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Flow Injection Analysis with Atomic Spectrometric Detection

(Review Article)

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Abstract

The combination of flow injection analysis with atomic spectrometry has considerably extended the capabilities of conventional atomic spectrometric methods in terms of efficiency, sensitivity, economy and freedom from interferences. These improvements are mostly related to the on-line sample pretreatment and the possibility of micro-sample introduction in the detection device. The basic concepts of flow injection analysis; the basic components of the flow injection manifold as well as the main applications of flow injection analysis are presented. Special emphasis is put on the coupling of flow injection analysis with detection devices based on atomic spectrometry – flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry. The possibilities and the restrictions of the separate combinations are discussed. Examples are given for the on-line flow injection separation/preconcentration-atomic spectrometric determination of a large variety of elements at trace- and ultra-trace levels in samples of complex matrix composition.

Keywords: Flow injection analysis, Atomic spectrometric detection, Knotted reactor

1. Introduction

The progress in trace element analysis of environmental and biological matrices is driven by three major factors: (i) the demand for quantification of an increasing number of elements at lower concentration levels; (ii) the interest in elemental speciation due to issues of bioavailability and toxicity and (iii) the need of minimizing contamination and sample manipulation.

Attempts to extend modern analytical methods to significantly lower detection limits are often fraught with problems of sampling and storage, on the one hand, and contamination from

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handling and reagents, on the other. There is a narrow link between the advances in instrumental detection capabilities and the methodology of sample pretreatment, which has encouraged the development of flow injection strategies through minimization and miniaturization of sample handling and pretreatment and its on-line implementation to the detection instrument. Complex chemical processing accomplished on-line alleviates the need for extensive and costly clean room facilities while permitting information to be obtained using small-size samples.

1.1. Flow injection analysis

Flow injection analysis (FIA) has now reached a well-established position in modern chemical analysis. It is recognized that FIA may serve as an interface between solution chemistry and analytical instruments. This is evident from the numerous (more than 15 000) monographs and papers [1] published since the first paper on FIA by Ruzicka and Hansen appeared in 1975 [2]. Three key attributes of FIA ensured its rapid development and wide acceptance: (i) the fundamental principles are easy to understand and implement; (ii) the instrumentation can be readily assembled from simple, inexpensive and accessible components and (iii) it provides a simple means of automating many manual chemical analytical procedures [3]. Practically, FIA can be coupled with all methods of detection that are used in contemporary chemical analysis.

2. Basic concepts of FIA

It is very difficult to give a precise definition of what flow injection analysis really is. Some authors [4] explain this by its high versatility, so that definitions are rapidly outdated by new developments. One of the definitions for FIA, given by Ruzicka and Hansen in their monograph published in 1988 [5] is: “A technique for information-gathering from a concentration gradient formed from an injected, well-defined zone of a fluid, dispersed into a continuous unsegmented stream of a carrier”. According to Ruzicka и Hansen, FIA is based on three main principles: (i) sample injection; (ii) controlled dispersion of the injected sample zone and (iii) reproducible timing of the movement of the injected zone from the injection point to the detector.

In 1995 Fang [4] emphasized on another characteristic of FIA, namely the thermodynamically non-equilibrium conditions, under which the processes are performed. According to Fang: “FIA is a flow analysis technique performed by reproducibly manipulating sample and reagent zones in a flow stream under thermodynamically non-equilibrated conditions.”

The simplest flow injection (FI) manifold, the single-line manifold, is represented on Fig. 1. It consists of pump, sample injector, reaction coil and detector. The pump is used to propel the carrier stream through a narrow tube. The role of the injector is to reproducibly inject a defined volume of sample into the carrier stream. The main function of the reaction coil is to promote reproducible radial mixing of two or more merged components through generation of secondary flows. The resulting species is sensed by the detector as a transient peak. The height and area of the peak are proportional to analyte concentration.

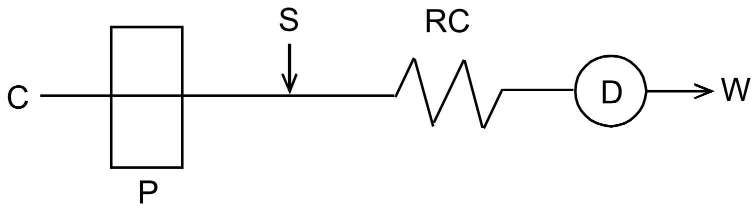

Fig. 1. Schematic diagram of a single-line FI manifold. P – pump, C – carrier stream, S – sample injector, RC – reaction coil, D – detector, W – waste

The flow injection manifold has become considerably complicate to fulfill the new requirements due to the expanded application of FIA. Thus, the basic principles of FIA should be understood in much broader sense, for example, sample injection should be understood as introduction of any liquid zone or series of zones into a flow by any reproducible means.

Dispersion during the transportation of a sample injected in a unsegmented stream of a carrier is the most important physical phenomenon in all flow injection systems. The specific feature of dispersion processes in FIA is that they are reproducible and controllable through the manipulation of flow parameters and geometrical dimensions of the flow conduits.

The dispersion process typical of FIA systems is shown in Fig. 2. The driving forces active in dispersion of the injected zone into the carrier stream are convection and molecular diffusion. Convection occurs as a result of (i) linear flow rate differences of fluid elements located at different points along the radial axis of the conduit and (ii) secondary flows created by centrifugal forces perpendicular to the flow direction in non-straight conduits. Convex parabolic front of the injected zone and concave parabolic tailing edge are developed with penetration into the carrier stream, the extent increasing with the distance traveled. The main experimental parameters influencing the dispersion of an injected zone are: sample volume, geometrical dimensions of transport conduits (internal diameter and length), configuration (straight, coiled, knotted) and flow rates of carrier and merging fluid streams. The dispersion of the injected zones increases with use of small sample volume, straight long transport conduit with large inner diameter and high flow rates. Thus, under the specific conditions applied in FIA and with a fixed conduit, the acting forces are well under control, so that no random turbulence occurs. As a result perfectly reproducible concentration-time relationships may be obtained, which provide the basis for obtaining reproducible readouts under the physically and chemically non-equilibrium conditions specific for FIA.

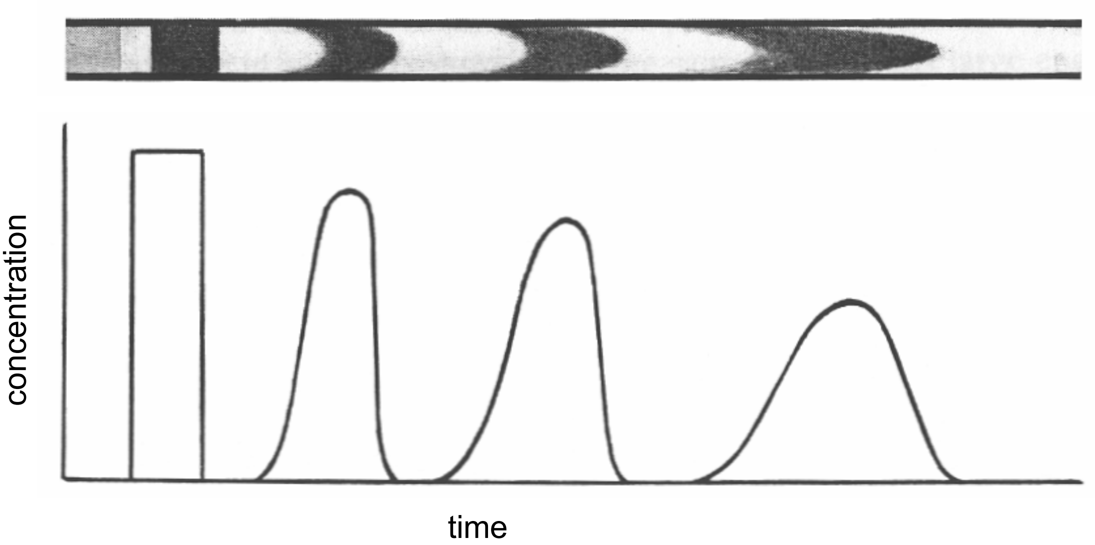

Fig. 2. Dispersion process of an injected fluid zone in an FI system

In order to provide a quantitative criterion to evaluate the extent of dispersion, Ruzicka introduced the term “dispersion coefficient, D” [6]. D is defined as the ratio of the concentration of the constituent of interest in a fluid element of the injected zone before and after dispersion, expressed by:

$D = C_o/C$,

where C_o is the original concentration of the constituent of interest in the solution before dispersion and C is its concentration in the fluid element of the dispersed zone from which analytical readout is extracted. When the fluid element with the highest concentration (peak maximum) is used for readout, the equation is:

$D = C_o/C_{max}$.

The dispersion coefficient is a dimensionless value equivalent to the dilution factor of the fluid element under consideration. D is therefore always greater than unity.

FI systems may be classified according to the value of their dispersion coefficient as: systems with limited dispersion ($D < 3$), medium dispersion ($3 < D < 10$) and large dispersion ($D > 10$). Limited dispersion is observed in FI systems where only transport processes occur. The use of these systems permits to achieve high sampling rates and sensitivity. FI systems with medium dispersion are designed for studies involving processes additional to the transport (usually a chemical reaction). Sample throughput and sensitivity are generally lower than for the previous ones. FI systems with large dispersion are characterized by a high degree of mixing between carrier, reagent and sample, resulting in a well-defined concentration gradient. Their application is restricted to FI titration and some other gradient modes of operation.

3. Basic components of the FI manifold

The main property of the FI instrumentation is the high degree of flexibility for solution handling. The FI manifold can easily be adapted to a variety of particular needs of the analyst. Many configurations of FI manifolds have been proposed in the literature and are reviewed in most of the monographs on FIA [4,5,7]. Basically the FI manifold consists of a propulsion device, an injection valve, transport conduits, connectors and mixing reactors.

3.1. Propulsion devices

Considering the versatility and precise timing features of FI systems, the general requirements to the propulsion devices used for FIA applications may be summarized as: short- and long-term reproducible flow rate, low-pulse delivery, multi-channel capability, easily adjustable flow rate for each channel and resistance to corrosive reagents and solvents. These requirements are not easily satisfied by the available equipment on the market but some of them are more adequate than others for specific applications.

The peristaltic pump is one of the most frequently used propulsion devices in the FI systems. Its main advantages are the multi-channel capabilities provided by parallel pump tubes and the accessibility due to its low cost. On the other hand, it suffers many limitations like relatively high pulsation and deficiency in long-term flow rate stability. However, most of these drawbacks can be avoided to give acceptable performance when the pump is used properly.

3.2. Injection valves

Initially, the reproducible introduction of a defined volume of sample into a moving carrier stream was accomplished by an injector. Nowadays the injector is replaced by an injection valve which enables additional manipulations to be performed, e.g., switching flows between conduits and changing flow directions.

The main requirements to the injection valves used in FIA are: multi-functionality, possibility for automatic control, solvent resistance and small dead volume. The most common valves are: the six-port rotary valve, the multifunctional eight-channel valve and the commutator valve.

3.3. Transport conduits and connectors

The transport conduits provide connections between the various components of the FI manifold. PTFE tubings of 0.35-1.0 mm i.d. are often used because of their inert properties. Tubings with bores less than 0.35 mm i.d. are seldom used, owing to the risk of blockage by accidentally introduced suspended particles in the flow stream. Tubings of over 1 mm i.d. are mainly used in systems involving high dilution factors or in systems with evolution of gases.

Connectors are used for connecting the tubes to different components of the FI manifold or prolongation of tubes.

3.4. Mixing reactors

Mixing reactors of various geometries can be used in a FI manifold. They can be classified into coiled reactors, knotted reactors and stirred chambers. The main function of coiled or knotted reactors is the promotion of reproducible radial mixing of two or more merged components through generation of secondary flows. Knotted reactors are widely used in the separation and preconcentration of trace elements. Mixing chambers are mainly used for FI titration and dilution.

4. Applications of FIA

The main applications of FIA are for sample digestion, sample dilution, separation and preconcentration of trace elements.

4.1. Sample digestion

Sample digestion constitutes an important part of sample pretreatment prior to AS detection of the species of interest and is often the rate-limiting factor on sample throughput. Digestion procedures almost always involve operations at elevated temperatures which cause operational difficulties in closed flow systems such as evolution of gases during digestion, high pressure build-up, and incomplete mineralization of the sample owing to the short reaction times and large percentage of non-absorbed power. This appears to be the reason for the rather late development of on-line digestion procedures [4]. Examples of FI on-line digestion can be found in [8, 9].

4.2. Sample dilution

Dilution is often a basic stage of the sample preparation process. It is necessary, for example, when AAS is used for detection because of its relatively narrow dynamic range – usually not more than three orders of magnitude. Although the different FI methods for sample dilution are based on different principles, there are some general features: (i) no volumetric glassware is involved in the dilution process; (ii) no precisely defined dilution factors are pursued but actual dilution factors may be evaluated when required; (iii) standard solutions for calibration are made to cover the concentration range of the undiluted samples since the calibration standards undergo the same dilution process as the sample; (iv) dilutions are performed on-line with the dilution system directly connected to the spectrometer [4]. A method involving FI on-line dilution is described in [10].

4.3. Separation and preconcentration of trace elements

Developments in analytical instrumentation allow trace and ultra-trace analysis in diverse kinds of samples. Despite these advances it is still often necessary to use separation and preconcentration procedures prior to detection. Preconcentration steps aim at reducing the limits of detection of the existing analytical techniques by removing interferences and/or increasing the concentration of the species of interest. Conventional preconcentration techniques, such as ion exchange, adsorption, extraction, coprecipitation, a.o., when operated in the batch mode, are time-consuming, labor-intensive, require large sample and reagent volumes and suffer great risks of contamination and analyte loss [11]. With on-line operation using FI techniques the drawbacks of batch-wise operation can be overcome to a great extent and currently on-line preconcentration may be achieved almost as efficiently as a simple AS determination, both in terms of sample throughput and reagent consumption. In fact, up to now the most dramatic improvements achieved in FI-AS have been in the field of on-line preconcentration.

A number of criteria can be used to better compare the efficiency of the different techniques and procedures. The most frequently used are: (i) the sample throughput, (ii) the sample consumption and (iii) the enhancement factor (EF) [4]. The latter is defined as the ratio of the concentrations before and after preconcentration. In practice EF is approximated with the ratio of the slopes of the linear sections of the calibration curves before and after preconcentration.

In FI preconcentration systems, samples may be introduced either on a volume basis or on a time basis. With volume-based sample loading, the amount of sample processed is determined by the sample loop and the filled sample is subsequently transferred from the loop by a suitable carrier. This approach is used when injection of a small defined volume of sample is required. With time-based loading, the amount of sample processed is determined by the sampling flow rate and the sampling time. The time-based loading is often used in separation and preconcentration FI manifolds as it is less time-consuming, easy to accomplish and permits handling larger sample volumes.

Liquid-liquid extraction is based on the distribution of the species of interest between two immiscible phases, usually aqueous and organic [12]. Although liquid-liquid extraction is a well-established procedure for separation and preconcentration of trace elements from a variety of samples, its adaptation to FIA was difficult. The first paper concerning FI liquid-liquid extraction was published in 1981 by Nord and Karlberg [13]. However, this kind of preconcentration systems has seen slow development. This seems to be a result of the difficulties associated with organic solvent manipulation, both in maintaining stable flows using conventional FI fluid delivery equipment, as well as in providing efficient and reliable phase separation. Examples for the FI on-line liquid-liquid extraction separation and preconcentration of traces of Ni and Cr can be found in [14] and [15], respectively.

Precipitation and coprecipitation performed off-line have been successfully used for matrix separation and trace element preconcentration with subsequent AS detection. The earliest attempts at using FI systems for preconcentration by precipitation with AS detection were made by Valcarcel et al. in 1987 [16] and the first report on coprecipitation appeared in 1991 [17]. Although preconcentration by on-line precipitation or coprecipitation is equally feasible, the precipitation approach is limited by the relatively small number of available selective precipitation reactions which produce precipitates with sufficiently low solubility products to fulfill the requirements of trace analysis. The analytes are usually precipitated as hydroxides [18,19] or organic compounds [20,21]. Coprecipitation methods are less demanding on the solubility of the precipitate formed, since trace analytes may be also precipitated by adsorption, occlusion and formation of isomorphic crystals through the use of an appropriate precipitate carrier. Therefore, coprecipitation is more universal with less interferences from coexisting constituents. However, the adaptation of coprecipitation procedures into FI systems was rather late. The reason for this delay was probably the difficulty associated with the manipulation of a relatively large amount of precipitate in a continuous flow system [4]. Filters [20,22] initially used for precipitate collection have limited capacity and the collected precipitate caused pressure build-up. Such difficulties have been overcome to a large degree through the implementation of knotted reactors (KRs) as filterless precipitate collectors which feature relatively large collection capacities and low flow impedances. The main mechanism of collection was assumed to be the development of a sustained centrifugal force in the stream carrying the precipitate, as a result of secondary flows created in the reactor. Apart from precipitate collection, the reactor also ensured rapid mixing of sample and reagent solutions and limited dispersion of analyte following dissolution when transported to the detector [12]. KR FIA-AS has been successfully utilized for separation and preconcentration of Pb [17], Mo [23], As [24], Se [25], Cd, Co and Ni [26], Cd, Ni and Pb [27], Cd, Cu, Fe and Pb [28], Cd, Cu, Fe, Ni, Pb and Zn [29], coprecipitated with organic, e.g., (Fe(II)-hexamethylenedithiocarbamate (Fe(II)-

HMDC) [17,26], Co(II)-pyrrolidinedithiocarbamate (Co(II)-PDC) [29], Fe(II)-PDC [23], Cu(II)-diethyldithio-carbamate (Cu(II)-DDC) [27], Ni(II)-DDC [28]) or inorganic ($La(OH)_3$ [24, 25], $Hf(OH)_4$ [24]) precipitation agents.

Solid phase extraction in miniature columns packed with various sorbents has been used most frequently in FI on-line separation and preconcentration techniques. The advantage of on-line sorption column systems is the relative ease of operation and the robustness of the equipment, when compared to on-line liquid-liquid extraction systems. The large choice of sorbent materials along with various chelating reagents and eluents made the solid phase extraction technique very attractive. However, some flow instability can occur due to flow impedance of packed columns particularly when using fine-particle packing. In some cases drawbacks such as sorbent volume changes (swelling or shrinking at different experimental conditions) and limited number of sorption/elution cycles, have been observed [30].

There are many published papers dealing with a large number of sorbents modified with different reagents for higher selectivity, as well as sorbents used to retain already formed complexes. C_{18} (octadecyl bonded silica gel) has been most frequently used to retain organic metal complexes. Successfully used complexing agents were dithiocarbamates (DC) [31], 5,7-dichlorooxime [32], 1-nitroso-2-naphtol [33], O,O-diethyldithiophosphoric acid [34-36], a.o. Microcolumns of pure alumina [37] or alumina modified with 2-nitroso-1-naphtol [38], DC [39] have been also used. Fullerenes (C_{60}) [40] have been used to sorb metal complexes with DC and 8-hydroxyquinoline (HQ) [41,42]. Microcolumns of cellulose modified with oxime [43], 2,2'-diaminodiethylamine [43], or 8-hydroxyquinoline-5-sulphonic acid [44] have been applied to element separation and preconcentration. PTFE turnings packed in a mini-column have been used to retain DC complexes [45]. TiO_2 nanoparticles modified with 1-(2-pyridilazo)-2-naphthol [46]; polyurethane foam [47,48] modified with 2-(2-benzothiazolylazo)-*p*-cresol [49]; ion-exchangers with iminodiacetate functional groups such as Muromac A-1 [50-52], Chelex-100 [53,54], Toyopearl AF-Chelate-650 M [8,55], as well as cation-exchange – Type 732 [56], AG50W-X8 [57] and anion-exchange – Dowex 1-X8 [58,59] resins have been also used for separation and preconcentration purposes.

As mentioned above, a knotted reactor (Fig. 3) made from Microline tubing by tying interlaced knots was first introduced as a filterless collector of organic precipitates in on-line coprecipitation-dissolution for FAAS by Fang and co-workers [17] to overcome the difficulty associated with the manipulation of a relatively large amount of precipitate in a continuous flow system. Later on, in 1994, the same authors have found that metal complexes could be retained on the inner walls of a PTFE KR without precipitate formation [60]. Scanning electron microscopic observation of the KR wall surface were made [60] to verify that the retention mechanism of the Cd-DDC complex formed on-line was different from that of a coprecipitation system using an Fe(II)-HMDC collector (see Fig. 4): no observable particles were found on the KR walls for the Cd-DDC under 200-fold magnification while precipitate particles were obvious for the Fe(II)-HMDC coprecipitation system. It was assumed therefore, that the retention of Cd-DDC on the KR walls takes place through molecular sorption. The retained Cd-DDC was eluted with IBMK and the eluate was analyzed by FAAS. 30-fold preconcentration of Cd was registered as an evidence for the presence of Cd-DDC on the inner walls of the KR. Since this first study, the KR has been extensively and successfully investigated as sorption medium in on-line FI preconcentration coupled with AS.

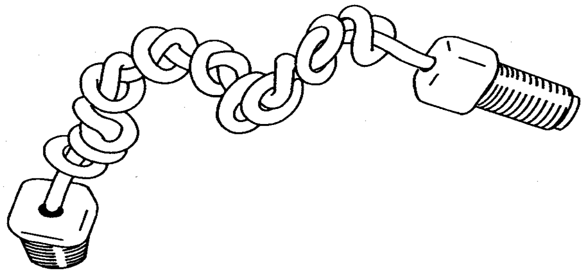

Fig. 3. Knotted reactor

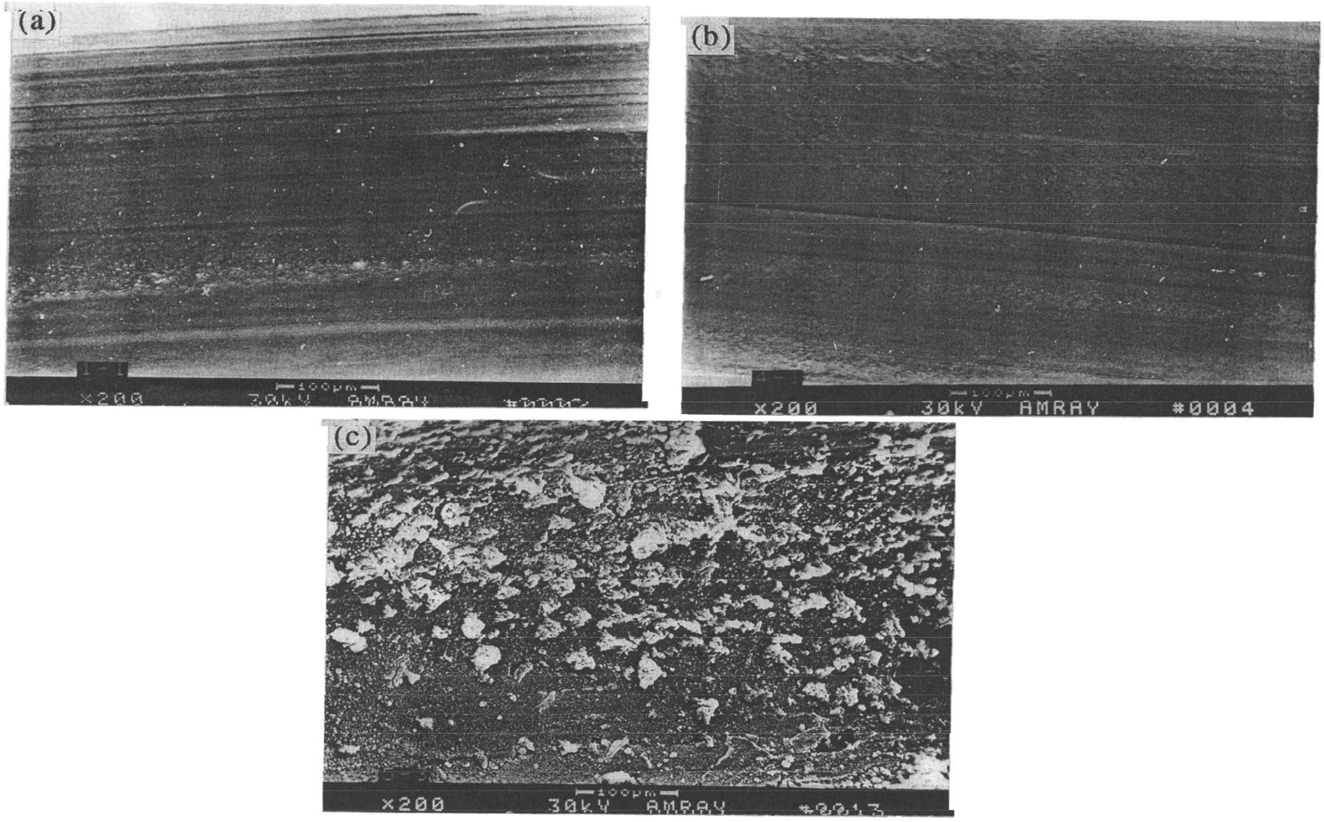

Fig. 4. Scanning electron micrograph of the inner walls of a PTFE KR (200-fold magnification). (a) Untreated walls; (b) Cd-DDC sorbed on the walls for 50 s; (c) Cd-DDC - Fe(II)-HMDC coprecipitate collected on the walls [60]

There are several advantages of on-line systems using KRs instead of packed columns: (i) higher enhancement factors due to higher sample flow rates (lower hydrodynamic impedance in the reactor); (ii) unlimited lifetime; (iii) KR is easily made in laboratory; (iv) no need for packing material; (v) lower cost [61, 62]. A disadvantage is the lower capacity of the KR.

The scheme of the FI manifold used for separation and preconcentration of trace elements by sorption of their complexes onto the inner walls of a KR has undergone essential development since its first use. Initially, the flow injection scheme consisted of two steps only: (i) on-line formation of a neutral analyte complex and its subsequent sorption on the inner walls of the KR and (ii) on-line elution of the sorbed analyte complex for FAAS detection [60]. Later on, Chen et al. [63] modified the system by sandwiching the eluted sample zone with air segments, thereby avoiding mixing of the neighboring phases of eluate and eluent under fast elution rates. Further, other developments in the FI manifold were adopted such as rinsing with a suitable liquid [64,65] or blowing with air of the KR and connecting tubing before elution [66].

An improvement in the scheme of FI on-line separation and preconcentration using a KR was proposed in 1999 by Ivanova et al. [70]. The authors divided the preconcentration stage of the procedure into two separate stages – (i) immobilization of the reagent onto the inner walls of the KR and (ii) formation of the analyte complex with the immobilized reagent. The new scheme offered several advantages in comparison with the conventional preconcentration scheme of on-line merging of sample and reagent solution: (i) higher sensitivity owing to the more favorable conditions of analyte complexation with the immobilized reagent; (ii) better optimization of the separate processes of reagent sorption on the KR and analyte preconcentration, (iii) no analyte losses due to adsorption of complexes outside the KR, (iv) no need of a pre-fill step between samples of different analyte concentrations [70].

FI on-line sorption onto a KR was successfully applied as a separation /preconcentration procedure for a number of elements in various matrices using reagents such as NaDDC (Cd [60], Cu [63,71], Pb [67], Pb [72]), APDC (Pb [66], Sb [68], As [69], Co [73], Tl [74], Cr [75,76], Pt [77], Fe [78], Cu, Ni [79], Co [80], Ag, Cd, Co, Cu, In, Mo, Ni, Pb, Sb [81]), DDPA (Pb [62], Bi [82], Cd, Pb [83]), HQ (Cu, Mn, Ni [79], Co [80], Co [84]), 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) (Co [80], Cu, Mn [70], rare earth elements [85]), 2-nitroso-1-naphtol-4-sulfonic acid (Co [80]), nitroso-R-salt/tetrabutyl ammonium bromide (Co [86]) and dithione (Cd, Co, Cu, Zn [64]). Methods for speciation of Sb [68], As [69], Tl [74], Fe [78], and Cr [75, 76, 87] were also developed.

4.4. Flow injection analysis with atomic spectrometric detection

Flow injection analysis was successfully coupled to detection devices based on different principles, mainly atomic spectrometry (FAAS, ETAAS, ICP AES, ICP MS). The combination of FI methodologies with AS has attracted considerable interest in the past 25 years owing to the great potential in enhancing the relative sensitivity and selectivity of these analytical techniques by combined systems. Additionally, the analytical procedures can be automated and considerably simplified for samples with complicated matrices owing to the separation and preconcentration of the analytes achieved during the preconcentration process.

The general advantages of FI-AS are:

- expansion of the analytical range of the detection device by more than six orders of magnitude through on-line dilution (four orders of magnitude to higher concentrations) and preconcentration (two orders of magnitude to lower concentrations);
- selectivity enhancement by on-line matrix separation or modification;
- lower sample and reagent consumption, typically over 90 % saving in sample and/or reagent;
- enhanced reliability in ultra-trace analysis owing to decreased contamination risks by automated sample processing in an inert closed system.

A unique feature of the FI-AS procedures is that all advantages mentioned above can be simultaneously realized.

5. FIA coupled with FAAS and ETAAS

AAS is one of the most widespread techniques for trace element analysis in various samples. The main advantages of FAAS are: high sensitivity for volatile elements, high selectivity due to almost full absence of spectral interferences, low cost and easy calibration with aqueous standard solutions. The reliability, high productivity and relatively simple sample preparation of FAAS have made it a routine method in practically all areas of analysis. ETAAS has also gained high popularity because of its low detection limits and capabilities for microanalysis. The limitations of FAAS and especially of ETAAS in the analysis of samples with complex matrices come mainly from the matrix interferences which worsen the metrological characteristics of the method. To overcome these limitations, preliminary separation and preconcentration of the trace elements is needed.

Coupling a flame atomic absorption spectrometer to a flow injection system is not technically problematic, as both systems work in continuous mode. The coupling is accomplished by connecting the sample introduction capillary of the spectrometer to the capillary coming from the FI system. Specific for the FI separation and preconcentration - FAAS detection system is the possibility of improving the nebulization efficiency through optimization of the sample introduction flow rate. Additional enhancement in sensitivity can be achieved by introduction of organic solvents often used as eluents [4].

The specific features of ETAAS operation impose special requirements on the design and operation of FI separation and preconcentration systems which differ from those of FAAS and can be summarized as follows:

1. Discontinuous operation - originally considered as the main obstacle, the discontinuous ETAAS operations and the continuous flow techniques are now successfully combined by synchronization through parallel computerized systems. FI operations are carried out in parallel with the furnace temperature program (i.e. one sample is processed in the FI system while the previously processed sample is being simultaneously treated in the ETAAS). In this way a higher sample throughput can be obtained.

2. Small volume of the graphite tube - an important limitation of the ETAAS is the volume of the sample that can be introduced. The maximum volume is typically about 50 µl. In order to meet such requirements, various approaches for introducing the concentrate obtained by FI pretreatment into the graphite tube have been proposed. These include:

- off-line collection of the eluate in a vessel, followed by conventional sample introduction into the graphite tube [132];
- on-line time- or volume-controlled eluate zone sampling [133, 134];
- on-line introduction of the eluate by slow injection into a preheated graphite tube [135];
- multiple injection of the eluate with intermediate drying [136] or via thermospray sample deposition [137].

In case of FI separation and preconcentration in a KR, the eluate volume can be minimized by:

- use of an eluent loop to fix a small eluent volume [67, 73, 80, 86];
- optimization of the KR length so that a small volume of eluent can be sufficient for quantitative elution of the analyte complexes [73, 76, 79, 80];
- removal of the residual solution in the KR and transport conduits by air flow prior to elution [73, 74, 86];
- use of air flow for moving the eluent from the eluent loop to the KR and for the subsequent introduction of the eluate into the graphite tube [67, 73, 74, 86].

3. Difficulties in the analysis of complex matrices - as the introduction of a sample with a complex matrix into the graphite tube would cause serious interferences, rinsing of the KR and connecting tubing was introduced before elution [68]. This step aims at removing non-adsorbed or weakly adsorbed concomitant elements.

There are many scientific papers in the literature dealing with the FI-FAAS and FI-ETAAS analysis of clinical samples [88-90], foods [89,91-94], medicines [43,66,95,96], environmental samples, such as water [65,88,97-99,100-104], soils and sediments [88, 99,105,106] and plants [66,71,106]. Two reviews on FI-ETAAS appeared recently [107,108].

6. FIA coupled with ICP MS

In 1980 Houk et al. [109] demonstrated for the first time the successful combination between the argon inductively coupled plasma (Ar ICP) used in ICP AES and the quadrupole mass spectrometer (Q MS) known from gas chromatography (GC). As a result, in 1984 the first inductively coupled plasma mass spectrometer was produced. Since then ICP MS has become an established technique for trace and ultra-trace analysis. The main advantages of ICP MS are: capability for simultaneous multielement analysis (quantitative and semi-quantitative), high sensitivity (below ng L^{-1}) and large linear dynamic working range (8-9 orders of magnitude). In addition, its ability of determining separate isotopes and measuring isotopic ratios opens new exclusive possibilities like isotope dilution methods for accurate determinations of trace and ultra-trace levels of elements in various samples and measurement of stable isotope tracers, administered to living organisms in order to follow the metabolism of essential and toxic elements [110]. It must be noted, however, that ICP MS is still a comparatively expensive analytical tool with high maintenance costs; its adequate running demands highly qualified personnel and its suffers many interferences especially when complex matrices are analyzed [110]. The latter disadvantage is usually overcome by applying preliminary separation procedures.

Like FAAS, ICP MS works in continuous mode. This is the reason for its easy coupling to the continuously working FI system – the sample introduction capillary of the ICP MS instrument is connected to that coming from the FI manifold. However, there are some special features of ICP MS which the analyst must take into account and modify the FI manifold according to them. These are:

1. The introduction of solutions with high content of dissolved solids (over 0.2 %) may cause blocking of the sampling cone, drift of sensitivity, high interferences and poor precision. Accordingly, a rinsing step of the FI on-line preconcentration system is necessary before elution.

2. Organic solvents are very often used as eluents in FI separation and preconcentration systems. It is well known that loading of organic solvents to the plasma causes sensitivity drift when conventional pulverization is used because of carbon deposition on the sampling cone; instability or even extinction of the plasma; (iii) carbide polyatomic ion interferences [138]. The mentioned effects are usually reduced/eliminated by FI introduction of microliter volumes of organic solvent [34], use of cooled spray chamber [139] or ultrasonic nebulizer with membrane desolvation [81, 140].

FI-ICP MS has been widely used for trace and ultra-trace analysis of clinical samples [89,114-121], foods and beverages [89,118,122-124], plants [125-127], soils and sediments [126-130], medicines [96,131], biological samples [141,142], waters [21,111-113, 143], etc.

It may be hence concluded that FIA is a technique of wide possibilities covering all areas of sample preparation – digestion, dilution, trace element separation and preconcentration. It has been successfully adapted to various AS methods of detection. As a result, precise and reliable FI-AS methods for trace and ultra-trace analysis in a variety of sample types have been developed.

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