CHAPTER 1

INTRODUCTION

1.1 Preconcentration/sample pretreatment using flow injection system with column technique [1]

Flow injection (FI) is a powerful technique, which is not only for performing many analyses, but also sample pretreatment. The systems may also be classified according to their objectives for separation. Separations may be effected to overcome interferences to improve the selectivity, or to enhance the sensitivity through a preconcentration process, or both.

FI systems of separation and preconcentration exhibit some extremely favorable features over their batch or even continuous flow counterparts. The general characteristics of FI methods for separation with preconcentration involve high sample throughput, high enrichment efficiencies, low sample consumption, low reagent consumption, simple automated operation and low contamination risks.

1.1.1 Preconcentration

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry (AAS), there is a crucial need for the preconcentration of trace elements before their analysis, due to their frequent low concentration in numerous samples, especially water samples [2]. The determination of extremely low concentrations of elements usually requires separation and preconcentration steps. Various methods, including coprecipitation, liquid-liquid extraction, ion exchange and chelating sorbents, have been applied for the preconcentration of cations in batch and flow injection analyses [3]. Ion exchange preconcentration has proved to an effective means of increasing the sensitivity of atomic absorption spectrometry, as well as a means of removing interferences. Batch ion exchange preconcentration can increase the sensitivity of a procedure, but uses large sample volumes. And the conventional column mode of ion exchange preconcentration is tedious and time consuming. There has been interest in on-line preconcentration since 1980 and many modifications have been proposed to improve its performance. This approach increases the selectivity, sensitivity, detection limit and sample throughput [4,5]. Therefore, attempts have been made to apply on-line ion exchange to AAS determination with the aim of speeding up and simplifying the preconcentration step. The valve designs have been improved, and in addition to Chelex-100 resin, other ion exchange resins have been tested, and different flow systems have been proposed to increase the efficiency of the process [1]. Chelating resins have found widespread applications in FI-AAS systems owing to their selectivity and simple loading/elution reactions. The most widely used is Chelex-100 resin [6,7]. Various methods of achieving preconcentration have been adapted to an FI manifold, including liquid-liquid extraction, precipitation, ion exchange [3], immobilization [8], electrodeposition and solid-phase extraction. A configuration for an on-line column uses an in-valve mini-column as a small column located in the loop of the injection valve for sample preconcentration prior to Flame atomic absorption spectrometry (FAAS) determination. An FI in-valve preconcentration column provides the additional advantage of offering the possibility of a calibration using only a single standard solution [9,10].

1.1.2 Sample pretreatment

Sample pretreatment is necessary when the analytical method cannot provide good separation and quantification due to interferences from sample matrix components [11]. Sample preparation has been a growing area in chromatography over the past several years. Samples containing interfering substances can affect chromatographic performance. These substances may mask the peak of interest or be irreversibly retained on the analytical column, permanently damaging the column. To eliminate these problems, such samples need to be treated before injection [12]. Numerous analytical techniques have been employed in the determination of heavy and transition metals. But ion chromatography seems to be one of the most effective and simple techniques to determine cationic species owing to its high sensitivity, rapidity, selectivity and simplicity coupled with the possible advantage of simultaneous determination [13-15].

Ion chromatography is a common analytical tool for the determination of metals. A common problem in ion chromatography is poor resolution of an analyte ion from matrix ions that are present in relatively high concentrations [15-21]. Post column derivatization with a color reagent such as 4-(2-pyridylazo) resorcinol (PAR) or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) for visible spectrophotometric detection [13,14,22,23] has been used for good sensitivity and stable baselines. One of the most important aspects of developing an IC method is the ability to recognize when undesirable chromatographic effects are derived from sample matrix interferences [22,24,25]. Sample matrix effects can include shortened retention times, poor peak efficiency, poor resolution, poor reproducibility and irregular baseline [11]. Automation of sample pretreatment and manipulation within the manifold have increased sample throughput and decreased the potential for sample contamination [26,27].

FI systems were used for on-line sample pretreatment. Widely used column techniques were carried out with many categories of column and many kinds of packing materials as sorbents such as ion exchange, chelating resin, C_{18} bonded silica gel, etc. (see Table1.1).

Table 1.1 FI systems with sample pretreatment for determination of some cations

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
Solid phase extraction FI-FAAS	Pb	Natural water	- Using functionalized cellulose sorbent and several cation exchange resin - Nitric acid and ethanol for elution	- DL=0.17 $\mu g\ l^{-1}$	[28]
FI with solid phase extraction-spectrophotometry	Cd, Cu and Pb	Surface water	-Using extraction chromatographic resin, Lewatit TP807'84 containing di(2,4,4-trimethylpentyl acid as active component -pH of column : pH 3.2 and pH 5.5	- %R=80-120 - RSD=10%	[29]
FI with solid phase-spectro photometry	Zn	Human hair, pharmaceutical, and water sample	- Reaction of Zn(II) and1-(2-pyridylazo)-2 naphthol (PAN) immobilized on a Dowex cation exchanger	- 20-500 $\mu g\ l^{-1}$ at sample volume 2000 μl - DL=0.05 $\mu g\ ml^{-1}$ at sample volume 100 μl, 5 $\mu g\ l^{-1}$ at sample volume 2000 μl	[30]

Table 1.1 FI systems with sample pretreatment for determination of some cations (continued)

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
Solid phase extraction-ICP-AES	Cd, Cu and Pb	Sea water	- Anionic complexes with EDTA and 8-hydroxyquinoline-5-sulphonic acid	- DL=1.3, 3.1, 6.8 nM for Cd, Cu and Pb - Enrichment factor 10	[31]
FI with solid extraction-GFAAS	Pb	Sea water	- Micro-column filled with sorbent (boned silica with actadecyl functional group (C_{18})) - Ethanol for elution	- DL (3σ)=0.003 µg l^{-1} - Precision 1.9% RSD (n=11)	[32]
FI with coprecipitation-FAAS	Pb	Biological sample	- Coprecipitation of Pb and Fe (II)-hexahydroazepinium hexahydroazepin-1-ylformate (hexamethyleneammoniumhexamethylenedithiocarbanate) complex - Dissolved precipitate in isobutyl methyl ketone	- DL (3σ)=2 µg l^{-1} - Enrichment factor =20 - Enhancement factor=66 - RSD (n=12)=2.7%	[33]
On-line pretreatment-chelation ion chromatography	Pb, Cu and Cd	Drinking water	- Using chelating resin column (MetPac CC-1 column) - Oxalic acid and sodium nitrate as eluents - Post column with 2-((5-bromo-2-pyridyl) azo)-5-diethylaminophenol (5-Br-PADAP) at 560 nm	- DL below the µg l^{-1} level	[34]

1.2 Importance of some cation (Cd, Cu, Pb and Zn) determinations

The accelerated industrialization process of developing countries in combination with their rapid population growth and some agricultural activities have brought a risk of increasing the pollution index in natural environments such as soil, water or air. The unsuitable handling management of industrial waste has been recognized as pollution sources responsible for producing considerable loading of heavy metals (Pb, Cu, Cd, Co, Zn and Ni) to the environment [23]. The presence of residual ash deposits derived from the coal combustion process in an energy power plant could be a possible source of metallic pollutants. Traces of heavy metals, such as Cd, Pb and Zn, can have their origin from combustion residues, which could migrate or infiltrate into the aquifers for interacting and dissolving with natural ground water [23]. Heavy metals in wastewater are major threat to human beings and the environment due to their toxicity [35]. Two important features distinguish heavy metals from other toxic pollutants. There are not biodegradable and their toxicity is controlled by their physicochemical form [36]. Lead and cadmium commonly occur in the environment due to the contribution of anthropogenic sources, such as waste incineration and combustion of coal and oil, and are among the most toxic heavy metals for human health [37]. Lead belongs to those trace heavy metals which are of major interest in environmental protection owing to its cumulative toxicity. Lead is still emitted into the biosphere in considerable amounts owing to its application as a fuel additive [9]. Cadmium is one of the metals of prime environmental concern because of several dangerous effects that it may have on humans [38]. Copper is an essential micronutrient for animals and plants, occurring usually at low concentration in plant tissues (0.2-200 $\mu g\ g^{-1}$) and in natural water (<40 $\mu g\ l^{-1}$). This element has been considered also as an ambient contaminant; the demand for its determination is thus presently increasing [39]. The importance of Zn as an essential trace element in human and animal health is well known. The determination of trace metals in real matrixes has received increasing attention in recent years. Heavy and transition metals are toxic when their concentrations in water exceed certain values. The most toxic heavy and transition metals are Hg, Cu, Pb, Cd, Zn and Ni. They have special importance from the ecotoxicological point of view, both because of the high toxicity of their compounds and because they can accumulate in various organisms [34]. Cations of cadmium, copper, lead and zinc frequently exist together in many real environments. There is an increased need to measure several cations simultaneously and rapidly in the same sample with single injection and/or measurement in various fields like environmental and/or industrial control [40].

1.3 Analytical methods for cadmium, copper, lead and zinc determination with preconcentration

Several studies concerning determination of some cations (Cd, Cu, Pb and Zn) in water samples with preconcentration and/or separation of the analyte from its matrix have been reported [37]. Chemical analyses of cations have traditionally been carried out by AAS. Flame atomic absorption spectrometry (FAAS) is an analytical technique remarkable for its selectivity, speed and fairly low operational cost. However, sometimes this technique does not have enough sensitivity for a required analysis and the detection limits of FAAS have usually been high and consequently unsuitable for direct trace analysis in complex matrixes. A complex system consisting of a graphite furnace with AAS has good detection capabilities, but some chemical, ionization, spectral or physical interferences have limited their generalized use. Moreover, the use of simple or standard inductively coupled plasma (ICP) instruments has not been totally demonstrated to be sensitive enough for achieving the low detection limits required for trace analyses. Therefore, new and more complex technologies such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled argon plasma spectroscopy (ICAPS) have been coupled with chromatography for measuring cations at lower detection limits [23,29,41]. Unfortunately, these new high-cost technologies are often beyond the reach of most laboratories in developing countries. Hence, a great need still persists for investigating cheaper, faster, accurate and highly sensitive analytical methodology for the determination of cations at low levels. UV-visible absorption molecular spectroscopy is another possibility.

The off-line preconcentration and separation of trace constituents by using ion exchange, adsorption or solvent extraction batch procedures are effective in improving the sensitivity and selectivity of atomic spectrometric methods. Principal drawbacks of off-line separation procedures are that they are often time-consuming, frequently require a large sample volume, the sample may be contaminated, and the sample throughput is very low.

On-line separation and preconcentration have evolved into two of the most prominent contributions of the FI technique to FAAS. The procedures for an on-line preconcentration have been proposed to widen FAAS application [42]. Flow injection coupled to atomic spectrometric techniques offers many advantage such as selectivity and sensitivity, which are characteristic of atomic spectrometric analysis, in addition to the great speed typical for flow techniques [43-45]. Micro-columns containing chelating ion exchange, C18 octadecyl bonded silica gel, activated carbon and various other materials have been used for FI on-line preconcentration of analyte before determination with FAAS [45]. Chelate-forming resins have been widely applied as ion exchangers for various cations in different environmental and industrial areas. These resins show greater selectivity compared to the conventional types of ion exchangers. Many chelating resins with different functionalities have been emphasized for interaction with metal ions [35]. Initially Chelex-100 was widely used as a batch preconcentration material [46]. However, this resin could be used in on-line systems to preconcentrate metal ions [47].

With the implementation of on-line FI techniques for separation and preconcentration, such drawbacks no longer exist, while the beneficial effects are further enhanced: sampling frequency can be increased by one or two orders of magnitude and consumption of sample and reagent can be decreased by one or two orders of magnitude. On-line FI techniques also have better precision and are easy to operate automatically [40,48-50]. Flow injection analysis (FIA) has become an important technique as a result of its high speed and precision and the ease with which it is automated. The technique has been widely used. The FIA system could be used to introduce the sample into a detector such as AAS [51], ICP-AES, ICP-MS, ISE and IC [52] and to enhance the pretreatment step. FIA systems with on-line sample pretreatment are very beneficial. These include, for example, column, gas diffusion, dialysis, solid extraction and solvent extraction [10,53]. The on-line column in an FI system could be incorporated with FAAS to preconcentrate analytes at low levels [17]. Moreover, FI on-line columns could be used for sample pretreatment in the complicated sample matrixes prior to the determination step.

Various analytical techniques are available for determination of some cations (Cd, Cu, Pb and Zn) in environmental matrixes. The application have been reported in Table 1.2

Table 1.2 Summary of analytical methods for determination of Cd, Cu, Pb and Zn with preconcentration/sample pretreatment

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
FI with preconcentration-FAAS	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Natural water	- Using mini-column with poly (aminophosphonic acid) chelating resin (PAPh A, 20-30 mesh) - Sample pH 5.0 - 3.0 M HCl for elution	- DL=0.5, 5.0, 1.5, 1.6, 3.5, 0.6, 3.2, 3.1 and 0.4 $\mu g\ l^{-1}$ for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn - Precision (coefficient of variation) in the range 1.1 (Cd, Cu) and 3.3% (Co)) - Sampling rate 48 h^{-1}	[6]
FI with preconcentration-ion pair chromatography	Co, Ni, Cd and Mn	River water	- Using cellulose functionalised sorbent Cellex P for preconcentration - Post column derivatization with PAR - Spectrometric detection at 510 nm - Preconcentration time 25 min	- DL at sub $\mu g\ l^{-1}$ level	[7]

Table 1.2 Summary of analytical methods for determination of Cd, Cu, Pb and Zn with preconcentration/sample pretreatment (continued)

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
FI-Spectrometric detection	Cu	Plant digests and natural water	- Chelex-100 resin mini-column for preconcentration	- DL=0.09 $\mu g\ l^{-1}$ - %R=95-104	[39]
FI with photometry	Cd, Co, Cu, Ni, Pb and Zn	Drinking water, surface water and waste water	- Reaction of catins with dithizone at pH 6	-160 µl: 20 samples h^{-1} - 210 µl: 16 samples h^{-1}	[41]
FI-MPT with column preconcentration-AES	Cd, Cu, Mn and Zn	Water	- Using thiol resin microwave plasma torch (MPT) - 1.0 M HCl for elution - Sample uptake 1.2 ml min^{-1} - Sample pH 9	- DL=3.6, 2.2, 3.1 and 1.8 ng ml^{-1} for Cd, Cu, Mn and Zn - Enrichment factor (EF)= 4.2-4.9	[48]
FI with preconcentration-FAAS	Cu, Zn, Cd, Mn and Ni	Water sample	- Using pore glass based iminodiacetate resin compare with pore glass 8-hydroxyquinoline (CPG-8-HQ) resin	- Sample throughout 12 h^{-1} - %R=64-100	[54]
FI with preconcentration-FAAS	Zn	Water sample	- Dialkyldithiophosphates (DDP) complex with Zn	- Enhancement factor=35 - DL (3σ)=0.5 $\mu g\ l^{-1}$	[55]
FI with preconcentration-GAAS	Cd, Pb, Cu and Ni	Sea water	- Formation of metal-DDC complexes and sorption on the RP-C18 - Ethanol for elution	- Calibration range 0.1-0.3 $\mu g\ l^{-1}$ Pb, 0.01-0.03 $\mu g\ l^{-1}$ Cd, 0.2-0.6 $\mu g\ l^{-1}$ Ni, 0.1-0.3 $\mu g\ l^{-1}$ Cu at sample volume 3 ml	[56]

Table 1.2 Summary of analytical methods for determination of Cd, Cu, Pb and Zn with preconcentration/sample pretreatment (continued)

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
FI with preconcentration FAAS	Cd	Biological material	- Mini-column packed with polyurethane foam - 0.1 M HCl for elution	- DL=0.027 μg l^{-1} - LR=0.91-3 μg l^{-1} - pH range 6.50-9.25 for sample solution - Preconcentration factor=41	[57]
FI-ICP-MS	Mn, Co, Ni, Cu, Zn, Cd and Pb	Sea water	- 8-hydroxyquinoline immobilized on silicone tubing (Sil-8HQ)	- %R=35-90 - DL in ng l^{-1} range	[58]
FI-ICP-MS	Cu, As, Se, Cd, In, Hg, Ti, Pb and Bi	Water and biological material	- Analyte complexed with ammonium salt of o,o-diethyldithiophosphoric acid in HNO_3 on C18-mini-column - Methanol as eluent	- Enrichment factor in range 5-61 depend on analyte - LOD varied from 0.43 ng l^{-1} for Bi to 33 ng l^{-1} for Cu - Sample consumption 2.3 ml and sampling frequency 21 h^{-1}	[59]
FI with preconcentration-FAAS	Cu, Zn, Pb and Cd	Sea water	- Chelating exchanger column (Chelex-100, 50-100 mesh) - 2.0 M HNO_3 for elution	- DL=0.07, 0.03, 0.50 and 0.05 μg l^{-1} for Cu, Zn, Pb and Cd - Degree of preconcentration ranges 50-105 fold - Sampling frequency 60 sample h^{-1} - RSD=1.2-3.2% at μg l^{-1} level	[60]

Table 1.2 Summary of analytical methods for determination of Cd, Cu, Pb and Zn with preconcentration/sample pretreatment (continued)

Technique	Analyte	Sample	Condition	Analytical Characteristics	Ref
FI-with preconcentration-FAAS	Cd, Pb, Cu	Synthetic sea water and drinking water	- Micro column packed with bonded silica with octa decyl functional groups - Complexed formation of diethylammonium diethyldithiocarbamate - Sample loading time 20 sec at flow rate 3.3 ml min^{-1}	- DL (3σ)=0.3, 3, 0.2 µg $l^{-1}$for Cd, Pb and Cu - Enrichment factor 19-25 for Cd, Pb and Cu - Sampling frequencies 120 h^{-1} - Precision=1.4, 1.0, 1.3% (RSD) for Cd, Pb and Cu - %R=95-102%	[61]
FI with column exchanger -AAS or spectrometry	Fe, Cu, Zn	Multi-vitamin tables	- Chloro-complex with cations - Thiocyanate complex with Fe - 480 nm for Fe - 0.1 M HNO_3 for elution	- % RSD=2.5-4.2 - Accurate relative error<2% - Linear range= 0.83+0.08 μg^{-1} for Fe, 0.32+0.03 μg^{-1} for Cu and 3.87+0.12 μg^{-1} for Zn	[62]
FI-chemiluminescence detection	Cu	Sea water	- Reaction of Cu with 1,10 phenanthroline	- DL=0.1 nM - LR=1.3-3.1 nM	[63]

1.4 Liquid-core waveguide sensor

A liquid-core waveguide (LCW) can be made from tubing in which the wall material has a lower refractive index than the liquid-core material. Under this physical condition, it is possible for light to be launched into the core of the waveguide and be guided over a significant length. A commercially available material capable of guiding light through water is the amorphous copolymer of 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole. This material, trade named Teflon-AF 2400, has been investigated as an aqueous-core optical waveguide because the refractive index is n=1.296 and the polymer will support internal reflection from aqueous solution (water, n=1.333). Teflon-AF 2400 is quite physically and optically stable and is transparent in the spectral range from 200 to 2000 nm [64].

Teflon-AF 2400 has been used as either a LCW or liquid waveguide capillary cell (LCW) for absorbance spectroscopy [65], fluorescence [66,67], liquid chromatography [68], gas chromatography, an Raman spectroscopy [69-71], and used as a Raman detector for liquid chromatography [72-74]. The major advantage of using an optical waveguide for Raman spectroscopy is that the signal is significantly enhanced by integration of Raman scattered light along the length of the waveguide.

1.5 Aromatic compounds (benzene, toluene and xylene) determination and analytical methods

Benzene, toluene and xylene are increasingly ubiquitous contaminants in ground and surface water, entering the aqueous environment as industrial effluents, municipal waste discharges, atmospheric fallout, and accidental and intentional spills. Because these compounds are known to be toxic to humans, their sensitive and rapid determination is of critical importance [75].

Available drinking water standards, relevant physical and chemical characteristics, common fuel oxygenates, and the aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylene isomer (BTEX), are presented in Table 1.3.

BTEX properties are presented for comparison since these compounds are the most soluble compounds in gasoline. When gasoline comes into contact with water, the fuel oxygenates will rapidly partition out of the fuel and into water because of their high aqueous solubility [76].

Table 1.3 Drinking water standard and aromatic hydrocarbon[a]

Compound	Drinking water standard[b] (μg l^{-1})	Aqueous solubility (mg l^{-1})	Vapor pressure (mm l^{-1})
Benzene	5	1780	76-95
Toluene	1000	535	28
Ethyl benzene	700	161	9.5
Xylene isomers	10000	146-175	6.6-8.7

Source: Properties of common fuel oxygenates and aromatic hydrocarbons are summarized from NSTC (1997) and Conrad (1995). Drinking water standard is from US EDA (2000).

[a] Parameter values are at 25°C unless otherwise noted

[b] US Environmental Protection Agency maximum contaminant level

Established methods for determination of aromatic compounds such as benzene, toluene and xylene contaminants in water include liquid-liquid extraction, solid phase extraction, solid phase microextraction, purge and trap gas chromatography and headspace gas chromatography [77]. While these methods exhibit high levels of sensitivity and selectivity, they still require relatively well-trained personnel for their successful operation. Specifically, when samples are taken for analysis the operator must be highly trained in the correct procedures for obtaining a representative sample. If the sample is improperly collected, leading to a non-representative sample, or if it is mishandled, leading to contamination and/or loss of analyte, the analytical result obtained using the best instrumentation is inevitably wrong. A related consequence of collecting and transporting samples is that the technique is both time and labor intensive. On this foundation it is evident that analytical technologies which are capable of achieving in-situ real time analysis of contaminants are needed [75]. Most extraction schemes are largely based on the relative solubilities of analytes and interferences in the two partitioned phases. Because an extraction phase is generally non-reflective, coextraction of analytes and interference may occur [78].

Reversed-phase liquid chromatography (RPLC) is a very popular separation and analytical technique employed in almost every chemistry laboratory worldwide. However, a mixture of relatively polar organic solvent and water (eg., methanol/water or acetonitrile/water) has to be used as the mobile phase in RPLC. Therefore, the major disadvantage of RPLC is the need for organic solvents that are expensive, are potentially harmful to the operator and the laboratory environment, and need to be disposed of [79,80].

Raman spectroscopy (RS) is a powerful analytical tool, which provides detailed vibrational information, as does fourier transform infrared (FT-IR) spectroscopy, and therefore has a high analyte identification potential. In contrast to FT-IR, it can easily be used for aqueous solutions, and is therefore suitable for biological samples. However, RS suffers from an extremely low sensitivity [73]. Raman scattering is a very week phenomenon; approximately 1 in 10^7 photons is scattered at an optical frequency different from that of the source radiation. RS is a particularly strong candidate for detecting BTEX analytes in water because it offers a high degree of selectivity (in contrast to visible absorption and fluorescence) and is compatible with aqueous matrixes (in contrast to infrared absorption). A problem with RS is that it is a weak process, resulting in relatively low-intensity Raman signal and poor signal-to-noise ratio of the Raman spectra. Various methods have been used to combat this problem, including resonance Raman scattering (RRS), and surface-enhanced Raman scattering (SERS) [72]. One way to increase the amount of the scattered light in conventional RS is to increase the absolute number of the Raman scattering centers by sampling more molecules within the excitation laser beam. The latter could be achieved by using liquid-core optical fibers.

1.6 Research aims

The aims of these studies are as follows:

1. To study preconcentration of some cations such as cadmium, copper, lead and zinc at trace levels by an in-valve ion exchanger mini-column in a FI system

2. To apply FI-in-valve column pretreatment with ion chromatography for determination of cadmium, lead and zinc

3. To develop a novel Raman liquid-core waveguide sensor as a preconcentrating column and flow cell for benzene, toluene and *p*-xylene

1.7 The relevance of the research work to Thailand

The research work concerns development of analytical instrumentation and methods with cost-effective approach. Analytical instruments are imported with high costs. Attempts were made to develop on-line sample pretreatment with simple instrumentation so that less complicate instrument can be utilized.

A simple flow injection (FI) system with in-valve mini-column using either very simple atomic absorption spectrometry (AAS) or a simple ion chromatography (IC) provides alternative economical procedures to determine some inorganic toxic elements namely cadmium, copper, lead and zinc in water or zinc ore samples.

A novel simple FI pretreatment for Raman spectrometric determination of some potentially carcinogenic substances in water namely, benzene, toluene and xylene has been developed and provides an alternative fast procedure.

The development of cost-effective approach using the FI systems is easily automated, and eliminates costly and time-consuming off-line operations.

The developed instruments and procedures are suitable for Thailand and elsewhere.