CHAPTER 2

Principle of Simultaneous Determination of Fluoride and Hydroxide by Flow Injection Analysis

2.1 Theory of flow injection analysis

Flow injection analysis (FIA) is an unsegmented continuous flow method based on an introduction of a liquid sample into a moving stream of another liquid along which it is dilute or dispersed and undergone chemical/separation processes prior to be continuously transported to a detector. Dispersion of the analyte or interesting species can be controlled through the geometry and fluid dynamics of the FI system. By the time the controlled dispersed zone is detected within a flow-through cell of a detector, the transient signals are obtained, at that point physical or chemical equilibrium has rarely been attained. Owing to the non-steady state employed in FIA the time between the injection point and the detector should be reproducible. The FIA method has briefly four important characteristics : non-segmented continuous flow, direct injection, partially controlled dispersion and reproducible run timing [1].

2.1.1 Flow injection system

A schematic diagram of the basic flow injection system which consists of four modules is shown in Figure 2.1.

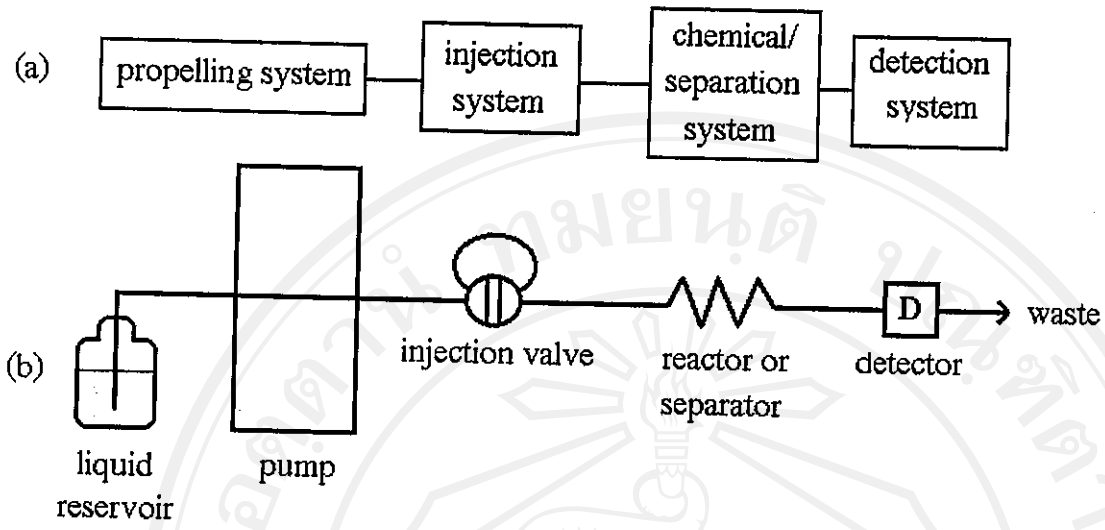

Figure 2.1 General scheme of a basic flow injection system; (a) block diagram and (b) basic manifold.

a. The propulsion system

The propulsion module has a function of propelling the liquid reagent or carrier at the constant flow rate into a system. The flow should be pulseless and reproducible to keep a dispersion and operational timing constant which are essential features in FIA. Because working pressure in the FI system is normally low compared to that in the HPLC system, the simple and inexpensive devices can be applied to assemble the FI manifolds. A common type of the propulsion unit is a peristaltic pump which has several channels (commonly four channels) that are suitable for the general routine FI work. The flow rate is varied by changing a diameter of the pump tube or changing the pump's roller speed. Other types of the pumps such as a syring pump can be used but not be widespread due to its high cost.

b. The sample introduction unit

The main function of the injection system is to introduce a well-defined zone of sample or reagent into the moving carrier stream without disturbance of the flow. The injection volume should be accurately and reproducibly measured, and be varied in an easy manner. The widely used insertion unit is a low pressure six-port valve which has low cost, ease of operation and rapidity.

c. The transport-reaction system

Chemical manipulation plays an significant role in the transport-reaction unit, converting an analyte into a detectable form, which can be 1) a mixing reactor 2) a packed reactor or solid phase minicolumn or 3) a separation unit. The mixing reactor is the most common device in this module and usually a small bore tube of inner diameter between 0.3-0.8 mm with various designs, as illustrated in Figure 2.2, to controll the dispersion.

d. The detection system (including data acquisition module)

An appropriate detector senses the detectable controlled dispersed plug from the transport-reaction system and record the absorbance, potential or other parameters which is proportional to the analyte concentration. Both optical and electrochemical detectors are widespread utilized in FIA. A flow-through cell is only conducted in a nondestructive detector such as a spectrophotometer and an ion selective electrode.

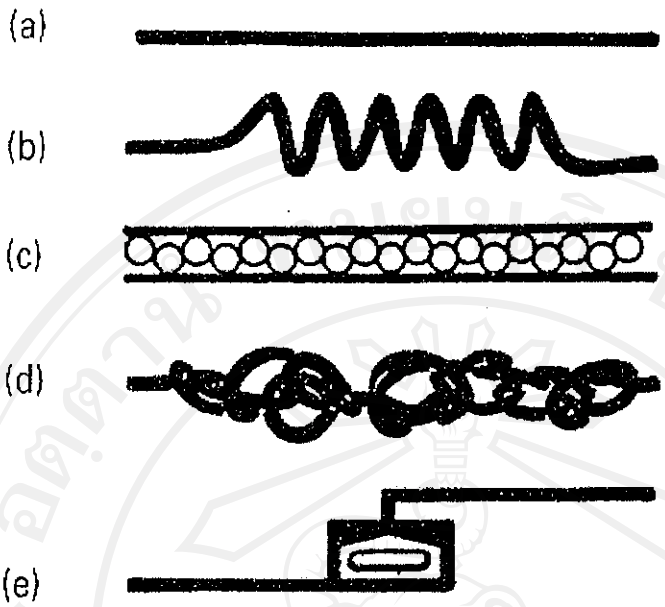

Figure 2.2 Reactor geometries. (a) Straight open tube; (b) coiled tube; (c) single bead string reactor; (d) knitted reactor; (e) mini-mixing chamber [1].

2.1.2 Dispersion in FIA

Dispersion is the most important physical phenomenon affecting the profile of the FIA signal although chemical reaction between the sample and regent concurrently occurs. It has hardly been reach a stead state but should be reproducible before the intermingling zone reaches a detector. Controlling the factors affecting the dispersion, namely 1) geometric configuration of the FI conduit, e.g. internal diameter and length of tubing, type of a mixing reactor, and 2) hydrodynamic conditions, e.g. flow rate, is the main key in FIA.

The crucial characteristics of dispersion in FIA are as followed:

1. Flow pattern in the FI channel is laminar. Dispersion in a narrow bore tubing, normally used in FIA, is depicted in Figure 2.3.
2. The dispersion in the most common FIA is convective-diffusional transport.
3. There are two types of dispersion, axial and radial (Figure 2.4), involving the FI peak.

Axial dispersion, or dilution in the direction of the flow, is dominant in a straight tube, causing more peak broadening than the another. Radial dispersion, as a result of a secondary flow pattern which circulates to the direction of the flow, provides well mixing with minimum dispersion and peak broadening. The more turns in the flow path, the more mixing efficiency caused by radial dispersion. Note that the reversal of the flow leads to the reversal of radial flow pattern (Figure 2.4). The knitted mixing tubing with many serpentines undoubtfully offers narrower peaks and greater sensitivity than the coiled reactor. Development of a new FIA methodology or modifying an existing one consequently requires the optimization of variables controlling the dispersion, for instance, liquid flow rate, injection volume, type of the mixing reactor, diameter and length of tubing.

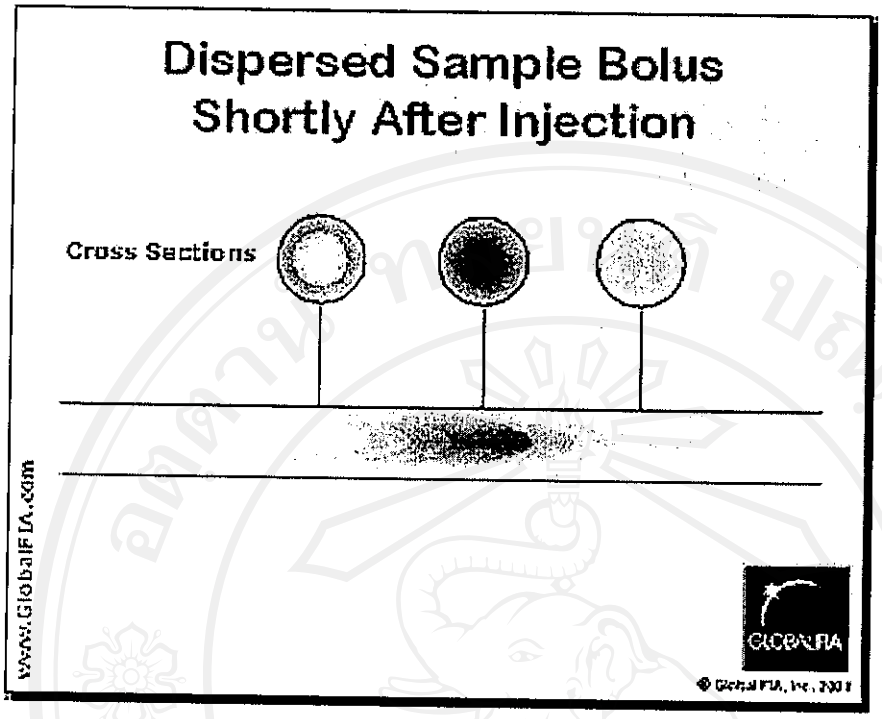

Figure 2.3 Dispersion in laminar flow [2].

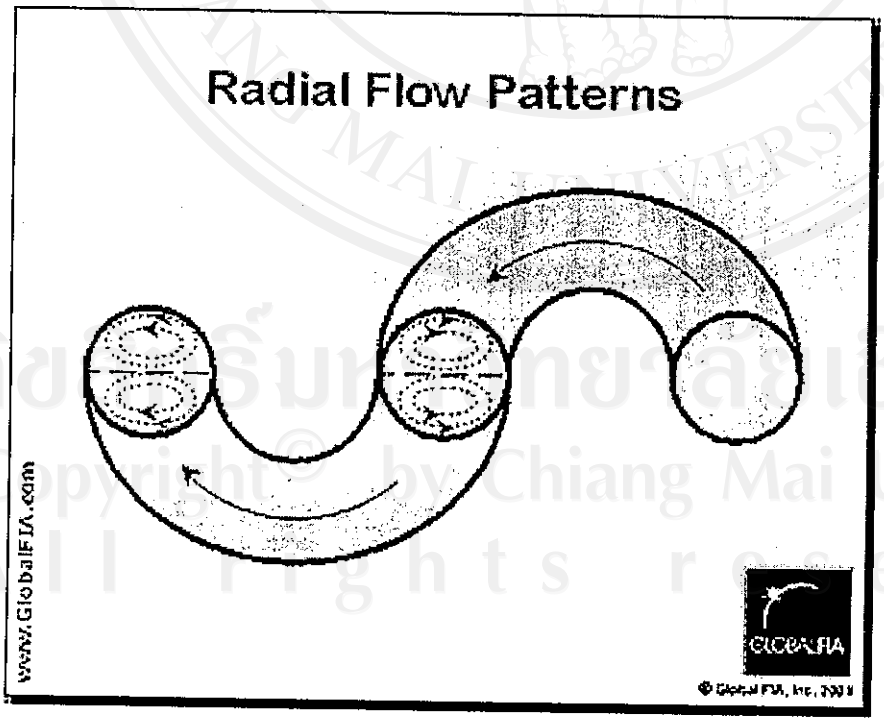

Figure 2.4 Radial flow pattern in FI manifold [2].

2.2 Spectrophotometric flow injection determination of fluoride

The analytical methods for fluoride have been extensively reviewed. Methodology for fluoride analysis in various matrices [3] including sample pretreatment and the measurement by an ion selective electrode, photometric methods, ion chromatography and atomic and molecular spectroscopy is summarized. Fluoride in biological materials is of particular interest due to its cariostatic effect and requirement of physiological indicators of human exposure to environmental fluoride. A review [4, 5] and "reaction paper" [6] are intensively discussed. Among the reviews published in the literature, development in the analysis of fluoride over the past two decades, followed the article of Venkateswarlu [7], are the outstanding series [8-12]. Database for flow injection determination of fluoride is additionally available online at http://www.fia.unf.edu or http://www.flowinjection.com.

Substantial systems, metal ions and organic complexing reagents, are proposed for fluoride quantification by spectrophotometry, classified as a classical technique. Zirconium is the most superior on account of its high formation constant for fluoride. Cerium, lanthanum and thorium are also well-recognized. Vast lists of organic reagents are proffered elsewhere [13, 14]. Details on the analysis by photometry, separation of fluoride from matrices and determination, are also provided in the books [15, 16].

Spectrophotometric determination of fluoride categorizes into two main bases according to an effect of fluoride on any species involving in the reaction.

2.2.1 An indirect method or substitution of a coloured complex with fluoride

Owing to fluoride seldom forms a coloured complex, almost all spectrophotometric measurements for fluoride are an in direct method in which displacement of organic ligands in a coloured metal complex by fluoride is principal. Bleaching of the coloured complexes of tri- or tetravalent cations such as Fe(III), Al(III), Ce(III), Th(IV) and Zr(IV) by fluoride results in the decrease in their absorbance. For example, a red complex of zirconium and SPADNS (sodium 2(*p*-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) in the standard SPADNS method [17] is broken down by fluoride to form a colourless fluorozirconium complex. The decrease in absorbance, monitored at 570 nm which is a maximum absorption wavelength of Zr-SPADNS depends on a fluoride amount contributing to the decolorization reaction.

2.2.2 A direct method or mixed ligand complex formation

Until now a few direct method, e.g. La(III)-alizarin complexone, has been reported. Fluoride and an organic reagent forms a coloured mixed complex with a metal ion. For instance, absorbance of Ce(III) or La(III) complex of alizarin complexone (1,2-dihydroxyanthraquinon-3-ylmethylamine-N,N-diacetic acid) increase with increasing of fluoride concentration as a result of formation of the metal-alizarin complexone - fluoride mixed complex.

The advantage of spectrophotometric determination of fluoride is its high sensitivity, nevertheless, it suffers from an interferent effect and a narrow dynamic range compared to another standard method, potentiometry. An appropriate separation

process normally overcomes the poor selectivity. In addition, it renders simplicity and rapidity with comparable accuracy and precision.

Despite many spectrophotometric methods for fluoride reported in the literature, application of flow injection analysis in this area is little published probably due to the two distinguished methods already carried out in FIA, no proper systems that free from the drawback of foreign ions and the incoming of the fluoride selective electrode. The extremely explored systems are of the zirconium complexes [18-20] or alizarine fluorine blue systems [21, 22]. However, development of a new flow injection method for fluoride by spectrophotometry is preferable to potentiometry because the former uses no special flow cell which is necessary for an ion selective electrode (ISE) in the latter. Moreover, it is uncomplicated to manage a single flow cell to concomitant determination of two anions, fluoride and hydroxide, rather than two flow cells and two ISEs (the pH electrode and F-ISE).

2.3 Simultaneous detection of fluoride and hydroxide

A prominent criteria for coincident flow injection determination of fluoride and hydroxide by a single spectrophotometer for investigation of an ion exchange process during fluoride removal by bone char is a suitable selection of reagents for both ions. The selected method for fluoride determination is based on decolourization of the ternary aluminium complex, aluminium - eriochrome cyanine R - cetyltrimethylammonium bromide, by fluoride. The diminishing of absorbance at its maximum absorption wavelength (λ_{max}) at 590 nm is proportional to fluoride

concentration. Hydroxide detection is achieved by modifying a classical method, using an indicator. A foremost feature of the interesting indicator is that its λ_{max} is closed to that of the aluminium complex, allowing a simple measurement at a single wavelength. Of four phthalein indicators, i.e. phenol red, cresol red, thymol blue and *m*-cresol purple, studied in the present work, the last with its λ_{max} at 576 nm is considerably favourable because of its high sensitivity and transition range covering the working pH. Any wavelength between 576 and 590 nm can be chosen for simultaneous determination of the two ions with satisfactory sensitivity.

The manifold for simultaneous detection of fluoride and pH by a single wavelength spectrophotometric flow injection analysis is represented in Figure 2.5. The dispersed plug of samples which are injected at the injection valve I1 is splitted into two lines for fluoride (MC1) and hydroxide. Difference in the length of mixing reactors (MC1 and MC2) leads to the difference in resident time of two ions. Switching the line switching valve I2 permits the detectable species of fluoride or hydroxide to pass through the spectrophotometer. Details on fluoride quantification, pH measurement and simultaneous determination of both are discussed in Chapter 4, 5 and 6 respectively.

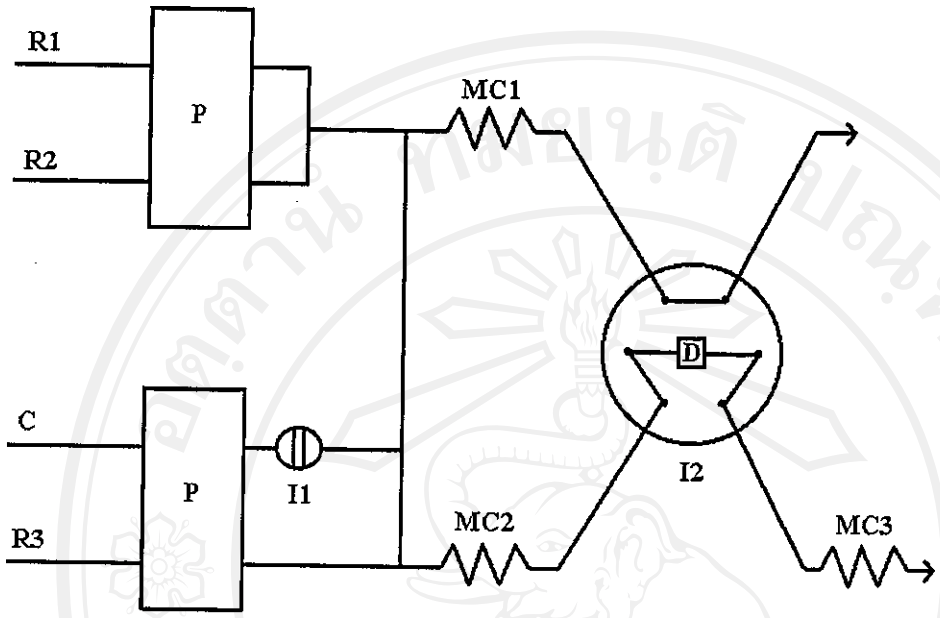

Figure 2.5 Flow injection system for simultaneous determination of fluoride and hydroxide. P: peristaltic pump, I: injection valve, MC: mixing coil, D: spectrophotometer, C: carrier (water), R1: aluminium solution, R2: eriochrome cyanine R / cetyltrimethylammonium bromide, R3: *m*-cresol purple.

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