is expressed in terms of the dispersion, D, which is defined by : (Figure 1.2)

$$D = C^0/C^{max} = const.H^0/H \qquad (1.1)$$

Where C^0 is the original concentration of the injection sample. C^{max} is the maximum concentration of the sample zone after it has undergone all the dispersion processes and is passing through the detector. H is the peak height recorded for the sample zone as it passes through the detector. And H^0 is the peak height corresponding to an undispersed sample zone.

The effects of the variables i.e. flow rate, sample size and tube length upon dispersion in an FIA system are shown in Figure 1.3.

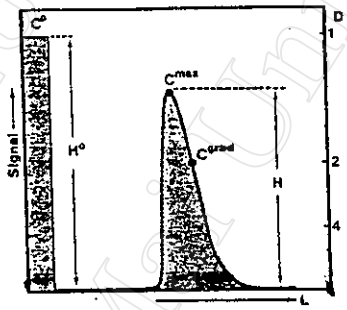

Figure 1.2 Dispersion, D in the system defined as the ratio between the original concentration, C^0 and the concentration of the dispersed specie, C^{max}. [3]

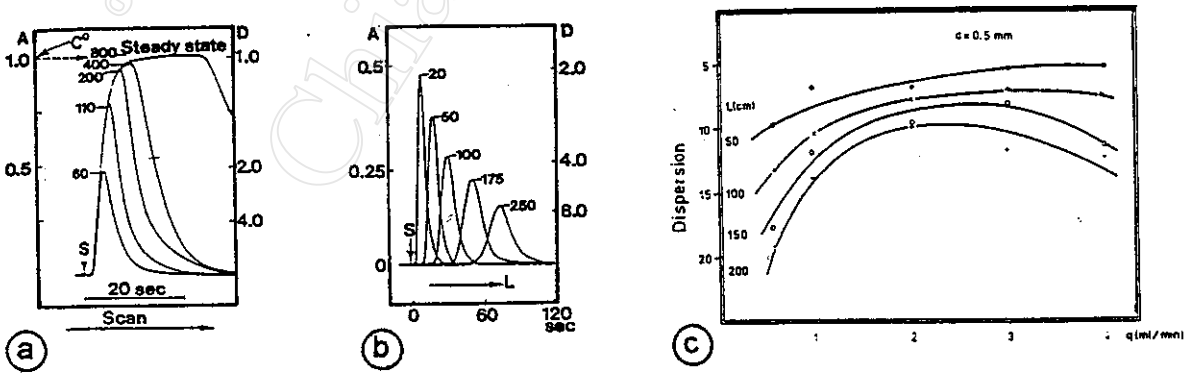

Figure 1.3 Response curves upon dispersion as function of (a) injection sample volume, with sample volumes of 60, 110, 200, 400, and 800 µl, (b) the tube length; L [4] is given in centimeters and (c) flow rate at various reactor lengths with a constant tube diameter [1].

Dispersion is classified as :

1. Limited dispersion (D = 1-3) : An FIA system designed for using this range of dispersion is for a sample being presented to the detector without reaction e.g. in FIA-AAS, FIA-pH measurement. Smaller sample size and greater sample throughput advantage.
2. Medium dispersion (D = 3-10) : It is used in most FIA systems which chemical reaction is required. Peak height decreases as dispersion increases.
3. Large dispersion (D ≥ 10) : When using a long tubing or a mixing chamber between the points of injection and detection, resulting peaks will be very broad. Such a system is useful for flow injection titration.

1.1.2 Basic Components of an FIA System

Basic components for a simple FIA (Figure 1.4) consist of :

1. A propelling system forcing the carrier stream through the different elementary units in a perfectly reproducible, pulse-free, constant and regular flow. This function can be performed by a peristaltic pump, aquarium air pump [5], a gas-pressure system or even gravitation.
2. An injection system for introducing accurate, reproducible and variable sample volume into the carrier stream. Syringe injection and valve injection could be used.
3. A transport system of reaction zone to interconnect the different elements and accomplish the desired extent of mixing or dispersion of the sample in the carrier stream as they flow along the system. There are straight tube, coiled tube, mixing chamber, glass bead column and knitted reactor.
4. A detection system for continuous monitoring of the carrier stream in order to provide qualitative and quantitative information. In general, detectors are designed for use in colorimetric, electrochemical and AAS/ICP-OES techniques.
5. A recorder is for the output from the detector as a peak by means of a chart recorder, a microprocessor, a computer or a microcomputer.

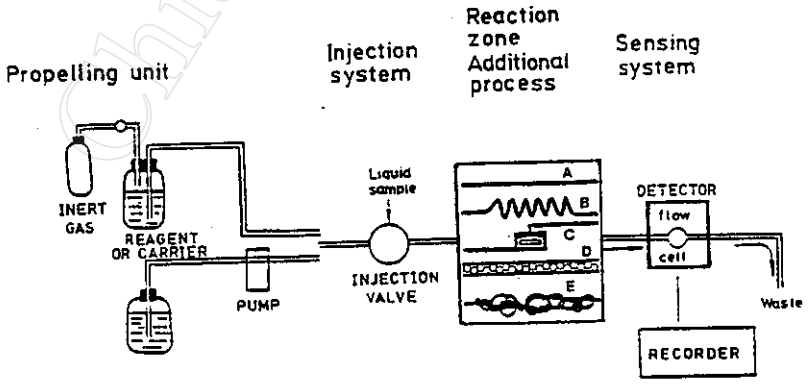

Figure 1.4 General arrangement of an FIA system, showing its essential components : propelling unit (peristaltic pump or gas-pressure unit), injection system, reaction zone (A : straight open tube, B : coiled tube, C : mixing chamber, D : single-bead string reactor and E : knitted reactor). Adopted from Vancarcel and Luque de Castro [1] and Ruzicka and Hansen [4].

1.2 Phosphorus/Phosphate [6,7]

Phosphorus (P) in the elemental form is particularly toxic and is subjected to bioaccumulation in much the same way as mercury. Phosphorus occurs in natural waters and in waste waters almost solely as phosphates that are one of the major nutrients required for plant and is essential for life. In excess of a critical concentration, phosphates stimulate plant growth. Phosphorus in various physico-chemical forms is used as a measure of water quality in waste water and sewage treatment plants because it is known to be a limiting nutrient for the growth of algae and aquatic plant and hence is implicated in a condition of accelerated eutrophication or aging of waters. However, phosphorus is not reported to be toxic to men, animals or fish. The major operationally defined forms of phosphorus are :

a). TP (total phosphorus), which can be considered to be the maximum potentially biologically available P. This includes particulate, colloidal and dissolved forms.

b). TDP (total dissolved phosphorus), which is the fraction that will pass through a 0.45 μm filtration membrane. This includes colloidal material which is less than 0.45 μm in diameter. TDP can further classified into a number of fractions as shown in Figure 1.5.

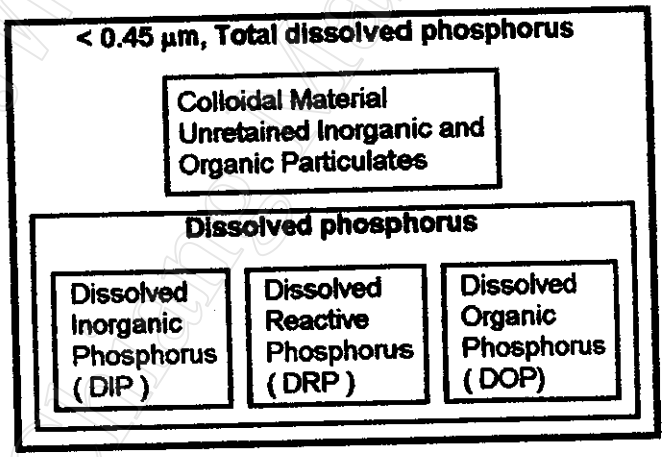

Figure 1.5 Representation of the operationally defined components of total dissolved phosphorus. [7]

Dissolved inorganic phosphorus (DIP) consists of orthophosphates (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$) and condensed phosphate (pyro-, meta- and other polyphosphate). Small amounts of certain condensed phosphates are added to some water supplies during treatment and larger quantities may be a major component of synthetic detergents. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm runoff and to a lesser extent with melting snow.

Dissolved organic phosphorus (DOP) components in natural waters are mostly the products of biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota.

Dissolved reactive phosphorus (DRP) is operationally defined as that fraction that is readily detected without the need for digestion or hydrolysis. It consists mostly of orthophosphates, as well as some condensed and organic P that are readily hydrolysed during detection.

In flowing water, there are two basic needs that must be met in establishing a phosphorus criterion : (1) to control the development of plant nuisances and, in turn, to control and prevent animal pests that may become associated with such plants and (2) to protect the downstream receiving waterway, regardless of its proximity in linear distance.

Phosphorus, in the form of organic or inorganic phosphate, is an important and widely distributed element in the human body. The adult human body contains between 500 and 700 g of phosphorus, of which about 85% is in the skeleton and the rest is located intracellularly in the soft tissues. Adult serum contains approximately 2.5-4.5 mg/l (0.81-1.45 mmol/l) of inorganic phosphate in the forms of monovalent and divalent phosphate anions ($H_2PO_4^-$, HPO_4^{2-}) [8].

Phosphorus analyses embody two general procedural steps : (I) conversion of the phosphorus form of interest to dissolved orthophosphate, and (2) quantitative of the orthophosphate formed that selected for interpretive purpose.

1.2.1 Spectrophotometry [9]

Most of the commonly used methods for the determination of phosphate are based on spectrophotometric measurement of the reactions of heteropoly yellow (molybdophosphoric acid reacts with vanadium, absorption at 400-490 nm) or heteropoly blue (molybdophosphoric acid reduced by ascorbic acid or stannous chloride, absorption at 690 nm) as following :

$$H_3PO_4 + 12H_2MoO_4 \longrightarrow H_3P(Mo_{12}O_{40}) + 12H_2O \qquad (1.2)$$

$$Mo(VI) \xrightarrow{\text{reduction}} Mo(V) \qquad (1.3)$$

Another group of methods is based on the ion-association complexed formed between molybdophosphate and various organic basic dyestuffs such as Malachite Green [10], Crystal Violet [11], etc.

1.2.2 FIA Method

Several FIA systems based on the aforementioned methods have also been developed. The spectrophotometric determination of phosphate by FIA based on the formation of molybdophosphate heteropoly acid has been widely studied [12-16]. Fluorescence quenching-FI is also reported by using ion association compound that is highly sensitive because of visible-light absorption and fluorescence quenching of the dye. In ion association type or ternary complex, the metal ion reacts with ligand to produce a charged binary complex which then forms an ion association complex with a second ligand of opposite charge, usually dyestuff. Of these, the determination of phosphate by fluorescence quenching-FI with Malachite Green (MG) [17] , Rhodamine 6G [18] or Rhodamine B (RB) [19] (Figure 1.6) is very sensitive. The example of ion associate formation of 1:3 complex [19] of molybdophosphate with RB is represented by the equations [20] :

$$PO_4^{3-} + 12(MoO_3) + 3RB \longrightarrow RB_3(PMo_{12}O_{40}) \qquad (1.4)$$

$$nRB_3\,(PMo_{12}O_{40}) \longrightarrow [RB_3(PMo_{12}O_{40})]_n \longrightarrow \text{precipitate} \qquad (1.5)$$

which excitation and emission wavelengths are 560 and 580 nm, respectively.

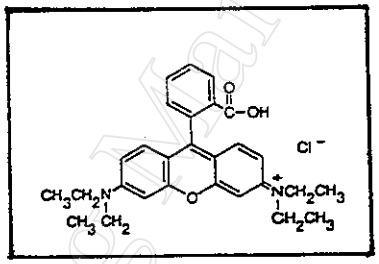

Figure 1.6 Chemical structure of Rhodamine B [21].

1.3 Nitrates and Nitrites [6,22,23]

Nitrogen levels in aquatic systems, as with phosphorus, are intimately linked with excessive algal growth. Two gases (molecular nitrogen and nitrous oxide) and five forms of nongaseous, combined nitrogen (amino and amide groups, ammonium, nitrite and nitrate) are important in the nitrogen cycle. Total nitrogen levels in waters can vary from as low as 0.1 mg/l to in excess of 10 mg/l in heavily polluted rivers.

Nitrogen species: Inorganic nitrogen species are chemically well characterized whilst organic nitrogen includes a number of naturally occurring compounds such as urea, proteins, peptides and nucleic acids in addition to numerous synthetic organic substances. Functionally , organic nitrogen is defined as organically bound nitrogen in the -3 oxidation states and thus, does not include all organic nitrogen compounds. Other operationally defined nitrogen fractions (Figure 1.7) include total dissolved nitrogen (TDN), dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN = nitrate + nitrite + ammonia). DON dominates the flux of total nitrogen from land to sea , generally making up to 60 %

of total export. It usually measured as the difference between TDN and DIN (i.e., DON=TDN-DIN).

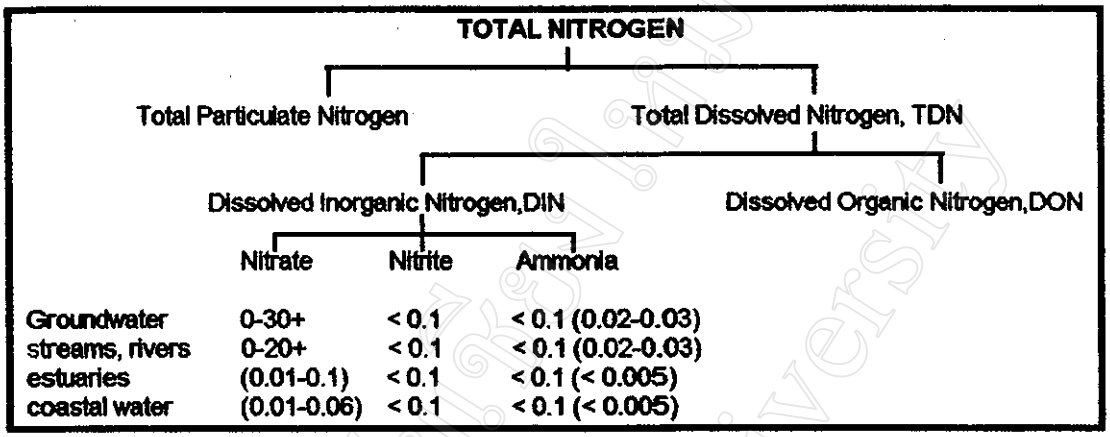

Figure 1.7 Nitrogen speciation in natural waters. Concentrations are expressed as mg nitrogen per litre. Values are quoted as ranges typically encounted in a variety of waters. The values in brackets represent indicative values at or above which problems have been known to occur, depending on a range of other factors.[22]

The forms of nitrogen of greatest interest in water are nitrate, nitrite, ammonia and organic nitrogen. These forms are all interconvertible with each other and with molecular nitrogen in biological process that can be shown in Figure 1.8.

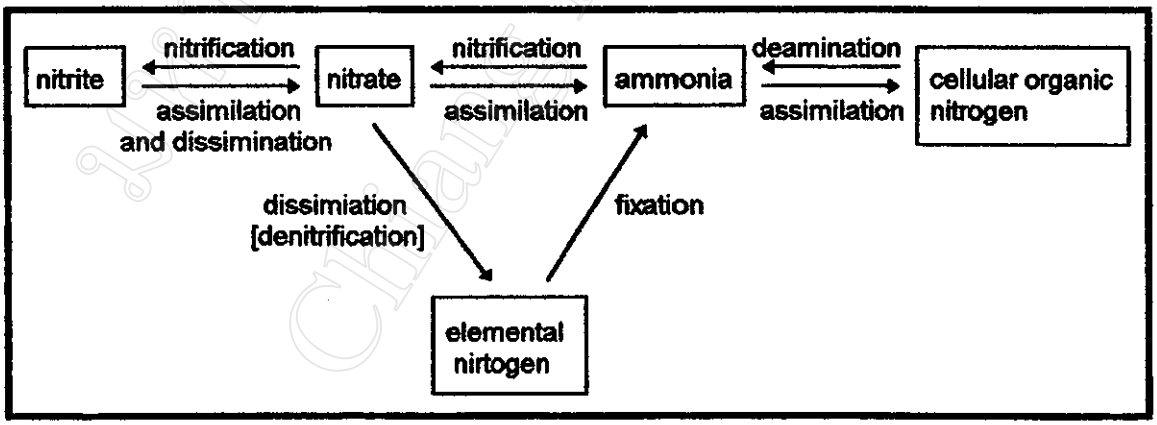

Figure 1.8 Main biological process involving nitrogen.[24]

The biological process in based on the following reactions :

$$\text{protein (organic N)} + \text{bacteria} \xrightarrow[\text{either aerobic or anaerobic}]{\text{saprophytic}} NH_3 \qquad (1.6)$$

$$2NH_3+3O_2 \xrightarrow[\text{aerobic}]{\text{Nitrosomonas}} 2NO^-_2 + 2H^+ + 2H_2O \quad (1.7)$$

$$2NO^-_2 + O_2 \xrightarrow{\text{Nitrobacter}} 2NO^-_3 \quad (1.8)$$

Sources of nitrogen : The cellular organic nitrogens (the amino and amide groups) are found in soil organic matter and as constituents of plant and animal protein. The ammonia (or ammonium ion) is either released from proteinaceous organic matter and urea, or is synthesized in industrial processes involving atmospheric nitrogen fixation. The nitrite ion formed from the nitrate or the ammonium ions by certain microorganisms found in soil, water , sewage and the digestive tract. The nitrate ion is formed by the complete oxidation of ammonium ions by soil or water microorganism; nitrite is an intermediate product of this nitrification process. In oxygenated natural water systems nitrite is rapidly oxidized to nitrate. Growing plants assimilate nitrate or ammonium ions and convert them to protein. A process known as denitrification takes place when nitrate-containing soils become anerobic and the conversion to nitrite, molecular nitrogen, or nitrous oxide occurs.

Nitrogen effects : Nitrate in drinking water is associated with a blood disorder in infants,under 3 months of age, called methemoglonemia. Development of this illness comes about by bacterial conversion of the relatively innocuous nitrate ion to nitrite in the gastrointestinal in the blood, to methemoglobin that cannot transport oxygen. This serious and occasionally fatal poisonings have occurred following ingestion of untreated well waters shown to contain nitrate at concentrations greater than 10 mg/l nitrate nitrogen. Large amounts of nitrates are also injurious to the dyeing of wool and silk and are undesirable in fermentation processes.

Nitrite is unstable in the presence of oxygen and is , therefore , absent or present in only minute quantities in most natural waters under aerobic condition. Nitrite in water is sometimes an indication of organic pollution. Recommended tolerances of nitrite in domestic water supplies differ widely. A generally accepted limit is 2 mg/l, but as little as 0.1 mg/l. Nitrite is undesirable in water used in dyeing wool and silk and brewing.

Selected methods for the determination of nitrite and nitrate include :

1.3.1 Colorimetric Method [9]

Usually the determination of nitrite is based on the Griess reaction : the diazotization of nitrite ion with sulfanilamide in acidic medium, followed which the values by reaction with N-(1-naphthyl)-ethylenediamine (NED) , give an azo dye with a maximum absorption at 540 nm. The dye formation can be easily monitored spectrophotometrically. Nitrate can be determined using the same reaction by prior reduction to nitrite.

1.3.2 Ion Chromatographic Method [9]

A water sample is injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated on the basic of their relative affinities for a low capacity. The separated anions are directed onto a strongly acidic cation exchanger in continuously flowing strongly acid solution. In the suppressor the separated anions are converted to their highly conductive acid the carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

1.3.3 FIA Method

The concept of FIA has been applied successfully to the simultaneous determination of nitrite and nitrate in water by using various techniques. In the most of the procedures nitrate is reduced to nitrite with copperised cadmium column [25-32]. Then sulfanilamide is diazotized with nitrite and the product is coupled with NED to form a highly coloured azo dye,the absorbance of which is measured at 540 nm. Although, reduction by hydrazine [33] has been successfully applied as an alternative to Cd-Cu method with the advantage that less calibration steps are needed, Cd-Cu has faster reaction.

1.4 Chromium [6,34]

Chromium (Cr) is the 17th most abundant nongaseous element in the earth's crust. Chromium forms a series of colour species corresponding to the +II,+III and +VI oxidation states. Chromium(VI) exists only as oxy species such as CrO_3,(CrO_4^{2-}) and ($Cr_2O_7^{2-}$) and is strongly oxidizing. Chromium(V) and (IV) exist in transient states only to disproportionate to Cr(III) and Cr(VI). A fair numbers of chromium(II) compounds are known, all of which are strong and rapid reducing agents. Chromium(III) forms large numbers of kinetically inert complexes. Although chromium has oxidation states ranging from Cr(II) to Cr(VI) the trivalent form is found most commonly in nature. In spectrophotometric analysis, chromic (Cr(III)), chromate(CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions are important. Chromic hydroxide ($Cr(OH)_2(H_2O)_4^{+}$), which precipitates at pH ~ 5 ,is amphoteric, dissolving in alkali (pH~13). Chromium(III) forms stable oxalate, tartrate and EDTA complexes.

Chromium dissolved in natural waters is present in two different oxidation states ; +III and + VI. Few of any water contain chromium form natural sources. Hexavalent chromium salts are used in metal pickling and plating , anodizing aluminum , and in the manufacture of paints, dyes, explosives , ceramics , paper and many other substances. Trivalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industries , and in photography. Chromium is a corrosion inhibitor and may be present in treated cooling waters. The some industrially important inorganic chromium compounds are listed in Table 1.1 waste products from many of these activities may contain chromium.

Table 1.1 Some industrially important chromium compounds [35]

Formular	Industrial use
$Cr(CH_3COO)_3$	tanning leather, catalyst
$CrBr_3$	in catalysts for polymerization of polymers
Cr_2O_3	pigment, latex paints, catalyst, dyeing polymers
CrO_2	high energy magnetic tapes
CrO_3	corrosion inhibitor, oxidant, catalyst, plating metals
$BaCrO_4$	anticorrosive pigment
$CaCrO_4$	corrosion inhibitor, depolarizer in batteries
$CuCrO_4$	in fungicides, seed protectants, wood preservation
$K_2Cr_2O_4$	tanning leather, dyeing, painting, corrosion inhibitor, oxidizer
$PbCrO_4$	pigment
$ZnCrO_4$	in anticorrosive pigment

The U.S. Public Health Service Drinking Water Standard (USPHS,1962) states the concentration of hexavalent chromium shall not exceed 0.05 mg/l in drinking water on carriers subject to Federal quarantine requlations ; no limit is given for the trivalent form. Chromium is not acutely toxic to human [34]. This is due to the high stability of natural chromium complexes in abiotic matrices. However, Cr(VI) is more toxic than Cr(III) because of its high rate of adsorption through intestinal tracts. In the natural environment, Cr(VI) is likely to be reduced to Cr(III), thereby reducing the toxic impact of chromium discharges. The toxicity of chromium salts to aquatic life differs widely with the species ,temperature, pH, valence of chromium and other factors.

Selected methods for the determination of chromium include :

1.4.1 Diphenylcarbazide Method [9,36,41]

This method determines only the hexavalent chromium(Cr(VI)) in solution. Diphenylcarbazide(sym-diphenylcarbazide or diphenylcarbohydrazide) reacts in acid medium with chromium (VI) ions to give red-violet solutions that absorbs light at 540 nm which is the basic of this sensitive method. For the determination of total chromium, all the chromium is converted to hexavalent state by oxidation with an oxidant such as : $KMnO_4$,$(NH_4)_2S_2O_8$ in the presence of silver ions, perchloric acid, bromine ,silver (II) oxide , sodium peroxides, cerium (IV) [37-40] or sodium bismuthate [41] and determined with diphenylcarbazide.

1.4.2 Chromate Method [41]

The spectrophotometric method for the determination of chromium ,based on the colour of $Cr_2O_7^{2-}$ or CrO_4^{2-} ions , is a good example of a precise but rather insensitive method. It may be based either on the yellow colour of chromate (CrO_4^{2-}) ions present in alkaline solution , or on the orange colour of dichromate ($Cr_2O_7^{2-}$) ions , formed from CrO_4^{2-} ions by acidification of the solution. The absorption spectra of dichromate and chromate shows in Figure 1.9 . If chromium is present as Cr(III) , it must first be oxidized to Cr(VI). This method has been used for

determining chromium in steel ,aluminium and bauxites and the raw material used in match production.

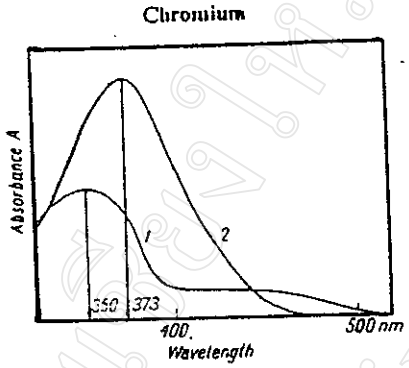

Figure 1.9 Absorption spectra of (1) dichromate (in M H_2SO_4) and (2) chromate (in ammonical medium). [41]

1.4.3 Atomic Absorption Method-Chelation Extraction [36]

The chromium is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the atomic absorption spectrophotometer. A number of papers have described specific analytical procedures for the speciation of chromium ions using atomic absorption and atomic emission spectroscopy [42-44].

1.4.4 FIA Method

Flow injection (FI) procedures for the sequential spectrophotometric determination of Cr(III) and Cr(VI) using 1,5-diphenylcarbazide (DPC) have been recently reported [45-48]. Sperling et al [49] reported , the differential determination of Cr(III) and Cr(VI) in natural waters. In this method, Cr(VI) is preconcentrated selectively on a C18 bonded silica column using sodium diethyldithiocarbamate (NaDDTC) as the chelating agent and detection by electrothermal atomic absorption spectrometry. However, recently, FIA systems comprising on-line ion-exchange has been applied to simultaneous determination of Cr(III) and Cr(VI). Milosavlojevic et al [50] used an ion-exchange column to simultaneous determination of Cr(VI) and Cr(III) by FIA-AAS with a chelating ion-exchange FIA system, whereas Cox et al [51] utilized a column of activated alumina and ICP-AES detection for simultaneous determination of Cr(III) and Cr(VI) in aqueous samples and Yoshimura [52] reported the application of ion-exchanger phase absorptiometry with DPC as coloring agent to direct determination of Cr(VI) in natural water using flow analysis.

1.5 Calcium [6,36]

Calcium is dissolved from practically all rocks but is usually found in greater quantities in water leaching deposits of limestone ($CaCO_3$), dolomite ($CaCO_3$. $MgCO_3$), gypsum ($CaSO_4.2H_2O$), or gypsiferous shale, water associated with granite or siliceous sand may contain less than 10 mg Ca/l. Water from limestone areas contains 30 to 100 mg/l, and water that traverses gypsiferous shale may contain several hundreds mg/l.

Calcium imports the property of hardness to water. Water hardness is caused by the polyvalent metallic ions dissolved in water. In fresh water these are principally calcium and magnesium although other metals such as iron, strontium, and manganese contribute to the extent that appreciable concentrations are present. Hardness is commonly reported as an equivalent concentration of calcium carbonate ($CaCO_3$).

The concept of hardness comes from water supply practice. It is measured by soap requirments for adequate lather formation and as an indicator of the rate of scale formation in hot water heaters and low pressure boilers. A commonly used classification is given in Table 1.2.

Table 1.2 Classification of water by hardness content. [6]

conc. mg/l $CaCO_3$	Description
0-75	soft
75-150	moderately hard
150-300	hard
300 and up	very hard

Natural sources of hardness principally are limestones which are dissolved by percolating rainwater made acid by dissolved carbon dioxide. Industrial and industrially related sources include the inorganic chemical industry and discharges from operating and abandoned mines.

Hardness in fresh water frequently is distinguished as carbonate and noncarbonate fractions. The carbonate fraction is chemically equivalent to the bicarbonates present in water. Since bicarbonates, generally are measured as alkalinity , the carbonate hardness usually is considered equal to the alkalinity.

Limits on hardness for industrial uses are quite variable. Table 1.3 lists maximum values that have been accepted by various industries as a source of raw water.

Table 1.3 Maximum hardness levels accepted by industry as a raw water source. [6]

Industry	Maximum Concentration mg/l as $CaCO_3$
Electric utilities	5,000
Textile	120
Pulp and paper	475
Chemical	1,000
Petroleum	900
Primary metals	1,000

However, hardness may provide protection by preventing dissolution of lead and cadmium from water pipes ; both these metals can produce high blood pressure, one of the precursors to heart attacks and some of the trace elements in hard water many provide protection such as lithium is thought to be beneficial in reducting anxiety.

Selected methods for the determination of calcium include :

1.5.1 Complexometric Method [36]

Disodiumdihydrogen ethylenediaminetetraacetate (Na_2EDTA) forms a slightly ionized colorless stable complex with calcium ions. Murexide (5,5'-Nitrilodibarbituric acid monoammonium salt) (Figure 1.10(a)) is dark purple in the absence of calcium but with calcium, it forms a light salmon-colored complex which has an ionization constant higher than the Na_2EDTA complex. Hence, by using murexide as an indicator, a solution containing calcium ions may be titrated with Na_2EDTA. The optimum pH of the titration is 10.4 or above. One of other dyes, Eriochrome black T (sodium 1-(1-hydroxy-2-naphthylazo)-b-nitro-2-naphthol-4-sulphonate) (Figure 1.10(b)) or calmagite (1-(hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid) (Figure 1.10(c)) may be added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0±0.1, the solution becomes wine red. If EDTA is added as a titrant,the calcium and magnesium will be complexed with Eriochrome black T at the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. This method is applied for the determination of total hardness. [9]

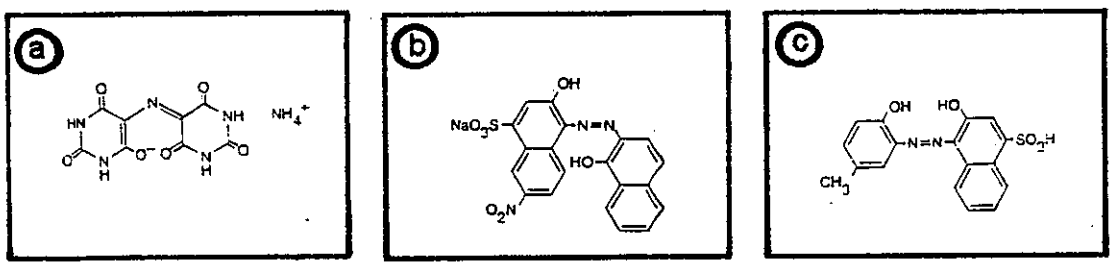

Figure 1.10 Chemical structure of (a) Murexide, (b) Eriochrome black T and (c) Calmagite. [21]

1.5.2 Atomic Absorption Method - Direct [9,36]

Calcium is determined by atomic absorption spectrophotometry. Lanthanum chloride is added to mask interferences.

Hardness can be calculated using the relationship :

Hardness, mg equivalent $CaCO_3$/l = 2.497[Ca,mg/l] + 4.118[Mg,mg/l]

1.5.3 FIA Method

Various color forming reagents have been proposed for the determination of calcium and hardness by FIA,e.g., Erichrome black T [53] ,Murexide [53-54], Chlorophosphonazo III [55], Calmagite[56] and o-cresolphthalein complexon (CPC) [57].

A method of Canete et.al.[53] was proposed for the simultaneous determination of calcium and sum of calcium and magnesium (hardness) in water by FIA. The procedure is based on FIA spectrophotometric titration. The chemical principle is based on conventional ones ,i.e., murexide-EDTA for calcium and Eriochrome black T-EDTA for the sum of calcium and magnesium. The manifold is shown in Figure 1.11.

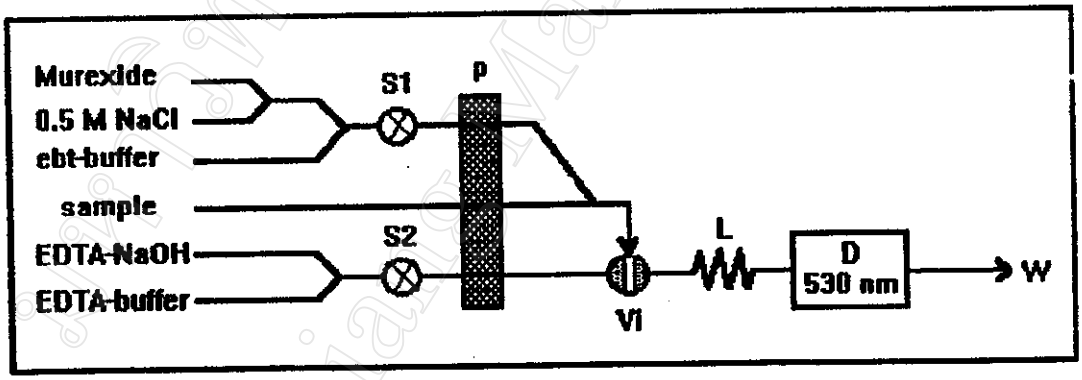

Figure 1.11 Manifold for the simultaneous determination of calcium and sum of calcium and magnesium (hardness) [53] ; ebt=Eriochrome black T, buffer = NH_4Cl/NH_3 buffer solution, Vi= injection valve, p=pump, L=reactor length , D= detector , W= waste , S1 and S2= selecting valves.

1.6 Aims of the Thesis

The aims of this research work are summarised as follows :

1. To develop flow injection analysis systems for the determination of phosphate, nitrite, nitrate, chromium and calcium.

2. To apply the procedures developed to determine of phosphate, nitrite, nitrate, chromium and calcium in water samples.