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

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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 1995 to late 2002 and including lots of technical innovation and developments of the this coupled system which typically utilisese 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 mentioniny that a relatively large percent of persent publication of the system were abstracted from INTERNET.

الخلاصة

تستعرض المراجعة تحريات بحثية تتعلق بمسح شامل للادبيات التحليلية الكيمياوية المنشورة لتقنيتي الحقن الجرياني والامتصاص الذري المهجلتين وذلك ابتداء من 1995 ولغاية 2002 بشكل انتقادي تبرز فيه الملامح البناءه لاسباب الدمج بين هاتين التقنيتين بمنظومة موحدة تتضمن الجمع بين حساسية وخصوصية ودقة مطيافية الامتصاص الذري من جهة وسرعة وبساطة وخفض كلفة التحليل التي تتسم فيها تقنية الحقن الجرياني من جهة أخرى. كما تضمنت المنظومة المهجنة كل ما هو جديد ومنشور في المجلات والدوريات العالمية من تطورات وتحديثات وباسلوب يفسح المجال للباحث لتقصي الحقائق العلمية حولها وبدون عناء . ومن الجدير بالذكر ان نسبة كبيرة من مساحة المسح قد جرت بمساعدة الشبكة العالمية للمعلومات (انترنيت) الامر رفع عدد المراجع التي تمت مراجعتها. ونظراً لهذا العدد الكبير من المراجع وما احتوته من ايضاحات واشكال وجداول فقد اصبح من الضروري تجزئة الموضوع إلى جزئين متسلسلين ينشران تباعا كل مكنهما يعبر عن مرحلة زمنية معينة.

Introduction

In part (I) of this article the published literature concerving the hyphenated (FIA-AAS) system was reviewed up to late (1994); in present paper we are going to review the published literature from early (1995) forward, late (2002).

FIA – AAS Hyphenated Techniques

Das and Chatterjee determined the concentration of aresenite and arsenate in different samples of water used by peoples for drinking, cooking and other house hold purpose; also analysed large number of urine, hair, nail samples several skin scales and some liver tissues samples of the people drinking the arsenic contaminated water, and showing arsenical skin lesions, (FI-HGAAS) system have been used for their analysis (1).

An on-line column preconcentration technique for (FI-AAS) has been developed (2) for determination of trace metals in natural water. For 2nd samples, detection limits of 0.5, 5, 1.5, 1.6, 3.5, 0.6, 3.1 and 0.4 μ g/L for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn respectively were achieved. The precision obtained was in the range between 1-1 (Cd and Cu) and 3.3% Co. Accuracy was also investigated and results agreed with the certified values of the references material. The sampling rate was 48/hour. The method used to determination trace amount metals in natural water sample.

Analytical performance of (FI-FAAS) was evaluated in terms of precision and sensitivity (3). For direct aqueous-solution introduction and alcoholic-elute introduction after on-line sorbent extraction, the influence of the interfacing parameters was investigated, including the nebulizer uptake rate, sample-introduced flow rate and coupling tube length-high.

A sensitive method for the determination of strontium has been developed (4). In this work strontium was determined by (FAAS) using a continuous copreconcentration dissolution procedure based on the formation of lead sulfate followed by elution with hot (EDTA) solution. Manifold parameters and chemical condition are described in detail. A concentration factor up to 61 can be achieved at a sampling rate of (20-30)/h. The detection limit for strontium was 0.9 ng/ml (3 sigma) and the (RSD) was 3.5% (n = 8) at concentration level of 100 ng/ml.

The determination of salicylic acid was carried out by reaction of drug with CuCO3 entraped in a polymeric material in solid – phase reactor the released cupric ions were monitored by (FAAS) at 324.8 nm (5). The calibration graph is linear over the range 4.0-7.5 ug/ml of salicylic acid with RSD of less than 1.5% and sample throughput of 25/h. The influence of foreign compound was studied and the method was applied to pharmaceutical formulations.

The heavy industry on the murmansk region in Russia is releasing huge amounts of waste into the air, including heavy metals and sulphur compounds, a pilote study was carried out involving serum and hair samples from (11) persons monitored in Ivalo in (1982) and (1991) (6). Total Hg content determined by (FIA) and the amalgam system pointed to a decrease in concentration in the hair of inhabitants of Ivalo. No trend towards an increase or decrease was found in Cu and Zn concentration in hair and serum as determined by AAS. Selenium has been thought to act as an antagonist to the heavy metal Hg.

(FIA) offers some special possibilities for calibration in (AAS). One of these procedures the interpolative standard addition method (ISAM) has been eritically investigated and compared to conventional calibration procedure (7), both theoretically and experimentally using the influence of Al on the determination /Mg by (FAAS) as examples, it has been proved that in principle the (ISAM) is not able to correct the interference effects.

Two types of injectors are described for introducing solid sample as slurries in (FIA) (8). A time based and volume based injector based on multitube solenoid pink valves were built, both can be characterized as hydrodynamic injectors – reproducibility of the injections of dispersed solids (less than or equal to 150 μm) was tested with several concentration of slurry samples up to 30mg/ml, the injected volume was 1mL. For both injectors dye and slurry samples could be injected with good precision (RSD for the peak area less than 2%). Data analysis and operation of injectors were automated.

A method was developed for determination of V(V) in presence of V(IV) using FIA (9); in this method V(V) forms a colored complex with 4-(2-pyridylazo) resorcinal (PAR) while a complexing agent 1, 2-cyclohexane diaminetera-acetic acid. (CDTA) was added to mask the interference, from V(IV) in the sample.

The V(V) was determined in the range (0.05-1.5)g/l, RSD 0.1 g/l V(V) level (n=10) was 0.3%.

A calibration method known in (FIA) as a gradient ratio calibration method has been verified in respect of capability of applying to determination by (FAAS) (10). It has been revealed that the performance of this method is possible to be different and rather unpredictable if the interference effect occurs in the analysis system examined. The calibration procedure has been attempted to be improved by means of such approach as the integration of signals processed and the use of spectrochemical buffers.

The speciation of Cr(VI) in stainless-steel welding dusts have been studied. The approach used for the analysis of Cr(VI) and total Cr relies on (FIA) equipped with different sequential detectors (11).

The system measures Cr(VI) by colorimetry with (1, 5-diphenyl) carbohydriazide) and total Cr content by (FAAS). The extraction of the samples of welding-fume dusts is achieved in a buffer solution (acetic acid and sodium acetate at PH = 4). This extraction procedure gives 96% recovery of Cr(VI). The (FIA-AAS) system that has been described is also more sensitive, has a lower detection limit (0.005 μg/l) and gives a better precision (<1%).

The use of cellulose –sodium sulphate and/or thiourea mixture for the micro determination of Cd, Cr, C, Fe, Ni, Pb, Zn and VO2+ ion in Nile Sea and waste water samples at different PHs was carried out employing the (AAS) technique (12). The effect of concentration of sodium sulphide thiourea, mass of cellulose, shaking time and the PH values of the sample on the preconcentration were studied. The reaction mechanism of preconcentration of the investigated metal ions on cellulose is based on either adsorption co-precipitation of the sparingly soluble metal-sulphied or formation of thiourea metal cellulose complexes. The method is simple and easily applicable for the micro determination of nine heavy metal ions at ppb level in different water sample.

A small range of new commercially available chelating resins are compared with a resin prepared in-house in terms of their applicability for on-line precencentration and matrix separation (13). The flow injection manifold was designed for rapid matrix seperation and the resins were tested for the determination of Cu, Zn, Cd, Mn, Ni. The resin based on controlled pore glass was found to be better for this rapid procedure because it did not require conditioning. Although the polymer based resins had better capacities. The commercially available controlled pore glass based iminodiacetate (IDA) resin had a comparable performance to the in-house controlled pore glass 8-hydroxyquinoline (CPG-HO) resin. The (IDA) resin had a much higher capacity than the (8-HO) however as with all (IDA) based resins. The sample through put was (2/hour).

A simple and inexpensive procedure is proosed for extension of the dynamic range (FAAS) measurements using on-line dilution (14).

The proposed methodology is based on the use of a manifold with two coupled dilution chambers and a zone injection system. The samples are prediluted in a closed system which includes a variable volume mixing chamber (10-20ml) and two injection valves. The samples are injected through one of these valves and the other is employed to take 100 μl of prediluted samples which are then passed through a new dilution chamber volume (1-10ml) and aspirated by the nebulizer of the instrument. A third injection valve mounted in the last part of the manifold is used for the direct injection of diluted standard solutions. Various dilution factors are obtained, ranging from 2-130000 times thus extending the analytical range of Cu determination to more than 100000mg/L.

Another work reports on the development optimization and application of an (FIA) manifold to the sequential determination of Ca and Mg cations in haemodialysis solution (15). A tubular electrode sensitive to Ca and an (AAS) to measure Mg were used as detection process. The system includes a dialysis is unit to enable sample dilution since they presented high levels of the species to be determined. The system performance was optimized to obtain the maximum slop of calibration lines to Ca and Mg cations by means of the Taguchi Parameters Design (TPD).

A method for the determination of trace amount of Bismuth (FI-AAS) with hydride generation was developed (16). The introduction of 50 μl of sample and tetrahydroborate solution in HCl and aqucons carriers in merging zones manifold allows the formation of Bismuth in which is separated from the liquid phase in an on-line stripping-type generater/gas liquid seperatar. The calibration graph is linear from (0.1-100)ng/ml Bi with a detection limit (3 sigma) of 320 Pg/ml Bi, the RSD for 20 replicates varies from 10% for (0.1) ng/ml Bi to 1.9% for (100) ng/ml Bi, with an injection frequency of up to 150 sample per hour; Ni, Co, Ag, Hg, Se and Sb interfere, but they can be masked with a thiourea-KI solution.

In order to achieve areproducible on-line pretreatment of slurry samples in (FIA) the dispersion behaviour of these sample has to be examined (17). This paper reports the effect of flow rate and some configuration of reaction manifolds. The reaction manifolds were a straight tube and two helically coiled tubes with different aspect rates and spatial orientation. The slurry samples consisted of spheres of different densities suspended in a Triton X-100/water solution, the particle diameter (up to 75 um) were relatively large compared to the internal diameter of the tubing (0.75 mm), for the straight tube theoretical calculation were found to give a reasonable impression of the experimental flow behavior of the spheres.

FIA system based on on-line microwave assisted digestion was tested as a tool to-perform silicate rock dissolution in acid medium (HF+HNO3) (18).

A 50 ng portion of the powdered rocks was dispersed with the acid mixture and stirred for a few minutes using a (3.8) ml/min flow rate; the sample slurry was digested inside a microwave over for 10 sec. A 20 μl volume of the digested sample slurry was introduced to an aqucons carrier stream and mix with a reagent stream containing boric acid before introduction into the (AAS) system. Chemical variables were studied and the best conditions were obtained with (4 M HF + 1 M HNO3), Mg was selected as a test element. The developed procedure enable about ten samples to be analyzed per hour.

Levels of Zn, Cu and Fe were measured in blood serum samples (19) of 320 children, ages between (7-14) years, the metals were determined using (FIA-FAAS), there was a tendency for serum zinc (SZn) to increase with age. Serum copper (SCu) decreases significantly ($P<0.05$) with age in male children, whereas it increases in female children, the concentration of serum iron (SFe) tends to be lower than that reported in the literature. The study should include metabolic balance and associations between SZn, SCu, SFe and anthropometric variables (height, weight, body mass index and skin fold thickness).

A standard addition method in (FIA-AAS) has been described (20). The method was applied to determination of Ca in synthetic samples with and without chemical interference. The influence of parameters of how injection system was studied. The results showed that the proposed method was independent of such parameters. RSD% within and between analyses were found to be 1.61 and 1.8% respectively at the 1.5 ug/ml Ca level. The method used for determination of Ca in tap water.

Also (FIA-HAAS) method was developed for determining Se in human milk and whole blood (21), after microwave digestion of the samples. The sample (2ml human milk or 0.25 ml blood) was introduced into the microwave vessel with 1.5 ml HNO3 and 0.25 ml H2O2. The digestion was completed by heating to 140 degree (2-3) hour, Se(VI) was reduced to Se(IV) with HCl. The instrument for (FIA-GAAS) (concen. of reducing agent, and carrier acid, flow rate of argon carrier gas and sample volume injected) were optimized, detection limit = 0.23 ng/mL (assay) or 115 Pg Se (absolute) in biological samples (1.15 ng/mL milk, 10.4 ng/mL blood). The precision values were 5% milk, 4.0% blood, the accuracy was evaluated with 2 reference materials.

A simple, rapid and reliable method was developed for determination total Hg in biological samples (22). Samples were solubilized using tetramethyl ammonium hydroxide (TMAH). The organically bond Hg was cleaved and converted to inorganic Hg by on-line addtion of KMnO4. The decomposed Hg together with inroganic Hg originally present in samples was determined by (FI-CVAAS), after reduction to elemental Hg vaper using NaBH4. A sample throughput of 100 measurements per hour was achieved after 30 min. dissolution with (TMAH), RSD% or 20 ug/l Hg was 1.3% (n = 11) and limit of detection was 0.1 ug/l. (3 sigma).

A simple and convenient method has been developed for the speciation of inorganic Se in aqueous solution (23), using alumina microcolumn. Both Se(IV) and Se(VI) are retained on the micro column in widely PH range solution. The successive gradient elution of preconcentrated species with NH3, allows to different between them Se(VI) and Se(IV) were eluted with 1ml of mole/l NH3 and 6 ml of 4 mole/L NH3 respectively and determined by graphite furnace (AAS). The detection limit for Se(VI) is 0.8 μ g/ml and for Se(IV) 49 μ g/l. The method has been applied to the speciation of inorganic Se in natural water sample.

The flow injection calibration procedure has been developed to correct for interference in (FAAS) (24). For this purpose a sample and standard solution were injected one after the other into the carrier stream containing some reagents known to usually produce strong interference effects. Affecting the analyte in both zones to the same extent they were able to act as spectrochemical buffers. As an example Ca in synthetic samples containing Al, Ti and Fe ore samples was determined.

A new (FIA) manifold for rapid determination of chemical oxygen demand is presented and evaluated (25). The (FIA) manifold combines sample digestion by mean of an oxidant solution (potassium dichromate, mercury sulfate), and acid solution (sulfuric acid and silver sulfate) in a domestic microwave oven with the liquid-liquid extraction of Cr(VI) with tributyl phosphate (TBP). Finally the remain (non-reduced) Cr(VI) is determined in organic phase by (AAS). The application range extends from (40-1200) mg/l, whereas the lowest limits of detection and quantification are 13.5 and 45 mg/l respectively. The interference of Ci can be compensated for at least up to 10,000 mg/l Cl-. Up to 9 samples per hour can be analyzed.

A new (FIA) procedure is proposed for the indirect (AAS) determination the cyanide (26). The (FIA) manifold is based on the insertion of the sample into a distilled water carrier then the sample flows through a solid phase reactor filled with silver iodide entrapped in polymeric resin beads. The calibration graph is linear over range (0.2-6.0) mg/l of cyanide. ($r = 0.9974$), detection limit is (0.1)mg/l; the sample throughput is

193/h, RSD% (0.8%). The method was applied to determination of CN in commercial samples.

In other method the gas-liquid membrane separator achieves high measurement sensitivity and show a very fast response because of its minimum dead volume several reduction systems were used to reduction of As(V) to As(III) in the on-line arrangement (27). The best results were obtained using solution of 15 g KI in 100 ml of 6 M HCl at the reaction coil temp 60C° detection limit of 150 Pg for As (III), 80 Pg As (III+V) and sampling rate of 25 sample per hour.

Example of application of on-line (FIA-AAS) combination are presented for the trace heavy metal analysis of environmential and biological samples, the influence of various parts of flow injection system e.g. type of flow injection mode, seperation and preconcentration and detection mode on analytical signal is discussed (28).

The analytical performance of method for determination of hydride forming elements has been improved recently by development of procedures in which the hydride is trapped on the interior surface of graphite furnace atomizer. The relationship between detection limit and sample volume are proportional to sample volume determined (29).

A method has been developed for the trace determination of total and inorganic Hg in natural water by cold vaper generation trapping and atomization in graphic furnace by selective reduction NaBH4 and SnCl2 , indium, tungstate, zirconium coated graphite tube were investigated for preconcentration of Hg vaper (30), detection limits of 90 and 60 ng/l for total and inorganic Hg were obtained for a 1500 μl sample volume. The precision RSD% was between (0.7-2.1)%.

(FI-CV-AAS) method was developed to determine inorganic Hg and total Hg in mussel samples obtained from Galicia Coasts (31). The mussel samples were digested in a microwave over using an HNO3 /H2O2 mixture and then total Hg was determined using sodium borohydride as a reducing agent. In a separate subsamples following ultrasonic extraction in HCl medium inorgunic Hg was determined by selective reduction using SnCl2 in acid medium as reducing agent. The results revealed that the Hg contained in mussel samples was methyl mercury.

A simple, rapid, and reliable method was developed for determination of inorganic As in biological samples such as fish fillet (32), Inorganic As was distilled from the samples as AsCl3 with HCl. The separated inorganic As was determinaed by (FI-HGAAS) after prereduction with KI and HCl. The concentretion of As in samples were less than (0.1) mg/kg dry weight for fish fillet.

An on-line time based injection systems used in conjuction with (CVG-AAS) and microwave-aided oxidation with potassium persulfate has been developed for determination of different Hg species in fish-eggs (33). Oil samples, Inorganic Hg was determined after reduction with sodium borohydride, while total hg was determined after an oxidation step with persulfate prior to the reduction step to elemental Hg with the same reducing agent. A linear calibration graph was obtained in the range (0.1-2) ug of Hg2+ by injecting 0.7 ml of sample. The detection limits based on (3 sigma) of the blank signals were 0.11 and 0.12 ug/l. for total and inorganic Hg respectively. RSD of ten independent measurements were 2.8 and 2.2% for 10 ug/l and 8.8 and 9.0% for 0.1 ug/l amount of total and Inorganic Hg.

A simple and highly selective (FI) on-line preconcentration and seperation (FAAS) method was developed for routine analysis of trace amounts of Pb in biological samples (34). The selective preconcentration of Pb was achieved in a wide range of sample acidity 0.075 to > or = 3 mole/l NH3 on a micro column (142 μl) packed with a macrocycle immobilized on silica gel. The lead retained on the column was effectively eluted with an EDTA solution (0.03 mole/l, PH = 10.5).

A rapid and sensitive (FIA-AAS) procedure is described for determination of Fe, Co, Ni, Mg and Zn (35), based upon on-line preconcentration on a micro column packed with C-18 material, these metals were complexed with 5, 7-dichloro oxine from weakly acidic solution in flow system and absorbed on the column. The preconcentrated elements were eluted with acidified methanol $(PH \approx 2)$ and injected directly into the neubulizer for atomization in an air-acetylene flame to measurement. The retention efficiency >98%, resulting in sensitivity enhancement factor of 60, 80, 80, 80 and 60 for a 1 min preconcentration time for Fe, Co, Ni, Mg and Zn respectively. The respective detection limits were 4.0, 1.0, 0.5 and 0.5 PPb. The throughput of samples was 30/h with loading time of 1 min. The method was applied to Seawater samples.

A rapid and sensitive sorbent extraction (HG-FIA-AAS) method is described for determination of As(III) and As(V) based upon on-line preconcentration on a microcolumn packed with activated alumina (36).

In the present procedure these arsenicals are complexed with quinolin 8-01-5-Sulphanic acid from neutral solution in (FI) system and adsorbed on the column.

In this study strongly basic anion exchange fiber was selected as the absorption material concentration HCl as complex agent, dilute HCl as eluant. Volume- based elution technique was proposed method (37). The enrichment factors are 19, 17 and 15 (compared with 40 μl) sample. The detection limits for the Cd, Pb and Zn are 1.1, 8.2 ans 2.6 ng/l respectively.

In this study Zn is preconcentration from acidic medium (PH=3) as its thiocyanate complex onto a polyurethance foam minicolumn placed in the loop of a four-way rate (38). The elution step is performed with a stream of 30% acetone in 2% HNO3 and Zn displaced is introduced directly into the nebuliser (FAAS). 1 min was used and detection limits of 3.0 μg /l was achieved with a throughput of 40 sample/h, at concentration of 20 μg /l and RSD% of 2.5% was obtained. For determination Zn in natural water a precontration time of 3 min was employed and detection limit of 0.85 μg /l was obtained, the system was slow with a throughput of 17 samples/h. the RSD% at 10 μg /l was 6%.

An analytical procedure for the reliable determination of Sb in digests of liquid-rich environmental matrices in the low ng/l range based on (FI-HG-AAS) has been developed (39); aliquots (250-320) mg of dry samples were mineralized with 3ml HNO3 and 0.5ml of each sulfuric and perchloric acid in open digestion vessels mode of glassy carbon in a heating block.

Because (AAS) seems to be simple at first glance its forthcoming end and replacement by more exciting techniques has been forecasted more than once over the past 45 years (40).

A method was developed for the determination of Se in serum by (FI-HG-AAS) following microwave digestion of serum samples and reduction of selenate to selenite (41). Detection limit = 0.3 μg /l. The results from the analysis of two seronorm standard reference materials showed good agreement with the certified values. The method was used to analyze Se in Sera of A ustrian and Slovenian peoples.

A method for the rapid determination of Co at ultratrace levels was applied in flour and flour byproducts obtained from various types of wheat that includes on-line preconcentration (AAS) is proposed (42). Solutions in 0.1 M HNO3 of milled wheat fraction subjected to wet a shing are preconcentrated in a straight forward system by flow injection system by sorption on (RP-CIB) column following chelation, the eluent ethanol is carried by an air-stream and the chelate is eluted and collected in 500 μL (PTFE) autosample cup. The determination of Co features aprecision (RSD % 6) for 0.2 ng/ml.

A method was developed for the generation of (cold vaper) of Cd by means of (FI-CVHG) from aqueous samples (43), the determination being conducted with (AAS). The limit of detection calculated as concentration giving a signal = 3 times the standard deviation of the blank was 16 ng/l and RSD% was 1.4% for the concentration 2 μg /l and 3.8% for 0.1 μg /l.

A continuous (FIA-AAS) system was used to develop an efficient on-line preconcentration of iodide traces. Cr(VI) is introduced into the flow injection system and is reduced to Cr(III) in acid medium proportionally equal to the iodide present in the samples (44). The Cr(III) reduced by iodide on micrcolumn packed with apoly aminophaosphonic acid chelating resins, while unreduced Cr(VI) is not retained.

A rsenic present at 1 μg /l in Sea water, as the following species, As(III), As(V) monomethylarsenic, dimethylarsenic and unknown organic compounds, the potential of the continuous (FI-HG) technique coupled to (AAS) (45) was investigated for the speciation of these major arsenic species in sea water. Two different techniques were used.

A direct, rapid and sensitive method for the determination Fe(II) and Fe(III) in water samples by (FIA-FAAS) system, on-line preconcentration with 1, 10-phenanthroline as the complex agent was developed (46). Various parameters affecting the complex formation and its subsequent adsorption such as PH of the mixture solution 1, 10-phen. concentration sample flow rate etc. A good precision (RSD = 1.1%), n=10, high enrichment factor 19 and sample throughput 80/h with detection limit of 3 μg /l were obtained. The Fe(III) determination with the recovery (94-105)% was found.

A flow system for Cu on-line preconcentration employing a tannin resin prepared from Encalyptns Saligna Sm, with determination by (FAAS) is propsed (47). The manifold was designed by assembling an automatic injectorcommutator and a set of three way solenoid values which were controlled by a microcomputer. The analyte was concentrated by pumping the sample solution through the resin column during 60 sec followed by elution with 1 M HCl, RSD%=3% (n=10) for a typical sample presenting concentration of 21.75 ng/mL Cu detection limit of 1 ng/ml and enrichment factor of 10 times were also achieved.

Six extraction medium (acetic acid, EDTA, tetrabutyl, ammonium hydroxide, NaOHlH2O, acetonitrile/H2O) were tested for their ability to extract Sb and As from free Ze-dried poplar – leaves, pine shoots and spruce shoots as well as from a peat matrix (48); additionally the extraction efficiency of Sb and As in fresh and freeze-dried elder leaves was compared, total concentration of Sb and As of aliquots $\approx$220 mg, were analysed by (FI-HG-AAS) after open vessel digestion with adequate mixture of HNO3, H2SO4, HCl and perchloric acid.

An electrolytic hydride generation system for sample introduction in (AAS) is described (49). The system uses a tubular electrolytic flow through cell with a concentric arrangement and packed cathodemade of vitreous carbon, the large cathode surface area (about 120 cm3) give efficiencies in hydride production of > 90% for As(III), Se(IV) and Sb(III); sample can be introduced in both continuous and (FI) systems.

A simple and quick procedure has been developed for the on-line preparation of one phase emulsion in (FI) system for Cr determination by (ETAAS) with Zee man effect back ground correction (50). The entire (FI) system was controlled by compute independent of the spectrometer. The method provided a linear range of Cr from (7-50) μg /l and detection limit of 4.0 μg /l which corresponds to 6 ng/g. the results were precise (0.6-0.8)%, the recovery (99.2-102.2)%. The method described is satisfactory for determination of Cr in new and used Lubricating 0.1 samples.

A minicolumn packed with poly aminophosphoric acid chelating resin incorporated in an on-line preconcentration system for FAAS was used to determine ultratrace amount of Pb in mussel sample at μg /l level (51). The RSD% (2.3%) for 25 μg /l and 2% for 50 μg /l, the sampling frequency was 45/h. The method was highly tolerant of interference and the results obtained for the determination of Pb in a reference material, and to determination of Pb at ultratrace level in biological materials such as mussel sample.

A field flow preconcentration system for copper determination in sea water is described (52). Sea water samples are collected and preconcentrated in sitn by passing them using a peristaltic pump through a minicolumn packed with amberlite XAD-4 impregnated with the comlexing agent 1-(2-pyridylazo) –2-naphthol. The analytical figures of merit for the determination of Cu are follows = detection limit (35), 0.06 μg /l, precision (RSD) 1.2% for 2 μg /l, enrichment factor 30 using 25 ml of sample and 83 microl of eluent.

A method is described for the determination of As by (HG-AAS) using a mixed acid as a pretreatment (53). (HG) is done by (FI) method. The others investigated in detail the temperature and time of decomposition using inorganic, organic As and environmental standard samples, pretreated with nitricperchloric –sulfuric mixed acid. By using mixed acid as a pretreatment agent at 220°C. The decomposition time could be shortened and the blank value of As from the reagents used was reduced. The mixed acid was also found to be effective as a pretreatment agent for organic As compounds in which a dimethylated compound sodium of biological samples. (Fig-1).

Flow injection on-line preconcenration-graphite furnace (AAS) method was also developed for determination of Cd (54). Cd in samples was adsorbed on an iminodiacetate- type chelating agent resin and than eluted with 2 M HNO3. The eluate was introduced into the injection tip of an autosampler. The eluate zone with highest analyte concentration was injected into the graphite furnace by cooperation of a peristaltic pump and a syring pump of the autosampler which controlled by a programmable controller. (Fig-2)

Volatile species of Cu, Au and Tl were generated at room temp. by the reduction of NaBH4 using (FI-VG-AAS) system (55). The 1, 10-phenauthroline, Sodium diethyl dithio-Carbamate (DDTC) and palladium (or gold, platinum) were used as enhancement reagent respectively, palladium combined with Rodamine B showed Co-enhancement effect on gold. The normal (FI) peak shape was obtained and the sensitivities where enhanced by 1-2 magnitude. The detection limit of (0.3-24) μg /ml (3σ) were obtained with 300 or 500 μL sample solution. The precision of 2.6-1.8% (RSD%) were obtained with the sample frequencies of 120-180/h. The (FI-VG-AAS) method were used for the determination of Cu in hair and rice sample and gold in the ore sample digests. (Fig-3)

A (FIA) on-line clean-up system was developed for determination of trace Pt, Pd, Au, in presence of Na, k, Ca, Mg, Fe and Al ions by electrothermal (AAS) (56). A column packed with strongly acidic Cation exchange resin (type 732) was used as a clean-up column, As , Pt and Au ions can form strong complex anions with Cl- in HCl medium, they can be seperated from coexisting cation by passing through the clean-up column.

The experimental results obtained for trace amount of gold, in reference material were in good agreement with the certified value.

A sequential injection (SI) on-line matrix removal and trace metal preconcentration procedure by using a movel micro column packed with (PTFE) bead is described and demonstrated for trace Cd analysis with detection by (ETAAS) (57), the analyste is inialty complexed with diethyldithiophosphate (DDPA) and adsorbed on to the column which is after words eluted with 50 μl of ethanol and subsequently with sample pre-treatment in the (SI) system. No flow resistance is encountered at flow rate of 9 ml/min through the column. The detection limits and precision (RSD 0.1 μg/l Cd) at the same level 1.3 μg/l LOD, (1.3% RSD) for packed column and 1.2% ng/l LOD, 1.5% RSD% for knotted reacter.

An on-line inorganic (InHg) and organomercury (OrHg) species seperation, pre concentration and determination system consisting of (CV-AAS) coupled to (FI) method was studied (58). The (InHg) species was retained on a column (id 3 mm, length 80 mm) charged with a Dowex (1X-8 resin) particle size 50-100 mesh. as the anionic complex formed with methylthoymol Blue (MTB) at PH=6.3 previous oxidation of (or Hg) species permitted the determination of total Hg, the difference between total and (InHg) determined the (or Hg) content in the sample the inorganic Hg was removed on-line from the micro column with 3M HNO_3.

The Hg Cold vaper generation was performed in an on-line system with 7.0% (w/v) $SnCl_2$ and 20% (v/v) HCl as reducing solution. A pre concentration factor of 180 was obtained for the preconcentration of 250 ml of aqueous solution. The detection limit for (InHg) and (OrHg) was 0.8 ng/l. The precision for ten replicate determination at the 15 ng/l Hg level was 4.4% relative RSD% calculated from the peak height obtained. The calibration graph using the seperation and preconcentration system for Hg species was linear with a correlation coefficient of 0.9994 at levels near the detection limit up to at least 100 μg/l, the accuracy of the method was evaluated by the analysis of a certified reference material QC metal LL3 Hg in water.

Conclusion

The above list of reference constitutes a selection B of FIA-AAS habradised topics. This list is by no means comprehensive nor is the comprehensive bibliography which is designed to direct the interested reader to recent review. A multitude of references 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.

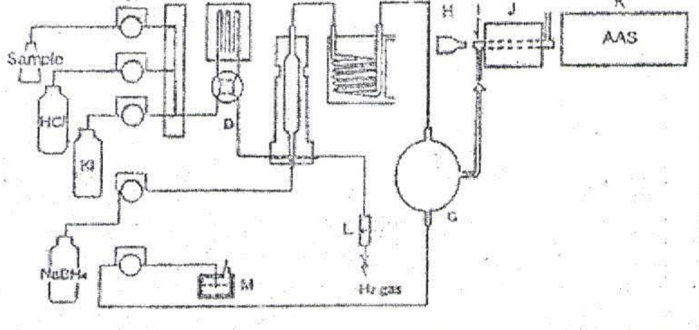

Fig. 1 Schematic diagram of the analytical apparatus: A, peristaltic pump; B, pre-mixer; C, pre-reduction furnace; D, switch cock; E, reactor; F, vapor-liquid separator; G, buffer tank; H, hollow-cathode lamp; I, heated quartz cell; J, electric furnace; K, atomic absorption spectrophotometer; L, flow meter; M, waste tank.

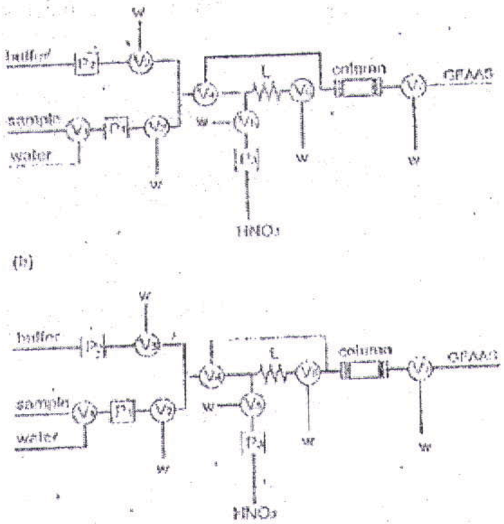

Fig. 2 Flow injection manifold for determination of cadmium by on-line preconcentration GFAAS analysis. (a) sample loading; (b) elution. V_1 - V_7, three-way solenoid valve; P_1 - P_3, peristaltic pump; L, eluent loop; w, waste.

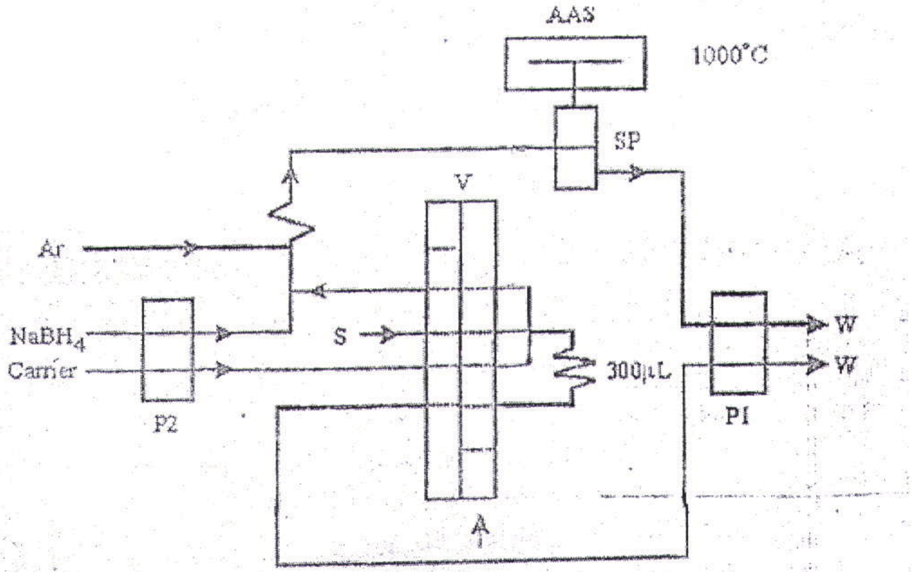

Fig.3 Manifold for the FI-VGAAS determination. The 300 mL sampling loop here is used for gold. For thallium and copper, the sampling volume were 500 mL. P1, P2, peristaltic pumps; AAS, quartz tube atomizer atomic absorption spectrometer; SP, gas-liquid separator; S, sample; W, waster; Ar, argon carrier gas.

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