CHAPTER 1

Introduction

1.1 Flow Injection Analysis (FIA)

1.1.1 Principle and Theory

The first definition for FIA, given by Ruzicka and Hansen in 1981 [1] in the first edition of their well-known monograph entitled "Flow Injection Analysis" was stated as: A method based on injection of a liquid sample into a moving unsegmented continuous stream of a suitable liquid. The injected sample forms a zone, which is then transported towards a detector that continuously records the absorbance, or any other physical parameters, as it continuously changes as a result of the passage of the sample material through the detector. The change will be proportional to the analyte concentration using controlled experimental conditions being kept equal both for samples and standards. The technique is based on a combination of sample injection, controlled dispersion, and reproducible timing [2]. The latter often referred to as the three basic principles or cornerstones of FIA. The simplest flow injection analyzer (Figure 1.1) consists of a pump, which is used to propel the carrier stream through a narrow tube of the FIA manifold. An injection port or valve, by means of which, a well-defined volume of sample solution is injected into the carrier stream in a reproducibility manner. A microreactor (usually a coiled reactor) in which the sample zone disperses and reacts with the component of carrier stream, forming a species that is sensed by a flow through detector where the FIA signals are recorded.

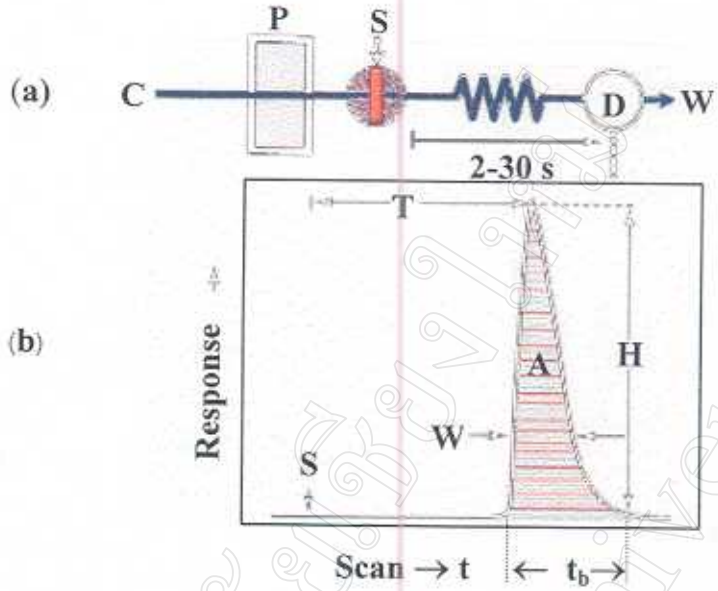

Figure 1.1 The basic components of an FIA system; (a) The simplest single-line FIA manifold utilizing a carrier stream of reagent; C is the carrier stream, P is the pump, S is the injection port, D is the flow cell, and W is the waste (b) The analog output has the form of a peak, the recording starting at S (time of injection t_o). H is the peak height, W is the peak width at a selected level, and A is the peak are, T is the residence time corresponding to the peak height measurement, and t_b is the peak width at the baseline [2].

A typical recorder output is as a peak and subsequently recorded as a function of time (Figure 1.1b). The height H, width W, or area A of which is directly proportional to the concentration of the analyte present in the samples. The time spent between the sample injection S and the peak maximum, 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. A sampling cycle is less than 30 s, and thus, typically, two samples can be analyzed per minute. The injected sample volumes may be between 1-200 µl, which in turn requires no more than 0.5 ml of reagent per sampling cycle. This makes FIA a simple, automated microchemical technique, capable of having a high sampling rate and a minimum sample and reagent consumption.

The FIA system itself provides the reproducible physical conditions, in contrast to batch methods or air-segmented continuous flow analyzers. In additional the low sample and reagent consumption, good sensitivity, reproducibility and high sample throughput are considered to be the main advantages of the flow injection method.

1.1.2 Basic Components of FIA [3,4]

A general scheme of FIA system showing the relationship of various components is presented in Figure 1.1-a. The basic components of the peristaltic pump used in the FIA system is shown in Figure 1.2.

(a) Propelling system

The liquid delivery unit is a critical component to drive or propel the solution in all FIA systems. There are three types of liquid delivery devices that are employed in the FIA systems namely; pressurized bottle (including constant head), peristaltic pump, and syringe pump. A peristaltic pump is a highly versatile propulsion device, which is no doubt used most frequently, not only in FIA but also in other continuous flow analysis systems, because it may accommodate several channels whereby, according to individual tube diameters, equal or different pumping rates may be obtained. The peristaltic pump consists of a motor-driven wheel with peripherally placed rollers and a compression cam (or band) which is squeezed against the rollers. One or several pump tubes are affixed so that they rest on a minimum of the rollers at all times (Figure 1.2).

(b) Injection system

The injection system is the important device to provide the necessary requirement to introduce the accurate and well-reproducible sample volumes into the carrier stream. The successful operation of any FIA system requires

injection of a well-defined zone into the analyzer channel, where the zone disperses in a controlled manner on its way toward and through the detector. The first injection system for FIA is a needleless syringe but it is difficult to ensure a constant volume. The rotary valve (GC type) was subsequently used. The other designs for injection system are proportional injector, solenoid valve, multi-injection and home-made low-cost rotary valve system. A modern pump also has a very small inner holdup volume, permitting rapid startup and short washout periods.

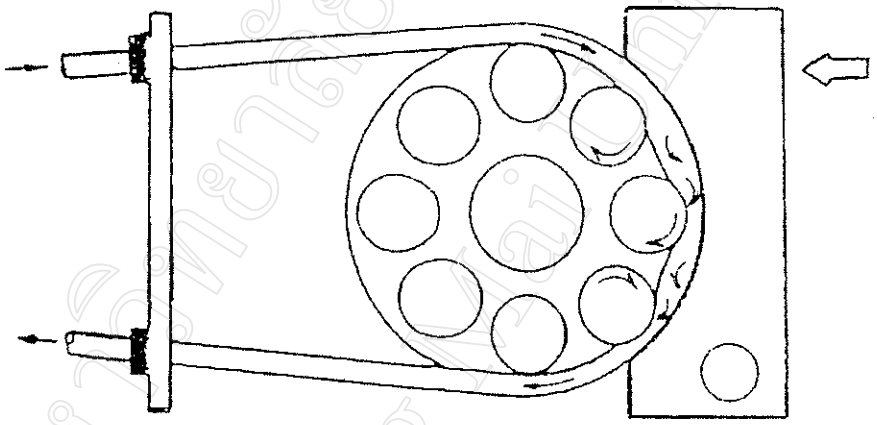

Figure 1.2 Relationship between the rollers of a peristaltic pump and the pump tubes [4].

(c) Reaction zone

The reaction zone composes of reactors, connectors, and other manifold components. The most frequently used reactors are made of plastic tubing, which can be coiled, knitted, or knotted. The most suitable tube material is Teflon (PTFE), which, besides being chemically resistant, adsorbs the least solutes on its surface. Polyethylene or polypropylene tubing is inexpensive and

easy to flange. PTFE tubings of 0.3-1.0 mm i.d. are often used for such purposes. To decrease the dispersion in short straight lines, often necessary to interconnect a manifold and a bulky detector, narrow tubing is useful. Mixing chambers and glass bead columns are utilized as mixing reactor. The connectors may be connected to the different components or prolonged either by push fitted, threaded, and permanently glued.

(d) Detectors

In theory, any detection system, which could be adapted for flow-through detection, may be used as detectors for FIA. Choice depends upon the method being used, the sensitivity and selectivity required. Recently, several detectors, including UV-VIS spectrophotometry, fluorimetry, chemiluminescent, AAS, AES, ICP, FTIR, nephelometric, thermometric, and various electrochemical detectors.

(e) Signal display device

The output from the detector is recorded as a peak by means of a chart recorder, microprocessor or a computer. Recently, microcomputers have been incorporated to store measured peak heights, peak areas and peak widths of the FIA signals.

1.1.3 FIA On-line Column Preconcentration System [3]

1) Among the various separation devices, packed sorption columns are most frequently employed in FIA on-line separation systems, because of their convenience of incorporating columns in the FIA systems. In the FIA on-line columns packed with any ion-exchangers or other sorbents have been reported for the removal of interferences, modification of the sample matrices, and /or preconcentration of trace analytes [3].

2) In practice, preconcentrations are often achieved with simultaneous separation of interfering matrices. General requirements of on-line sorption columns used in the FIA on-line system include the following:

- High sorption capacity.
- Low dispersion.
- Long lifetime of at least a few hundred or thousand cycles.
- Low hydrodynamic impedance.
- High reliability and stability over extended working periods.

3) Obviously these requirements are associated not only with mechanical and geometrical aspects of the column but also with the packing materials. It might be sufficient to state that packing materials should be mechanically stable towards different reagent media and provide high sorption capacities, but sorbent particles should not be fine or irregular as to create excessive back-pressures under normal sample loading flow rates.

1.1.3.1 Design and Operation

The column design strongly influences the column performance which fixed capacities, larger aspect ratio favour higher enrichment factors and stronger tolerance to interferences, but are limited by high back-pressure produced at high sampling loading rates. The capacities of the columns used in FIA preconcentration range from 15 μl to over 400 μl, depending on the specific purpose, but are generally much smaller than those used in batch procedures. The optimum column design for achieving high efficiency and low consumptive index depends on several factors, including: the sample loading rate and volume, the breakthrough capacity of the sorbent for the analyte, the specificity and the particle size of the packing materials, together with the extent of interference. The column performance will also depend considerably on the specific properties of the column packings.

1.1.3.1.1 Loading

In general, in preconcentration by sorption, the sampling sequence is always associated with loading samples on a packed column, either directly, by aspirating the sample from its container (time-based sampling), or indirectly, by displacing the sample from a fixed volume loop using a carrier stream (volume-based sampling). The enrichment factor value of a preconcentration system is directly related to the amount of sample loaded on the column, which in turn is determined by the loading time and the loading flow-rate. Volume-based sampling usually takes more time to load the same volume of sample when compared with the time-based alternative one owing to stronger dispersion effects.

1.1.3.1.2 Washing and Equilibration

The columns are usually equilibrated by washing with a buffer solution at the pH required for sample loading before the preconcentration, and washed again with distilled water after the sample loading to remove the residual sample in the column before elution. Such procedures simulated in the FIA preconcentration column using volume-based sampling by using the buffered sample carrier as a washing solution to achieve the above mentioned goals. However, the preclude used of the more efficient time-based sampling, or require more sophisticated manifolds with separate lines for washing, which all deteriorate the efficiency.

1.1.3.1.3 Elution

In the on-line elution, the kinetic features of the process are much more important than those for off-line batch procedures. The elution flow rate is an important parameter in column preconcentration, which is usually optimized for maximum sensitivity. However, the speed of elution is also a crucial factor for the efficiency of the on-line preconcentration systems, because in most

cases the eluent flow is connected directly (some after merging with reagent streams) with the detector. Ignoring the flow rate requirements of the detector, the optimum flow rate for elution will depend on how strongly the analyte is retained on the sorbent, and on the releasing strength of the eluent. When maximum enrichment factor is pursued, low elution rates are favoured. Experimentally, elution rates may be decreased until the enrichment factor approaches a steady value. If the optimum concentration efficiency value is the objective, then a compromise has to be made between the enrichment factor and the sampling frequency, and the higher elution rates giving somewhat the lower peak signals may have to be adopted.

1.1.3.2 Column Packing

The on-line preconcentration would demand special qualities for packing materials, which are not required or may be ignored in batch operations. These may include:

- Physical and chemical stable for at least over 500 preconcentration cycles.
- Negligible swelling and shrinking during a cycle of operation.
- Kinetic properties including easy retention and fast elution of sorbed analyte by an appropriate eluent.

The properties of various reported sorbents used in the on-line preconcentration systems have been reviewed by Fang [5].

1.2 Copper [6,7]

1.2.1 Physical and Chemical Properties

Copper is a reddish-brown, ductile and malleable metal. A chemical element copper (Cu) having an atomic number 29, is one of the transition elements group IB of Periodic Table. In compounds founded in the environment it usually has a valence of 2 but can exist in the metallic, +1 and +3 valence states. Copper is found naturally in a wide variety of mineral salts and organic compounds, and in the metallic form. The metal is sparingly by soluble in water, salt or mildly acidic solutions, but can be dissolved in nitric and sulfuric acids as well as basic solutions of ammonium hydroxide or carbonate.

Copper possesses high electrical and thermal conductivity and resists corrosion. The copper metal has a specific gravity of about 8-9, and melts at about 1,100°C.

1.2.2 Uses

Copper is one of the first metals, which have been used by humans. Its usefulness is accounted for by its combination of chemical, physical, electrical, and mechanical properties and its fairly abundant supply. Anthropogenic emissions include smelters, iron foundries and power station sources such as municipal incinerators. The major release of copper to land is from tailings and overburdens from copper mines and sewage sludge. Agricultural use of copper products accounts for 2% of copper released to soil.

Copper ores are mined, smelted and refined to produce many industrial and commercial products. Copper is widely used in cooking utensils and water distribution systems, as well as fertilizers, bactericides, fungicides, algicides and antifouling paints. It is also used in animal feed additives and growth promoters, as well as for disease control in livestock and poulty. Copper is used

in industry as an activator in froth flotation of sulfide ores, production of wood preservatives, electroplating, azo-dye manufacture, as a mordant for textile dyes, in petroleum and the manufacture of copper compounds.

1.2.3 Sources

Natural sources of copper exposure include windblown dust, volcanoes, decaying vegetation, the forest fires and sea spray. Wind is a significant factor in moving metal-laden soil particles around the land surface of the earth, which they can also reach from atmospheric sources by both wet and dry deposition. An important source of copper in aquatic sediments is from dead organisms, which settle out and contribute both copper and organic material.

Anthropogenic sources of copper include emissions from mines, smelters and foundries producing or utilizing copper, zinc, silver, gold and lead. Environmental copper can also arise from the burning of coal for power generation and from municipal waste incinerators. A major release of copper to land comes from mine tailings and overburden from mining operations. Other anthropogenic sources of copper include its use as an antifouling agent in paints, agriculture and animal and human excreta. Copper is also intentionally released into some water bodies to control the growth of algae.

1.2.4 Toxicity

Acute toxicity due to ingestion of copper in infrequent in humans and is usually a consequence of the contamination of beverages or from accidental or deliberate ingestion of high quantities of copper salts. Numerous case reports of single oral exposures to high levels of copper have been reported. Such exposures, including suicide attempts with copper sulfate, have occurred in youths and adults at doses ranging from 0.4 to 100 g Cu. Symptoms including vomiting, lethargy, acute haemolytic anaemia, renal and liver damage, neurotoxicity, increased blood pressure and respiratory rates. In some cases,

coma and death followed. There are also a number of reports showing copper toxicity of high dose copper ingestion in beverages.

1.2.5 Determination of Copper

The wide range of copper species, inorganic and organic, has led to the development of an array of sampling techniques, preparation and analytical methods to quantify the element in environmental and biological samples. Various analytical techniques are available for the determination of copper. Electroanalytical techniques, such as polarography, potentiometry and voltammetry, have been successfully applied, although they suffer from sensitivity to matrix interference. Recently, several techniques, including SIA, IC, ICP-MS, ICP-AES, XRF, and AAS have been used for copper determination in various sample matrices. Selection of the most appropriate method depends on parameters; on the purpose of the analysis, the nature of the analyze, the concentration of the copper, the presence and concentration of the other elements in the matrix, the accuracy required, and the methodology. A brief review for copper determination is shown in Table 1.1.

Table 1.1 A brief review of the methods for the determination of copper.

Method	Sample Conditions	Detection limit Precision Linear range	Reference
Differential-pulse polarography	sample = biological and water extraction with ethyl acetate reagent = N-phenylbenzohydroxamic acid	detection limit = 20 ng/ml	8
Differential-pulse polarography	sample = steel solvent extraction with dichloromethane reagent = bis(acetylacetone) ethylendiimine	detection limit = 0.8 μM linear range = 1-30 μM	9
Potentiometric stripping analysis	cysteine modified mercury film electrode	detection limit = 5×10^{-10} M (2 min deposit time) RSD = 2.9% (six electrode)	10

Table 1.1 (Continued).

Method	Sample Conditions	Detection limit Precision Linear range	Reference
Differential pulse anodic stripping voltammetry	sample = human hair microwave digestion	detection limit = 0.02 μg/g	11
Differential pulse anodic stripping voltammetry	sample = potable water and commercial lithium chloride N-phynylcinnamohydro-xamic acid modified carbon paste electrode	detection limit = 5×10^{-10} M RSD = 8.7% (5×10^{-7} M) linear range = 1×10^{-8}-1×10^{-6} M (preconcentration time 3 min)	12
Anodic stripping voltammetry	mercury electrode	detection limit = 3×10^{-9} M (preconcentration time 2 min) linear range up to 8×10^{-7} M	13
Anodic stripping voltammetry	sample = drinking and sea waters gold electrode	detection limit = 0.2 nM (90 s electrodeposition)	14
Anodic stripping square wave voltammetry	sample = aqueous medium carbon paste electrode modified with aminopropyl-grafted silica gel	detection limit = 3×10^{-9} M linear range = 5×10^{-8}-2×10^{-7} M	15
Differential pulse anodic stripping voltammetry	sample = human hair mercury electrode reagent = Bis(acetylacetone) ethylenediimine	detection limit = 1.6×10^{-8} M linear range = 5×10^{-8}-10^{-6} M	16
Differential pulse cathodic stripping voltammetry	sample = commercial salt and water mercury electrode reagent = benzylmonooxime	detection limit = 0.3 ng/ml (90 s accumulation time) RSD = 1.2 % (200 ng/ml) linear range = 1-850 ng/ml	17
ICP-AES with thermospray nebulisation	sample = natural water enrichment on Chelex-100	detection limit = 0.03 μg/l	18
ICP-AES	sample = molybdenite concentrate solution λ = 324-754 nm	detection limit = 0.11 mg/l	19
ICP-AES	samples = edible oils	RSD < 8%	20
USS-ETV-ID-ICP-MS	sample = fish (reference material) ultrasonic slurry sampling	detection limit = 5-50 ng/g RSD < 14%	21
ID-ICP-MS	sample = fish (CRM) off-line solvent extraction	SD = 0.742±0.007	22
ID-ICP-MS	sample = plant (CRM) microwave digestion and separated on Chelex-100	detection limit = 57 ng/g	23
LC (electrochemical and spectrophotometric detection)	sample = industrial waste water and biological electrode = glassy carbon reagent = butyl xanthate column = C_{18}	detection limit = 0.10 μg/l	24
HPLC (spectrophotometric detection)	sample = synthetic samples liquid-liquid extraction in water-acetic acid-chloroform reagent = 5,10,15,20-tetrakis (4*N* - pyridyl)porphine	detection limit = 5×10^{-9} M RSD = 3.2% linear range = 2×10^{-8}-4×10^{-7} M	25

Table 1.1 (Continued).

Method	Sample Conditions	Detection limit Precision Linear range	Reference
FAAS	sample = fresh eggs microvolume injection (10 µl)	detection limit 0.016 mg/l RSD = 2.6% linear range = 0.1-1.5 mg/l	26
FAAS	sample = serum	RSD < 5%	27
FAAS	sample = natural water preconcentration onto Amberlite XAD-2 loaded with calmagite	RSD = 2.42% (1.0 µg/sample)	28
FAAS	sample = natural and synthetic preconcentration with chemically modified chloromethylated polystyrene-PAN	detection limit = 4 µg/l	29
FAAS	sample = water solid phase extraction	detection limit = 4 ng/l	30
FAAS	sample = human milk with microwave digestion	detection limit = 0.07 mg/ml milk RSD = 2.9% (Intra-assay)	31
FAAS (after cloud point extraction)	sample = water and SRM reagent = 1(2-thiazolylazo)-2-naphthol surfactant = Triton X-114	detection limit = 0.27 ng/ml RSD = 1.6% linear range =0.27-100 ng/ml	32
GFAAS	sample = oil industry	detection limit = 9 µg/kg RSD = 29% linear range = 9-800 µg/kg	33
GFAAS	sample = river water preconcentration with yeast	detection limit = 85 pg/ml recovery = 93-100%	34
Spectrofluorometry	sample = ore, alloy, water and hair reagent=8-aminoquinoline derivatives (FCPAQ, FCPBSQ and BAQABP)	detection limit = 0.80, 0.20 and 0.50 µg/l linear range = 4.0-140, 1.0-200 and 3.0-150 µg/ml for the FCPAQ, FCPBSQ and BAQABP respectively	35
Fluorescence quenching	reagent = europium-terpyridine-aminopolycarboxylate chelate	detection limit = 7 ng/ml linear range = 0-300 ng/ml	36
Spectrofluorimetry	sample = brass and stream water fluorimetric reporter = 4,5-dihydroxy-1,3-benzenedisulfonic acid	detection limit = 3.83 (±0.09) $\times 10^{-7}$ M linear range = 5.0×10^{-7}-1.0×10^{-5} M	37
Electrochemilumi-nescence	sample = aqueous solution reducing agent = hydroxylamine hydrochloride complexing agent = 2,9-dimethyl-1,10-phenanthroline	detection limit = 0.1 mg/l linear range = 0.1-5 mg/l	38
Catalytic spectrophotometry	sample = tap water and biological material reagent = 3-methyl-2-benzo thiazolinone hydrazone and N-ethyl-N-(2-hydroxy-3-sulfo-propyl)-3,5-dimethoxyaniline in H_2O_2 λ = 525 nm	RSD = 2.6% (0.06 ng/ml)	39

Table 1.1 (Continued).

Method	Sample Conditions	Detection limit Precision Linear range	Reference
Derivative spectrophotometry	sample = river and tap water liquid-liquid extraction	detection limit = 2.8 ng/ml RSD < 2.1% linear range = 8-125 ng/ml	40
Derivative spectrophotometry	sample = alcoholic beverages, biological and standard alloy reagent = PAN in triton X-100	detection limit = 4.0 ng/ml linear range = 0.08-4 μg/ml	41
Derivative spectrophotometry	sample = steel, aluminum and nickel-base alloys reagent = 5-imino-3-(*p*-methoxyphenyl)-2-methyloxazolidine-4-thione	detection limit = 0.3 μg/ml (Zero order-λ 376 nm) linear rang = 0.25-3.01 μg/ml	42
Potoacoustic spectrometry	sample = biological sample solvent extraction (chloroform) chelate agent = 1,5-diphenylcarbazide	detection limit = 0.022 μg/l RSD = 1.5%	43
Spectrophotometry	sample = environmental (CRM) reagent = 3,3′-(1,3-propane-diyldiimine)bis-[3-methyl-2-butanone]dioxime	detection limit = 10 μg/l RSD = 0.74% linear range = 0.5-350 mg/ml	44
Solid phase spectrophotometry	sample = mushrooms, tea, drug and water sorbent = Dowex 1-X8 reagent = PAR	detection limit = 2.7 μg/l RSD = 1.8% (0.3-4.5 μg/l)	45
Spectrophotometry	sample = alloy and pig feeds solvent extraction (chloroform) chelate reagent = bis(acetylacetone) ethylenediimine	RSD =1.4% (50 μg/ml, n=10) linear range to 200 μg/ml (λ 545 nm)	46
Spectrophotometry	sample = pharmaceutical formulations environmental and foodstuff solvent extraction (methanol) reagent = S,S′-bis(2-aminophynyl) oxalate	detection limit = 11.5 μg/l RSD = ±0.66% (2 μg at 95%) linear range = 0.4 -150 μg/l	47
Spectrophotometry	sample = river water preconcentration by aggregate film formation reagent = *N*,*N*-dimethylthiocarbamate	RSD = 3.1% (3×10^{-6} M) linear range=1.6×10^{-9}- 8×10^{-8} M	48
Spectrophotometry	sample = serum and ground water reagent = bathocuproine disulphonate internal standard = bromophenol blue	detection limit = 0.03 mg/l RSD = 2.2% (0.5 mg/l) linear range = 0-2 mg/l	49
Sequential Injection Analysis with spectrophotometric detection	sample = plant food and water reagent = diethyldithiocarbamate λ = 460 nm	detection limit = 0.2 mg/l RSD < 4.5% linear range = 0.5-5.0 mg/l rate = 7 samples/h	50
Ion chromatography	sample = waters	-	51
Capillary electrophoresis	sample = duralmin alloys reagent = 1,10-phenanthroline derivatives	detection limit = 30 ng/ml linear range = 100-500ng/ml	52
Capillary electrophoresis	reagent = alizarin complexone and amine	detection limit = 200 ng/ml	53
Total reflection X-ray fluorescence spectrometry	sample = freshwater algae slurry sampling technique	-	54

Table 1.1 (Continued).

Method	Sample Conditions	Detection limit Precision Linear range	Reference
Total reflection X-ray fluorescence spectrometry	sample = spirituous beverages internal standard = vanadium	detection limit = 0.038 mg/l (crystal monochromator) and 0.020 mg/l (cut-off filter) RSD < 10%	55
Titration	sample = ores and alloys coplexing agent = EDTA standard solution = lead nitrate indicator = xylenol orange masking agent = 2,2'-bipyridyl	RSD <0.04 mg (for 2.54 - 25.40 mg of copper)	56

Among the reported procedures for copper(II) determination as shown in Table 1.1 only the batch methods are quoted in this section. The reported FIA methods for copper(II) determination will be review in the subsequent sections.

1.2.5.1 Previous FIA Method for the Determination of Copper

Flow injection methods offer great advantages such as flexibility, speed, inexpensive apparatus or instrumentations, high sampling rate and wide applicability in many fields. Initially the development of FIA methods was focused on finding and optimizing the measuring systems for selective and sensitive detection. A number of flow injection methods for the determination of copper(II) have been reported. Most flow injection systems have been increasingly used with various detectors, owing to their high sample throughput, performance and versatility. Table 1.2 reviews previous FIA determination of copper(II) during the last 5 years (1995-2000).

Table 1.2 A brief review of FIA for the determination of copper.

Detection system	Sample, conditions	Detection limit, precision, sample throughput	Reference
Spectrophotometry flow-through sensor (C_{18}-bonded beads packed in a flow-cell)	sample = catalysts and alloys reagent = 1,2 cyclohexanedione thiosemicarbazone	detection limit = 50 ng/l linear range = 0.1-10 μg/ml	57
Spectrophotometry	sample = blood serum and veterinary formulations reagent = zincon chemometrics	-	58
Spectrophotometry	sample = hair reagent = zincon	detection limit = 0.02 μg/ml linear range = 0.1-3.0 μg/ml rate = 20-30 samples/h	59
Spectrophotometry	sample = copper ores reagent = pyrophosphate λ = 240 nm	RSD = 1% linear range = 2-50 μg/ml rate = 70 samples/h	60
Spectrophotometry	sample = drinking, surface and waste water reagent = dithizone	-	61
Spectrophotometry	sample = milks reagent = 1,5-diphenylcarbazide	detection limit=1.41×10^{-3} mg/l RSD < 2% rate >120 samples/h	62
Spectrophotometry	sample = alloys and pig feeds reagent = bis(acetylacetone) ethylenediimine λ_{max} = 370 nm	RSD = 1.95% (n=10, 20 μg/ml) linear range up to 100 μg/ml rate = 20 samples/h	63
Spectrophotometry	sample = pepperbush catalytic reaction λ = 525 nm	RSD = 2.0% (0.05 ng/ml) linear range = 0.005-0.75 ng/ml rate = 40 samples/h	64
Spectrophotometry	sample = natural water catalytic reaction reagent = N-phenyl-p-phenylenediamine and m-phenylenediamine	RSD = 2.4% linear range = 0.1-2.0 ng/ml rate = 30 samples/h	65
Spectrophotometry	sample =river water (CRM) catalytic reaction reagent = cysteine and 1,10-phenanthroline	detection limit = 0.04 ng/ml RSD = 1% (1.0 ng/ml) linear range = 0.1-10 ng/ml rate = 30 samples/h	66
AAS	sample = multivitamin and mineral tablets Electrodialysis	detection limit = 1.44 mg/l linear range = 1-60 mg/l rate = 14 samples/h	67
GFAAS	sample = sea water preconcentration with chelating resin chelamine	detection limit = 3 ng/l SD = 0.4	68
GFAAS	sample = sea water	detection limit = 0.07 μg/l RSD < 10%	69
GFAAS	sample = old manuscript slurry sampling	RSD = 0.3-7.6%	70
GFAAS	sample = sea water separated and preconcentrate electrochemically on the graphite ridge probe	detection limit = 16 ng/l (10-min deposition)	71

Table 1.2 (Continued).

Detection system	Sample, conditions	Detection limit, precision, sample throughput	Reference
GFAAS	sample = algae slurry sampling and microwave digestion	limits of detection = 1.4 ng/ml for slurry-sampling and 8.0 ng/ml for microwave digestion	72
Fluorimetry	sample = food reagent = 5-(4-chlorophenylazo)-8-aminoquinoline	detection limit = 0.01 µg/l linear range = 0.05-5.00 µg/l	73
Differential pulse anodic stripping voltammetry	sample = water glassy carbon electrode supporting electrolyte = pyrophosphate	detection limit = 39 µg/l RSD = 14% rate = 8-12 samples/h slope = 0.49 µA µg/l	74
Chemiluminescence	sample = sea water reagent = 1,10-phenanthroline	detection limit = 0.1 nM	75

1.2.5.2 FIA for Copper On-line Preconcentration

The trace heavy metals determination is often dependent on analytical chemists. However, in many cases the available analytical instrumentation does not provide sufficient sensibility for the analysis of natural or real samples. Many types of preconcentration methods have been reported, such as precipitation, co-precipitation, using chelating resin, liquid-liquid extraction and solid-phase extraction [**76**]. It seems that the solid-phase extraction is superior to the conventional liquid-liquid extraction, because it is more efficient, reproducible and simpler in sample handling and transfer and low toxic organic solvent consumption. The solid-phase extraction technique has been used over 10 years ago to preconcentrate trace metals in water samples. Traditional off-line solid-phase extraction required very large sample volumes (500-1000 ml) for preconcentration, and only a small part of the eluate (10-100 µl) was used. This way several procedures have been developed for copper separation and preconcentration from environmental and biological matrices. On-line separation and preconcentration have been evolved into two of the most prominent contributions of the flow injection technique.

Automation of sample pretreatment and manipulation within the manifold have increased sample throughput and decreased the potential for sample contamination, which is critical in trace analysis. Recently, some on-line couplings of preconcentration techniques (e.g. solvent extraction and sorbent extraction [77]) have been extensively studied. Both of FIA on-line solvent extraction and sorbent extraction can readily enhance the detection ability of flame AAS [78]. Particularly, sorbent extraction is a preconcentration technique of rapidly growing importance in trace metal determination, which can be easily adapted to FIA on-line separation and preconcentration systems [79]. The main advantage of this is the possibility of using a relatively simple detection system such as spectrophotometry instead of other techniques, which require more expensive equipment and instrumentation.

1.2.5.3 Packing Materials for Copper FIA On-line Preconcentretion

The most commonly used materials for the on-line preconcentration of copper are: Ostsorb Oxin which contains chemically bound quinolin-8-ol functional groups, poly(aminophosphonic acid) chelating resins, Dowex 50W-X8, RP-C_{18}, immobilized algae and C_{60}-C_{70} fullerence. The analytical potential of synthetic zeolites as sorbent materials for the preconcentration of trace of copper by using flame atomic absorption spectrometry was investigated for the first time in 2000 [79]. Nevertheless, the potential of the synthetic zeolites from perlite as useful material has not yet been investigated. Perlites occurred naturally in Thailand (Lopburi province) and the synthetic zeolites from perlite are easily obtained by the simple zeolitization of natural perlites. This leads to the advantage that the synthetic zeolites from perlite should be used as a sorbent for copper enrichment and determination by on-line flow injection spectrophotometry. A brief review on flow injection on-line preconcentration of trace copper determination is shown in Table 1.3.

Table 1.3 A brief review of FIA on-line column preconcentration for the determination of copper.

Detection system, conditions	Samples	Detection limit, precision, sample throughput	Reference
ICP-MS sorbent = Amberlite XAD-4 resin acidic eluent	water	detection limit in low ng/l range	**80**
ICP-MS sorbent = iminodiacetate-based resin	blood and serum	detection limit = 3.5 μg/l rate = 6 samples/h	**81**
ICP-MS sorbent = C_{18} immobilized on silica eluent = methanol	sea water	RSD < 10% rate = 22 samples/h	**82**
ICP-MS sorbent = C_{18} immobilized on silica eluent = methanol	waters and biological (CRM)	detection limit = 33 ng/l rate = 21 samples/h	**83**
ICP-MS sorbent = Toyopearl TSK-immobilized 8-hydroxylquinoline resin	natural water	detection limit = 1.5 ng/l RSD < 5%	**84**
ICP-TOFMS sorbent = knotted reactor reagent = ammonium pyrrolidinedithiocarbamate	natural water and biological material	RSD < 5%	**85**
ICP-AES sorbent = silica immobilized 8-quinolinol eluent = 1:1 of HCl and HNO_3 mixture	sea water	detection limit = 0.07 ng/ml	**77**
ICP-AES sorbent=Chelex-100 and AG1 X-8 resin eluent = HCl 2.0 M	cow milk	-	**86**
LC sorbent = RP-C_{18} eluent = methanol/water (80:20 v/v)	water	detection limit = 0.41 μg/l RSD = 4.5% (0.1 mg/l)	**87**
HPLC sorbent = C_{18} reagent = 8-hydroxyquinoline λ = 400 nm	waste water and beverage	linear range = 40 μg/l – 5 mg/l	**88**
IC sorbent = chelate resin (MetPac CC-1 column) reagent = 2-[(5-bromo-2-pyridyl)azo]-5-diethylaminophenol λ = 560 nm	drinking water	detection limit = 0.2 ng/ml RSD = 4.7% linear range = 1.5-192 ng/ml	**89**
Chemiluminescence sorbent = immobilized 8-HQ on Toyopearl HW-75F resin eluent = 0.2 M HCl	sea water	-	**90**
GFAAS sorbent = C_{18} bonded silica	sea water	detection limit = 6.5 ng/l	**76**
GFAAS sorbent = C_{18} bonded silica eluent = ethanol	biological and environmental	detection limit = 0.05 μg/l RSD = 2% (3 μg/l)	**78**
GFAAS sorbent = Muromac A-1 chelating resin eluent = HNO_3	sea water	detection limit = 0.05 μg/l RSD = 3.8% rate = 18-26 samples/h	**91**
GFAAS sorbent = PTFE knotted reactor reagent = pyrrolidine dithiocarbamate	environmental and biologycal materials	RSD = 1.4-2.5% linear range = 4 –50 μg/g	**92**

Table 1.3 (Continued).

Detection system, conditions	Samples	Detection limit, precision, sample throughput	Reference
GFAAS sorbent = knotted reactor precoated with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one	certified reference materials	detection limit = 5.7 ng/l RSD = 2.4% (0.1 μg/l) rate = 21.6 samples/h	**93**
FAAS sorbent = spherical cellulose sorbent with chemically bound quinolin-8-ol eluent = 2 M HCl	-	detection limit = 0.3 ng/ml RSD < 5% (25ng/ml-5μg/ml)	**94**
FAAS sorbent = PTFE knotted reactor eluent = isobutyl methyl ketone	waters and rice	detection limit = 0.2 μg/l RSD = 1.7% (20 μg/l), 3.6% (2 μg/l) rate = 46 samples/h	**95**
FAAS sorbent = activated carbon eluent = isobutyl methyl ketone	waters	RSD = 1.8-3.5%	**96**
FAAS sorbent = C_{18} bonded silica eluent = methanol	sediment	detection limit = 1.4 μg/l	**97**
FAAS sorbent = Saccharomyces Cerevisiae immobilized on controlled pore glass eluent = HNO_3	reference materials	detection limit = 0.7 ng/ml	**98**
FAAS sorbent = poly(aminophosphonic acid) chelating resin eluent = 3 M HCl	natural water	detection limit = 1.6 μg/l rate = 48 samples/h	**99**
FAAS sorbent = C_{18} bonded silica eluent = ethanol	environmental	detection limit = 1.4 μg/l	**100**
FAAS sorbent = RP-C_{18} eluent = ethanol reagent = 1,10-phenanthroline	standard reference materials	detection limit = 0.3 μg/l RSD = 3.0% (50 μg/l) rate = 90 samples/h	**101**
FAAS sorbent = synthetic zeolite eluent = methyl isobutyl ketone	water	detection limit = 0.1 ng/ml RSD = 2.6% linear range = 2.5-30 ng/ml	**79**
FAAS sorbent = amberlite XAD-2 resin loaded with calmagite elutent = 1 M HCl	sea water and biological	detection limit = 0.15 μg/l RSD = 2.7-6.0% (0 –20μg/l)	**102**
FAAS sorbent = PTFE eluent = isobutyl methyl kotone reagent = ammonium pyrrolidine dithiocarbamate	water	detection limit = 0.05 μg/l RSD = 1.5% (2.0 μg/l) rate = 40 samples/h	**103**
Spectrophotometry sorbent = ion exchange packed in a flow-through cell	water	detection limit = 0.08 ng/ml	**104**
Spectrophotometry sorbent = Chelex-100	water	detection limit = 0.08 ng/ml RSD < 3.1%	**105**

Table 1.3 (Continued).

Detection system, conditions	Samples	Detection limit, precision, sample throughput	Reference
Spectrophotometry (catalytic) sorbent = Chelex-100 reagent = 2,6-dichlorophenolindophenol	plant digests and natural waters	detection limit = 0.09 μg/l RSD < 2% (5-70 μg/l) linear range up to about 100 μg/l rate = 60 samples/h	**106**
Spectrophotometry sorbent = poly(ethylenimine) reagent = PAR eluent = HNO_3 λ = 530 nm sample volume = 2 to 4 ml	residual and tap waters	detection limit = 25 and 13 μg/l RSD < 3% (0.05 and 0.5 mg/l) rate = 24 and 12 samples/h	**107**

1.3 Nitroso-R Salt

Disodium 1-nitroso-2-napthol-3,6-disulfonate (Nitroso-R salt) was first introduced in 1921 by Van Klooster for the determination of cobalt [**108**] and subsequently used by various investigators for the determination of cobalt [**109, 110**], iron [**111**], copper [**112-114**], and nickel [**115**]. The chemical structure of nitroso-R salt is shown in Figure 1.3. This agent forms soluble complexes with certain metal ions (e.g. Cr^{3+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, etc.). However, the sensitivity and the selectivity of the reagent have been achieved by controlling the pH of the solution.

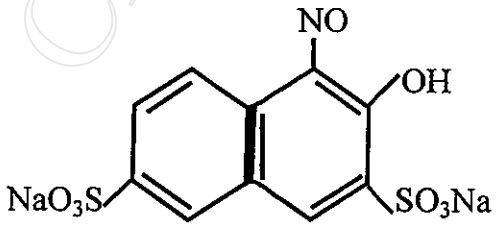

Figure 1.3 Chemical structure of Nitroso-R salt [**116**].

1.4 Perlite

1.4.1 Properties and Sources

Perlite is a glassy volcanic rock having the chemical compositions generally equivalent to rhyolite or granite but contains much higher water content (Table 1.4). Upon rapid high heating, perlite will be expanded into a frothy material of low bulk density, valued as a lightweight aggregate [**117**].

Table 1.4 Average chemical compositions of granite, ryolite, Lopburi perlite, Sardinian perlite, and World perlite [**118**].

Oxides (%)	Granite	Rhyolite	Lopburi perlite	Sardinian perlite	World perlite
SiO_2	70.41	71.33	72.58	70.59	71.0-75.0
TiO_2	0.45	0.42	0.25	0.2	-
Al_2O_3	14.38	14.77	12.57	13.37	12.5-18.0
Fe_2O_3	1.04	1.82	0.83	1.73	0.5-1.5
FeO	1.93	0.4	0.44	-	0.0-0.1
MgO	0.81	0.24	0.42	0.32	0.1-0.5
MnO	0.06	0.1	0.04	0.05	-
CaO	1.97	0.8	0.88	1.04	0.5-2.0
Na_2O	3.23	3.58	1.49	3.1	2.9-4.0
K_2O	4.95	4.57	5.68	5.29	4.0-5.0
P_2O_5	0.02	0.07	0.05	0.57	-
H_2O	0.55	0.16	4.35	4.0	3.0-5.0

Perlite deposits in Thailand are occurring in the Lumnarai Volcanic Complex (Lopburi Province) and associated with rhyolite and pyroclastic rocks. The Lopburi perlite contains the average major chemical composition of 71.56% SiO_2, 12.98% Al_2O_3, 8.3% (Na_2O + K_2O) and 4.2% of H_2O. The silica to alumina molar ratios range from 9-10 [**118**].

The primary use of perlite now is as an aggregate in insulation boards. Because of its low bulk density, and fire resistance perlite aggregate plasters hold many advantages over conventional plaster. As most perlites provide high silica contents, usually greater than 70%, and are adsorptive, they are chemically inert. Miscellaneous uses of expanded perlite include fillers or extenders in paint, enamels, glazes, plastic, and rubber; as a catalyst in chemical reactions, an abrasive, and as an agent for oil well cementing [**117**].

1.4.2 Zeolitization of Perlite

In nature, zeolites are formed by the reaction of saline water such as seas, lakes or percolating ground waters with volcanic glass, poorly crystalline clay or biogenic silica. Actually, the reaction is a devitrification of glass, which results in zeolitisation. It takes normally over tens or thousands of years to obtain zeolitically altered products, depending, however, on the composition of glass material, salinity, alkalinity, pressure and temperature of the systems. Zeolites have been synthesized from a variety of natural silicas and volcanic glasses including natural and expanded perlite [**119**]. Perlites have been experimentally converted to zeolites by many workers [**119-121**]. Zeolitisation of Lopburi perlite has been studied [**122**] and used as an adsorbent for Pb, Cd, and Zn.

1.5 Reasons for Undertaking This Work

There is speed to analyze for occurring toxic elements (such as Cd, Cu, Pb etc.). These elements can occur in trace amounts in industrial effluents, hence, the need to include a preconcentration steps in the analysis. The development of on-line sample preparation techniques that lead to improvement of selectivity, sensitivity, precision and accuracy of the determination will be undertaken.

1.6 Research Aims

The aims of this research work are as follows:

1. To develop a flow injection spectrophotometric procedure for the determination of trace copper(II) ion.

2. To develop a natural packing material for on-line preconcentration and separation flow injection system for trace copper(II) ion.

3. To apply the proposed procedure to the determination of trace copper(II) ion in environmental samples.