A review of Flow Injection Analysis Atomic Absorption Spectrometry Hyphenated Systems (part I)

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Abstract
This paper present a general review for chemical literature concerning the hybradised (FIA –AAS) system scanned over the years late 1970s to late 1994 and including lots of technical innovation and developments of this coupled system which typically utilise the adequate precision, sensitivity and specificity (AAS) on one hand and simplicity high sample through put and economy of (FIA) on the other hand. It is worth mentioning that a relatively large percent of present publication of the system were abstracted from INTERNET.

Introduction
Many reviews and books of flame and flameless atomic absorption spectrophotometry (AAS) of elements and (indirectly) compounds (1-4) have been published annually. On the other hand reviews covering publications of flow injection analysis (FIA) are growing steadily (5,6). AAS is well known as specific and selective technique compared with FIA which fast better through put and economical, simple and more easily hybridize able with other techniques such as AAS, ICP/AES, electrochemical and spectrophotometry.

Since the beginning of the eighties many experimental attempts were made to exploit the useful characteristic of these two complementary techniques as a robust micro analytical tool.

Recently a number of publications appeared in many analytical Journals (7) dealing with determination of a variety of substances using FIA-AAS system (8) from which one can deduce the suitability of this hyphenation, the present paper describes in details the overall review of the AAS- FIA combined technique right from the point of its appearance in 1979 till August 2002

1- Atomic Absorption Spectrometry (AAS)
measurement of atomic absorption of element could be classified into:

a) Flame atomic absorption where chemical flames (2) are used as a source for atomization.
b) Flameless - AAS which is either cold atomization where no heating is required to liberate atomic vapours but chemical reduction with reducing agents such as NaBH₄ or SnCl₂ is used. Or electrothermal atomization ETA-AAS where atomic vapour is produced by Ohmic heating of elements.

c) Hydride generation (HG) where the vapour of metal hydride is generated chemically and then swept into a heated absorption cell to obtain the free atoms through which the resonance line of element is passed where atomic absorption is proportional to concentration.

II- Flow injection analysis (FIA):
Flow injection (9-11) analysis (FIA) involves the introduction of a sample (Typically 50 µL) in a flowing stream of liquid (1 ml / min) in narrow bore (0.5 mm) non wetting tubing for quantitative analysis. A peristaltic pump is generally used to transport the liquid in a laminar flow pattern. A detection system which is used to measure the analyte concentration may virtually any instrument. An autosampler is often used to inject the samples into the flow stream. It is desirable to ensure good mixing by cooling the tubing tightly or packing the tubing with beads to produce a packed - bed reactor. The dispersion (D) of an FIA system is usually quantified by the ratio of the analyte concentration injected (C₀) to the analyte concentration at the peak maximum (Cₚ).

\[ D = \frac{C₀}{Cₚ} \]

The dispersion of an FIA system may be controlled experimentally by variation of several design parameters. E.g., D increases with tubing length, tubing diameter and the flow rate and decreases with volume injected, tight coiling and packing with glass beads.

III- FI - AAS Hyphenation
FI has been widely employed with flame AAS as a method for preconcentration since the early 1980s because of its compatibility with Continuous - flow system.

The combination of FI with GFAAS did not occur until the late 1980s but since then a number of publications have appeared in recent years. The interest in FI-AAS may be related to the ability to do automated preconcentration steps and to the availability of commercially available FI system (Perkin - Elmer, Norwalk CT) with use with AAS instruments (6,12).

An excellent practical guide to FIA-GFAAS hyphenated technique is written by Butcher and Sneddon (4) with references as early as 1997.

An example of an FI-GFAAS manifold and its automated operation for GFAAS for the preconcentration of Pb is shown in (Fig-1) and table (1). FI provides a convenient method for automated sample preconcentration, with typical enhancement factors of 20 to 50. FI has also been used with GFAAS as an interface for sample introduction into the furnace (2). One interesting applications of FI involves its coupling with in situ trapping of volatile hydrides in a graphite tube (7, 14) FI - HG- AAS system.

<table>
<thead>
<tr>
<th>Step</th>
<th>Duration</th>
<th>Pump</th>
<th>Function</th>
<th>Medium Pumped</th>
<th>Flow rate, mL/min</th>
</tr>
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<tbody>
<tr>
<td>a</td>
<td>10</td>
<td>1</td>
<td>Dispense eluate from previous preconcentration into furnace</td>
<td>Air</td>
<td>0.8</td>
</tr>
<tr>
<td>b</td>
<td>20</td>
<td>1</td>
<td>Elution of residual analyte from previous preconcentration</td>
<td>Ethanol</td>
<td>0.5</td>
</tr>
<tr>
<td>c</td>
<td>60</td>
<td>2</td>
<td>Sample change</td>
<td>Sample</td>
<td>5.0</td>
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<tr>
<td>d</td>
<td>30</td>
<td>1</td>
<td>Column rising</td>
<td>DDC solution</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Evacuation of eluate collector</td>
<td>Water</td>
<td>1.6</td>
</tr>
<tr>
<td>e</td>
<td>30</td>
<td>1</td>
<td>Sample elution and eluate collection</td>
<td>Ethanol</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Lead was complexed with diethyl dithiocarbamate (DDC) on line and separated using a 15-µL C₁₈ Minkxolumn (195).

The hydride generation (HG) technique involves the conversion of the analyte to a volatile hydride with a chemical reagent (usually sodium borohydride) which is then swept into an atom cell (generally a heated quartz tube) where the molecule dissociates gas atoms. Elements that form volatile hydride include Sb, As, Bi, Ge, Pb, Sc, Te and Sn.

Other volatile molecules have been used for sample introduction by similar procedures including chloride, fluorides, B-diketones and dithiocarbonate. In addition aqueous Hg may be reduced to the metal (15, 16, 17).

Disadvantages of these conventional HG procedures include dilution of the analyte by...
carrier gas and H2 and low atomization efficiency in quartz tube.

The insitu trapping technique involves flow of hydride into a heated GF that serves to decompose the hydride and condense the analyte within the tube. Recently Hg- GFAAS has been reviewed (14).

Tao and Fang (18) employed FI–HG–GFAAS system for the determination of tin in hair, serum, tap water and geological SRMs. The tin hydride was collected on graphite tube coated with Pb.

FIA-AAS Hyphenated techniques

A flow–injection analysis system is described for the automatic determination Ca, Mg, K in plant material by (AAS) and (FIA) (19).

Flow rates and damping factors were studied, the sample undergoes a dispersion of Ca, 40- fold with automatic incorporation of lanthanum when necessary. The proposed method allows 300 determinations per hour with atypical RSD of 0.5% and a reagent consumption of only 500 µg of lanthanum per determination which is about 1% the usual amount. The results for plant digests agree with those obtained by the standard (AAS) procedure (Fig-2).

A flow injection technique with an organic solvent carrier stream is recommended for determination of trace elements by (AAS) carrier streams of methyl isobutyl ketone and especially n- butyl acetate are effective in enhancing sensitivity (20). The proposed method permits about 300 determinations per hour with a relative standard of less than 5%; Ateflon tube through which a carrier solvent flowed was connected to the nebulizer of the burner via the sample injector (Fig-3).

The use of an atomic absorption spectrometer as a detector in flow injection analysis is briefly reviewed (21) where a new simplified model is described for the dispersion effects observed with such systems. The model is based on considering the dispersion to be due to a single hypothetical mixing chamber locally immediately prior to the measurement stage. The utility of this approach is demonstrated for two methods of calibration commonly used in (AAS) and it is shown that flow injection sample and standard handling techniques are comparable to manipulation with volumetric apparatus. Results are presented for the determination of chromium in standard steels.

A flow injection analysis procedure for the determination of rare amount of mercury by cold vapor atomic absorption (CVAA) method is measured (22). In order to make efficient use of the (FIA) technique, a new flow cell was developed to permit a rapid separation of elemental mercury from the carrier solution. The design of this device is based on the permeability of Hgo in commercially available teflon (PTFE) tap which acts as a membrane phase separator.

The calibration curve is linear up to 70 ng/ml (r=0.9996) using 15 cm open cell approach, with a detection limit of 1.4 ng/ml considering a signal to noise ratio of three.

The standard deviation is S = ± 0.004 absorbance unit, the sampling rate was 110 samples per hour. (Fig- 4).

A flow injection technique was applied to hydride – generation (AAS) (23). For the present reaction gas segmentation was found to be effective in minimizing the broadening of a sample zone with out an increase of noise levels.

When 0.5 ml of samples was used, arsenic, antimony, bismuth, selenium and tellurium could be determined with the detection limits (S/N=3) at 0.04-0.3 ng and RSD% better than 2.5%. About 120 samples could be determined within an hour.

The utilization of gas diffusion flow injection analysis (GD- FIA) has been demonstrated as an effective technique to increase the selectivity and sensitivity of an analysis method (24). In conventional (GI-FIA) a liquid phase donor stream that contains the sample is passed under another liquid phase, the acceptor stream which either contains reagent or will merge with the reagent downstream. The phases are separated by a micro porous membrane. In this configuration and under the conditions used only gases diffuse through the membrane of the gas diffusion cell. Even the rates that the different gases diffuse are dependent on the membrane and the physical properties of the gases. These differences can be exploited to increase selectivity, (Fig-5) and (Fig-6).

A review (25) is presented of recent sampling techniques including flow – dynamic injection and standard addition techniques for (AAS). Step-wise techniques are also described as applied to dilution correction, titration, and incremental dilution. Stop- flow and fast response determination and scanning.

An automatic analysis constructed from (PTFE) tubing 1.5 mm is described (26) in which equal volume of the sample solution containing 0.1-2.2 H g/ml of NO₃⁻ or 0.5-10 H g/ml of NO₂⁻ and the carrier solution (aq-CuSO₄ solution, 0.15 M hydroxyl ammonium sulphate) and 5ml of phosphate buffer solution (PH 4.5) are mixed by
passing through a 900 mm coil and are then extracted in a 3-6 m coil by segmented stream (0.36 ml/min) of a solution of dimethyl 1, 10-phenanthroline in 100 ml of MIBK.

Detection limits were 0.04 µg/ml for \( \text{NO}_3^- \) and 0.4 µg/ml for \( \text{NO}_2^- \). \( \text{NO}_2^- \) can be oxidized to \( \text{NO}_3^- \) by Ce(V) or reduced to N by H2SO4.

A review (27) is presented of the application of flow injection systems in (AAS) with consideration of sampling calibration and preconcentration procedure and hydride generation and cold vapor (AAS) techniques. Flow injection atomic absorption spectrometry (FI-AAS) with air compensation was studied and compared with (FI-AAS) using solvent compensation with conventional (AAS) (28).

It seems clear that air compensation offers important advantages as the great increase in nebulisation efficiency improves the sensitivity and selectivity. The reproducibility obtained for both peak height and peak area is similar to or better than that obtained using other (FI-AAS) systems and comparable to the given by conventional (AAS). (Fig-7).

Various improvement in flow injection systems involving on-line separation and preconcentration by gas diffusion, ion-exchange and liquid-liquid extraction are reviewed and their merits are discussed (29). Different gas/liquid separation devices for hydride generation and cold vapor (AAS) are compared. For combination of column preconcentration (Fig-8) with hydride generation cold vapor (AAS) (Fig-9) for determination of ultratrace selenium and mercury. An on-line liquid-liquid extraction (FAAS) system capable of achieving 60-fold enhancement for lead is reported, the limit of detection is 0.02 µg/ml.

The combination of flow injection techniques with flame atomic absorption and emission spectrometry is reviewed (30), with particular reference to the more recent contributions. The considerable growth in the number of direct coupled preconcentration and matrix isolation methods is noted together with the increasing number of reports of indirect methods for metals, inorganic, anions and even drug molecules. The conflicting requirement of obtaining freedom from stable - compound interferences coupled with good detection limits are discussed as means of obtaining the best detection limits. Modification to nebuliser and spray chamber design are suggest for maximizing peak height and for working with reduced uptake rates (to reduce stable compound interferences in flame based spectrometries). The single well stirred tank model is used to model nebuliser response and results are presented for (FI) behaviors of a Philips scientific SP9 instrument under condition of low flow rate shown reasonable agreement with the model.

A review (31) is presented with 27 references of development application and benefits of cited techniques over conventional methods.

The optimization of liquid transfer from (FI) system to (FAAS) (32) was studied in respect of e.g nebulizer uptake rate (≤10 ml/min) carrier stream flow rate (0.2-6 ml/min) air and water compensation at low carrier flow rates, and the use of a flow spoiler Pb and Ca were used as test analytes. Flow compensation was not generally necessary. Insertion of the flow spoiler gave improved precision which was also obtained by addition of air compensation of the carrier flow as ≤0.4 ml/min.

A brief review (33) was presented with 30 references of flow injection techniques used in conjunction with (AAS). The possible benefits of flow injection sample introduction at reduced flow rates to reduce were studied. The best approach for optimum detection limits in flow injection sample introduction is to maximize the peak height and minimize noise. By generation of a volatile metal chelate in (FI) manifold for subsequent determination and with appropriate solvent extraction and heated tubing. It is possible to increase considerably the atomization efficiently over conventional nebulization.

The sensitivity of (FIA) - (FAAS) for Vanadium determination has been enhanced using an online, preconcentration ion-exchange column (34). Various silica bonded ion-exchange resins have been evaluated for the preconcentration and separation of vanadium ions. A suitable strong anion exchange column was selected and integrated into the flow injection system with subsequent vanadium determination by (FAAS) using adinitrogen oxide-acetylene flame. It was established that V(v) species could be preconed on the selected column and quantitative identified at 50 PPb level with a corresponding RSD of 3%

Trace a mounts of copper were determined by (FIA-FAAS) (35) after extraction of the Cu chelate with ammonium pyrrolidinedithiocarboxylate (APDC) present in a concentration of 1 mg/ml from 0.2 M acetate buffer at PH 5.05 into 4-methyl-2- pentanone.
The limit of determination was (2ng/ml) for the injection of 150 μL of the organic phase into a continuous stream of air as the carrier medium. The max throughput was about 40 samples per hour. The method was applied to determination of copper in water samples from power station cooling circuits.

An online column preconcentration technique for (FIA-AAS) was developed (36). Diverse metal ions (Cd2+, Zn2+, Cu2+, Mn2+, Pb2+, Fe3+ and Cr3+). In solutions were concentrated quantitatively by a micro column packed with muromac A-1, which is an iminodiacetate chelate resin in a flow injection system. From the PH dependence of the uptake of the ions all the divalent metal examd were recovered quantitatively in the PH range (3-5). The 3σ detection limits were in the range 0.14-2.1 μg/l and the RSD for replicate measurement (n=3-4) were in the rang (0.7-1.7)%. The method was compared with flame and graphite furnace at absorption spectrometry. Application to the determination of Cd and Cu in several standard references materials are described.

An efficient flow injection system with online ion-exchange preconcentration for the determination of heavy metals by (FAAS) is described (37). The system features low sample consumption of only 1.6 ml per determination and a high sampling frequency of 120/h which is comparable to conventional (FAAS). Enrichment factors (E.F) of 25-31 (concen. Efficiency=50-62 E/F/min) were obtained for Cu, Cd and Pb. RSD were used with high nebulizer uptake rats to improve the nebulization efficiency.

Different strategies for coupling flow injection manifold to (AAS) to obtain better sensitivity were compared (38). Using T- connector interface, different carriers and flow compensation solvents were assayed in an attempt to improve the sensitivity of (FIA). Manganese and copper determination in sewage sludge were used as a test system and the analysis parameter of both batch and flow injection methods were compared.

A procedure for the direct analysis of Ca, Mg, Na and K in water by (FIA) using (FAAS) or flame photometry was developed using a well-stirred dilution chamber to extend the calibration rang and both a double injection and the merging zone technique to add a La solution to samples and standards (39). The results from the analysis of real samples agree with those found by a batch flame at procedure. The use of the dilution chambers makes it possible to carry out the calibration using dilution profile of a single concentration standard for each element.

A micro column of activated Al2O3 in the basic form was used in conjunction with (FAAS) for the preconcentration and determination of Ag in borehole water (40). The Ag was accumulated on the Al2O3 column by pumping sample solution at PH=4 through the column at a rate of 5 cm3/min for 3 min. by incorporating an injection value and a simple interfacing device into the system. Ag was determined by elution into the nebulizer of an (AAS) with 500 μL of 2 mole/l HNO3. Regeneration of the Al2O3 to its basic form was achieved by 0.15 mole/l NH3. Solution pumped through the column at 5ml/min for 2 min. A detection limit of 4 μg/l was measured based on a sample volume of 25ml. The RSD was ±5% at concentration levels >10 μg/l.

The automation of (F1) system for hydride generation of selenium and its subsequent determination by (FIIAAS) is described (41). Pre-treatment of the sample and details of automated equipment are reviewed. For the (FIIAAS) Se analysis a volume of 350 μL of acid- digested sample solution is injected, the online generated hydride is delivered by the gas liquid separator and is transported together with an Ar stream to the heated quartz cell for the (AA) determination. The absolute detection limit is 35 Pg Se, the RSD 0.1 μg/l Se. The absolute detection limit in real biological samples is 110 Pg Se, the relative detection limit 0.31 μg/l Se.

The selectivity of immobilised 8-hydroxy quinoline for Pb to be improved by the use of making agent during preconcentration (42) prior to determination by (FAAS). Interference by iron, copper, aluminum and zinc is suppressed by including triethanolamine, thiourea as fluorid, acetylayaceton or cyanide in buffer masking agent. Species such as Fe or Cu can completely prevent the preconcentration of Pb. This is shown to be over come by using a buffer consisting of 0.2M boric acid 2% triethanolamine 2% thiourea and 2% acetylayaceton even when the interfering species is in a 200-fold excess over lead. Recoveries for tap water samples, to which various amount of Pb had been added, ranged from (94-108)% results of analysis of tap water sample using this method were in good agreement with those obtained by electro - thermal (AAS).
A fast and reliable procedure for the determination of total and free Ca in milk is described (43). The method is based on (FI) technique, total Ca is determined by (AAS) (422.7 nm) and free Ca by spectrophotometry (580 nm). Interference in determination of free Ca is eliminated by using a dialyser, which also separates the total and free Ca. The system is suitable for the simultaneous determination of total Ca (RSD% less than 1.3 %) for (1300-1500) mg/dm³ of total Ca, and free Ca (RSD less than 0.85) for (120-70) mg/dm³ in milk at a sampling. A procedure of determination glycine is described (44). The method is based on the reaction of the analysis with finely powdered. Solid Cu++ carbonate in a continuous flow assembly. The optimum experimental conditions of PH, Temperature, sample volume, flow rate, column length and internal diameter and linear range of calibration were standied. Interference from foreign substance that a company this amino acid in pharmaceutical formulation was studied and the method was applied to determination of glycine.

A rapid sensitive and selective method for the differential determination of Cr(III) and Cr(VI) in natural water is described (45). Cr(VI) can be determined directly by (FI) on-line sorbent extraction preconcentration coupled with (ETAAS) sodium dithyldithiocarbamate as the complexing agent and C18 bonded, silica reversedphase sorbent as the column material total Cr can be determined after oxidation Cr(III) and Cr(VI) by potassium peroxysulfate.

A 12-fold enhancement in sensitivity compared with direct introduction of 40µL samples was achieved after preconcentration for 60 Sec., giving detection limits of 16ng/l for Cr(VI) and 18ng/l for total Cr (based on 3 sigma). Results obtained for sea water and river water. RSD 10% in the range 100-200ng/l. The selectivity of the determination of Cr(VI) was evaluated by analysing spiked reference materials in the presence of Cr(III) resulting in quantitative recovery of Cr(VI).

Flow injection analysis is applied to sample introduction in conjunction with automated hydride generation and (AAS) for determination As and Se in environmental samples such as soil (46). Vegetation, water, sediments and industrial wastes. Large sample loop was used to provide high sensitivities with an absorbance of 0.4 for 10 ng/ml for both As and Se.

The detection limit for both As and Se are 0.3 ng/ml equivalent to 75 ng/g in solid sample. Precision is 2.6%, RSD results for standard reference materials agree closely with the certified value.

The subject of this study (47) was the behaviour of new high- pressure pneumatic nebulizer with a single- bore for the passage of both liquid (sample) and gas (nebulizing gas) streams used as a method for introduction sample in atomic spectrometry. As a standard for comparison we used a meinhard-type concentric pneumatic nebulizer and (FAAS) to obtain the analytical signal. The results obtained indicate that for the same liquid and gas flow, the new singlebore high-pressure pneumatic nebulizer generation aerosols whose primary and tertiary droplet size distribution are finer than those obtained with a meinhard-type nebulizer. This leads to higher values in total analyte mass and solvent mass transport rates while the characteristics of the analytical signal in (FAAS) are improved. The operating conditions under which the new nebulizer shows the greatest improvement in comparison with the meinhard type are: Low gas flow, high liquid flow and small outlet section.

An analytical method based on microwave decomposition and (FIA) coupled to (HGAAS) described (48). This is used to differentiate As(III), As(V) monomethyl arsionic acid (MMA) and dimethyl arsionic acid (DMA) from organo arsenic compound usually present in seafood, with out microwave digestion, direct analysis of urine by (HGAAS) give the total concentration of As(III), As(V) MMS and DMS. The max As concentration was found in the urine samples collected approximately between (4-17) hour after eting sea-food, however the ingestion of organoarsenic containing seafood such as crabshrimp and salmon showed no effect on the urinary extraction of inorganic arsenic MMA and DMA.

A continuous ppt system for indirect determination of reducing sugars in various types of wine (49) based on the classical reaction with Fehling’s solution is reported copper(I) oxide is precipitated by injection the Fehling’s solution in wire carrier, which is directly as pirated. This allows reducing sugar to be determined in the range 10-110 µg/ml with RSD of 2.7% at 50 glucose/ml. The proposed method requires a number of samples pretretments. The results obtained in the analysis of six white and red wine were critically compared with those provided by standard manual methods.

Arsenic is determined in environmental samples containing metal ions up to 10000 mg/l Cu,
200mg/l Pb, 200mg/l Fe and 200mg/l Ni by using (FL-HAAS) technique (50). In the presented sample preparation method arsenic is pre reduced and the interfering metal ions are precipitate. As signal depressions from metal ions are excluded, a detection limit of 1μg/l arsenic is achieved. The use of a permeation tube for the production of liquid stream calibration standards in the flow injection determination (51) of ammonia was investigated. By varying the flow rate from (0.5-4.0) ml/min calibration standards over the range (1.5-18) ppm could be product. The relation between concentration of the resulting solution and the reciprocal of flow rate was shown to be linear. The inherent high temperature dependence of release rate necessitated the tubes being used under thermostated condition. Two methods were investigated for determination of traces of beryllium (52). One was developed using polyethylene powder as absorbent for preconcentration of the stable complex from between beryllium and chrome azurin S. After elution the preconcentrated metal was determined by graphite furnace (AAS), with the analytical procedure developed for water analysis, detection limit of 0.8μg/l, RSD deviations of (2.5-4.1)% and recoveries of (92-104) % can be achieved for beryllium in tap water. A method has been developed (53) for determination of (In Hg) and methyl mercury (Me Hg) in sloublized tissues with continuous (FI-CVAAS) kidney liver and brain tissues were spiked with (Me Hg) and (In Hg) and solubilized at an elevated temp in solution containing 90g/l (NaOH), 2g/l L-cysteine and 4g/l (NaCl). Total Hg determination was achieved by continuous (FI-CVAAS) using an in let system. The yeast saccharomyces cerevisiae was covalently immobilized on controlled pore glass (CPG) using a modified method of enzyme immobilization (54). This species was packed in a mini-column and incorporated in FI manifold system for trace determination of some metals prior to quantification with (AAS). The possibility of using alumina loaded with 1-nitroso-2-naphthol-3, 6-disulphonate for the online preconcentration of Co2+ was investigated (55). The relatively high capacities of this simply and reproducibly prepared material and the absence of swelling complications allow for its effective use in a (FIA-AAS) system. In the time-based system with a 20 min.

preconcentration time a detection limit 0.44μg/l was obtained with a precision of 2.3% (RSD%) at the 10μg/l level. A 97% recovery was obtained for artificial ocean water spiked with 1μg/l of Co2+. The method was applied to the determination of Co in oriental tobacco leaves certified standard material. A survey is give over various methods for separation and enrichment of trace elements and their speciation aquatic media using membrane filtration (56). The methods are mainly used for three purposes: Studies of size distribution patterns for trace elements in order to estimate the association of the elements with suspended particles and soluble compounds of different nature. Preseparation interfering constinues of solutions to be analysed in continuous flow instruments. Separation and preconcentration of inorganic ions in membrane filtration cell with and without chemical reagents. To obtain calibration graphs a standard solution of the analyte was pumped using an increasing flow rate while pure water aspirated for compensation, through a T-piece. In this way an on-line concentration gradient was obtained and a constant flow was supplied to the nebulizer (57). The absorbance was monitored via a computer which facilitated data acquisition and handling. Two microwave heated digestion techniques have been tested with a view to the evaluation the effectiveness of wet decomposition procedures a high-pressure/ temp. focused micro-wave heated and an on-line microwave heated system (58). The efficiency of decomposition was studied using a number of biological reference materials as well as urine and sewage plant effluent. Oxidation reagents included mixtures of HNO3, H2O2 and peroxodisulphate. The residual carbon content of the digestate was determined coulometrically pressurized decomposition of a TFM-teflon vessel is the most effective procedure. Various methods of analyte preconcentration for (AAS) are a viable for trace metals in aqueous samples (59). Among the drawbacks of many of these techniques are the generation of hazardous or toxic wastes. Poor pre concentration efficiencies and cumbersome on-line implementation of the particular techniques. Preconcentration of trace metal by sorbent extraction utilizing a low injection method is
described. The detection limit using the (quinolin-3-01) (DDC) chelates are at low parts-per billion levels, with enhancement factors between 50 and 100. The combination of (FIAS-HG) and transversely heated graphite atomizer- (THGA-AAS) has been applied for the sensitives detection of organolead compounds(60) (e.g. detection limit of trimethyl-lead species (Tri ML): $32 \mu g/l$ for 0.5 mL sample loop in the presence of inorganic lead.
A mixture of hydrochloric acid and ethylene diamineterta- acetic acid (EDTDA) as carrier solutions in flow injection system suppressed interference of inorganic lead. Calibration with various organolead compounds in the range (0.25-8) $\mu g/l$ was carried out in the presence of $10 \mu g/l$ Pb+2 with out any interference; additionally statistical aspects of the determination of (TriML) have been studied.

Conclusions
The above list of references constitutes a selection of FIA – AAS habrised topics. This list is by no means comprehensive nor is the comprehensive bibliography which is designed to direct the interested reader to recent reviews. A multitude of reference still surround the coupling of micro processes of FIA – AAS. It is to be hoped that thoughtful research will help to ravel some of these very basic problems of hyphenation where AAS contributes to sensitivity and specificity and FIA to simplicity and specificity of analysis.

References

27. Fenxi, Z., (1986), Huaxue Tongbao, 14(7), 549-556.