University of Al-mustansiryah

College of Science

Department of Chemistry

Master Degree

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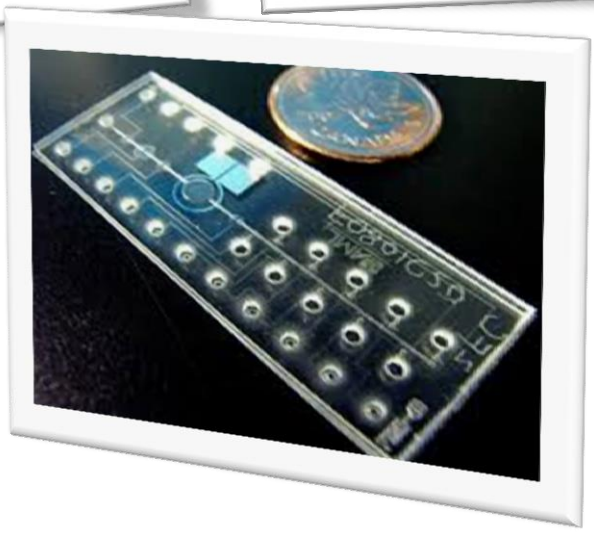
FLOW INJECTION ANALYSIS



Definition of FIA

The earliest definition was put forward by the parents of this technique, Ruzicka and Hansen, who in 1975 defined FIA as "the sequential insertion of discrete sample solutions into an un segmented continuously flowing stream with subsequent detection of the analyte" . In their later monograph on FIA, they expanded the original definition as follows: "a method based on injection of a liquid sample into a moving un segmented continuous stream of a suitable liquid. The injected sample forms a zone, which is then transported toward a detector" that continuously records the absorbance, electrode potential, or any other physical parameter, as it continuously changes as a result of the passage of the sample material through the flow cell" .

This definition has been revised seven years after by Ruzicka and Hansen to describe a technique for "information gathering from a concentration gradient formed from an injected well-defined one of a fluid, dispersed into a continuous un segmented stream of a carrier". Another definition was given by **Fang** **"A flow analysis technique performed by reproducibility manipulating sample and reagent zones in a flow stream under thermodynamically non-equilibrated conditions".**

Atypical definition describes FIA as "A simple and versatile analytical technology for automating wet chemical analysis, based on the physical and chemical manipulation of a dispersed sample zone formed from the injection of the sample into a flowing carrier stream and detection downstream"

Principle of FIA

The concept of FIA depends on three combinations:

1- Injection of samples volume
2- control of sample dispersion
3- The timing necessary to injected sample across the flow system.

The simplest flow manifold (FI) Fig. 1. It consists of pump, sample injector, file interaction and detection. The pump is used to push the carrier current through a narrow tube. The role of the injector is to re-inject a specific amount of sample into the carrier stream. The main function of the reaction coil is to encourage the reproducible reproduction of two or more integrated components by generating secondary inflow

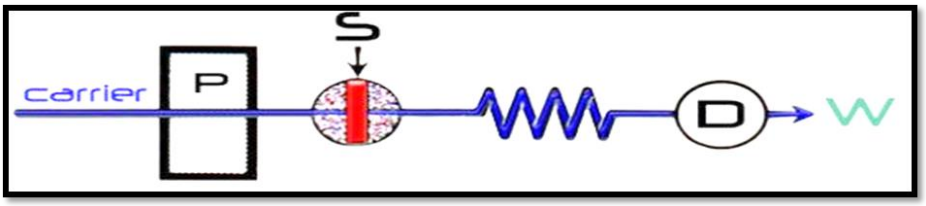


Fig.1: A single-line FI manifold; P: pump; C: carrier stream, S: sample injector, RC: reaction coil, D: detector and W: waste

The time span between the sample injection S and the peak maximum, which yields the analytical readout as peak height H, is the residence time T during which the chemical reaction takes place. A well-designed FIA system has an extremely rapid response, because T is in the range of 5-20 s. Therefore, a sampling cycle is less than 30 s (roughly T + tb), and thus, typically, two samples can be analyzed per minute. The injected sample volumes may be between 1 and 200 µL (typically 25 µL), which in turn requires no more than 0.5 mL of reagent per sampling cycle. This makes FIA a simple, automated micro-chemical technique, capable of having a high sampling rate and a minimum sample and reagent consumption .A FIA peak occurs due to two processes, one involving the simultaneous physical process of zone dispersion and the second involving the chemical process resulting from reaction between sample and reagent species Fig 2.

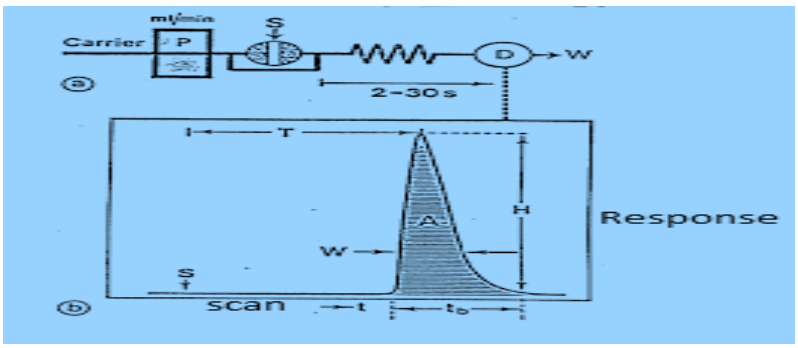


Fig. 2: The analog output has the form of a peak, the recording starting at S (time of injection to). H is the peak height, W is the peak width at a selected level, and A is the peak area. T is the residence time corresponding to the peak height measurement and t_b is the peak width at the baseline

Classification of Flow Systems

A: Segmented Flow Analysis (SFA)

The terms segmented flow analysis (SFA) and segmented flow analysis with sample aspiration (SFASA) have also been used .The segmented flow analyzer divides the sample into discrete segments separated by air or gas bubbles. As shown in (**Fig. 3a)** , the bubbles provide barriers to prevent the sample from spreading out along the tube due to dispersion processes. The bubbles thus confine the sample and minimize cross contamination between different samples. They also enhance mixing between the samples and the reagents. Samples are introduced at the sampler as plugs, some broadening due to dispersion occurs by the time the samples reach the detector. Hence, the type of signal is typically used to obtain quantitative information about the analyte **(Fig.3b)** .

Generally, a steady-state signal is used for determination of the analyte concentration. The precision and accuracy of the steady-state methods are much less sensitive to fluctuations in the recorded signal compared to those where the quantitative evaluation is based on a transient value. Samples can be analyzed at a rate of 30 to 120 samples per hour.

The liquid stream is segmented by bubbles of air or another gas with the aim of separating subsequent samples and avoiding the

broadening of the discrete analyte zones. It helps to maintain stable flow conditions, suppresses the sample carryover, and facilitates the mixing of sample with reactants in liquid segments.

Disadvantages of the SFA

1- Difficulty controlling the size of empty air bubbles

2- The inability to control and stop the movement of the carrying current

3- The compressibility of the air is high, and this causes an irregularity in the flow of the current inside the system

4- Failure to respond quickly and get unsatisfactory results because the device is complicated

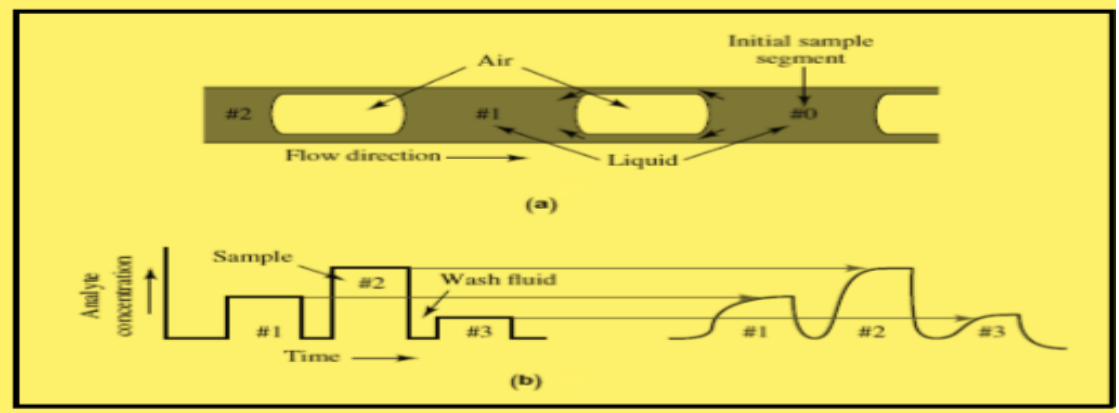


Fig. 3: (a) The segmented sample. (b) The analyte concentration profiles at the sampler and at the detector

B: Continuous Flow Injection Analysis (CFA)

In 1975 Ruzicka and Hansen introduced FIA (calling it initially non segmented continuous flow analysis) showing that bubble separation was unnecessary to prevent carry over and that it also introduced uncertainty in the reproducibility of the sample residence time inside the system. With the non-segmented technique the integrity of the sample pulse is kept by careful control of the hydrodynamic conditions of the system. With FIA, samples are injected from a sample loop into a flowing stream containing one or more reagents. The sample plug is allowed to disperse in a controlled manner before it reaches the detector. The concentration profile of the analytes entering the detection cell depends upon the mode of the sample introduction, the flow parameters, and the geometry of the FIA channel situated between the sampling point and the detection site (often called the reaction or dilution section). Therefore, a symmetric or asymmetric peak-shaped transient signal (rather than a steady-state plateau) is obtained as the detection signal. The extent of sample dispersion determines the analysis frequency (or throughput), i.e., the number of analyses per time unit . Samples can be processed with FIA at rates varying from 60 to 300 samples per hour .

Different between Continuous flow injection and segmented flow injection

Variable	Continuous flow injection	Segmented flow injection
Streamlined analytical stream	Non segmented	Segmented by air or gas
Insert sample	Injected	Suction
Volume of sample	Small (100) µL	Large (200)µL
System	Simple	Complex
Velocity	Fast	Slowly
Reagent consumption	Little	A lot
Mixed of sample	The injected sample is diluted and mixed with carrier	Interference occurs between the air bubbles ,the carrier and tube wall during each section under turbulent flow conditions
Recovery %	Good 1%	Good 1%
carrier stream	As no bubbles ,the carrier is fixed	Because of the air pressure ,the current is in the form of pulses

C: Reverse Flow Injection Analysis (rFIA)

Reverse flow injection analysis (rFIA) involves injection of the reagent into a continuous flowing stream of the sample (Fig.3b). Johnson and Petty were the first to discuss the effect of the rFIA approach on the analytical sensitivity through the determination of phosphate in seawater. rFIA is one of the FIA modes used to minimize reagent consumption, decrease sample dispersion, improve mixing efficiency and enhance the sensitivity. This simple, inexpensive approach is also applied to multi-component analysis by sequential injection of different reagents in the flowing

stream of the sample. rFIA is particularly important in water analysis due to the abundance of the sample, for determination of cations, anions, and organic substances, and also applications, such as pharmaceutical, biomedical and industrial analysis .

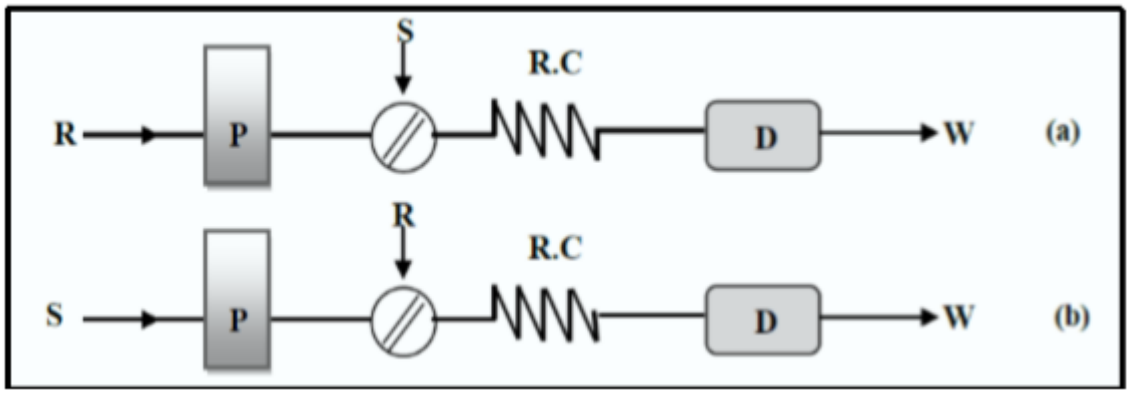


Fig. 3: Schematic diagrams of the basic (a) Normal FIA, (b) Reverse FIA; R, reagent; P, pump; S, sample; R.C, reaction coil; D, detector; W, waste.

D: Stopped Flow Injection Analysis (sFIA)

Amongst modern techniques derived from FIA, it seems that "stopped flow" techniques are the easiest to implement and the most versatile .In these techniques, the sample is injected as in conventional FIA but the carrier flow is stopped when the sample and the reagents reach the flow cell (at the detector) giving rise to several advantages .

While physical dispersion is minimized, as the driving force is diffusion only, chemical reaction proceeds (uncoupling both processes) increasing sensitivity as there is a longer reaction time

and lower dispersion of the products. Thus, reagent consumption and waste production diminish and, by controlling the stopping time, the concentration range can be selected, which is of the utmost importance for kinetic determinations at different wavelengths. However, stopped flow has the disadvantage of requiring a very robust and reproducible time control in order not to affect precision . sFIA is a very powerful tool for determining analyte species participating in enzymatic or cellular assays .