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Flow injection analysis coupled with atomic spectrometry

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The basic concepts of flow injection analysis, the components of the flow injection manifold as well as the main applications of flow injection analysis are presented. Special emphasis is put on the use of knotted reactors for flow injection separation and preconcentration of trace elements. 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 – is discussed. Examples are given for the on-line flow injection separation/preconcentration – atomic spectrometric determination of a large number of elements on trace- and ultra-trace levels in samples of complex matrix composition.

Key words: flow injection analysis, atomic spectrometric detection, knotted reactor.

INTRODUCTION

The progress in trace element analysis of environmental and biological matrices is driven forward by three major factors: (i) the demand for quantification of an increasing number of elements on lower concentration levels; (ii) the interest in elemental speciation in view 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 originating from handling and reagents, on the other. There is a close link between the advances in instrumental detection capabilities and the methodology of sample pretreatment, which has encouraged the minimization and miniaturization of sample handling 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.

FLOW INJECTION ANALYSIS

The 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 15000) monographs and papers [1] published since the first paper on FIA by Ruzicka and Hansen, which 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 simple means of automating many manual chemical analytical procedures [3]. Practically, FIA can be coupled with all methods of detection that are used in modern chemical analysis.

Basic concepts of FIA

It is very difficult to give a precise definition of what flow injection analysis really is. Some authors, e.g., Fang [4], explain this by its high versatility, so that definitions are rapidly outdated by new developments. One of the early 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 and 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.

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In 1995 Fang [4] emphasized on another characteristic feature 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 in 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 inject reproducibly 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 the analyte concentration.

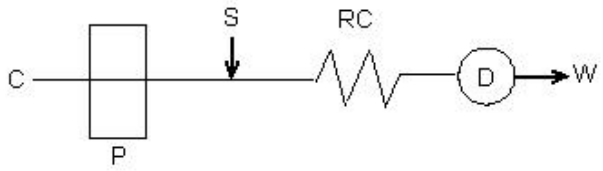

Fig. 1. Schematic diagram of a single-line FI manifold. P – pump, C – carrier stream, S – sample injector, RC – reaction coil, D – detector, W – waste.

The flow injection manifold has become considerably complicated to fulfill the new requirements due to the expanded applications 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*" [4].

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 features of dispersion processes in FIA are 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. The 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 upon 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 the 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.

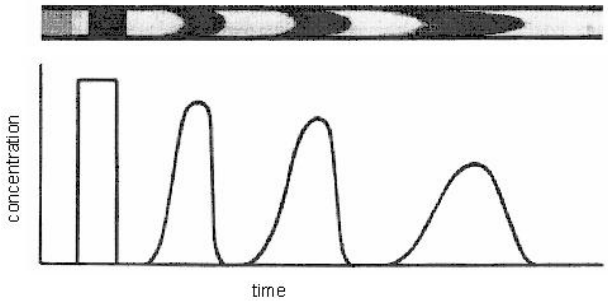

Fig. 2. Dispersion process of an injected fluid zone in an FI system.

Components of the FI manifold

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 follows: 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. A 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 from 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.

Injection valves. 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.

Transport conduits. The transport conduits provide connections between the various components of the FI manifold. To this purpose, PTFE tubings of 0.35–1.0 mm i.d. are mostly used.

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.

Applications of FIA

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

Sample digestion. Sample digestion constitutes an important part of sample pretreatment prior to AS detection of the species of interest and it 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 ref. [6, 7].

Sample dilution. Dilution is a 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 can be evaluated when required; (iii) standard solutions for calibration are prepared 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 [8].

Separation and preconcentration of trace elements. Developments in analytical instrumentation allow trace and ultra-trace analyses in diverse kinds of samples. Despite these advances it is still often necessary to use separation and preconcentration procedures prior to detection. Upon 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 separation/preconcentration [9].

Several criteria were introduced in order to compare the efficiency of the different techniques and procedures: (i) the sample throughput, (ii) the sample consumption and (iii) the enhancement factor (EF) [4]. The latter is defined as the ratio of the analyte concentrations before and after preconcentration. In practice EF is approximated as the ratio of the slopes of the linear sections of the calibration curves before and after preconcentration.

Liquid-liquid extraction. 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 [10]. The first paper concerning FI liquid-liquid extraction was published in 1981 by Nord and Karlberg [11]. However, this kind of preconcentration systems has seen slow development. This seems to be the result of 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 [12] and [13], respectively.

Precipitation and coprecipitation The earliest attempts at using FI systems for preconcentration by precipitation with AS detection were made by Valcarcel *et al*. in 1987 [14] and the first report on coprecipitation appeared in 1991 [15]. 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 fulfilling the requirements of trace analysis. The analytes are usually precipitated as hydroxides [16, 17] or organic compounds [18, 19]. Filters [18, 20], initially used for precipitate collection, have limited capacity and the collected

precipitate caused pressure build-up. Such difficulties have been overcome to a large extent 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 [10]. KR FIA-AS technique has been successfully utilized for separation and preconcentration of Pb [15], Mo [21], As [22], Se [23], Cd, Co and Ni [24], Cd, Ni and Pb [25], Cd, Cu, Fe and Pb [26], Cd, Cu, Fe, Ni, Pb and Zn [27], coprecipitated with organic, e.g. (Fe(II)-hexamethylenedithiocarbamate (Fe(II)-HMDC) [15, 24], Co(II)-pyrrolidine-dithiocarbamate (Co(II)-PDC) [27], Fe(II)-PDC [21], Cu(II)-diethyldithiocarbamate (Cu(II)-DDC) [25], Ni(II)-DDC [26]) or inorganic ($La(OH)_3$ [22, 23], $Hf(OH)_4$ [22]) 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. 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 under different experimental conditions) and limited number of sorption/elution cycles, have been observed [28].

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) [29], 5,7-dichlorooxime [30], 1-nitroso-2-naphthol [31], O,O-diethyldithiophosphoric acid [32-34], and others. Microcolumns of pure alumina [35] or alumina modified with 2-nitroso-1-naphthol [36], DC [37] have also been used. Fullerenes (C_{60}) [38] have been used to sorb metal complexes with DC and 8-hydroxyquinoline (HQ) [39, 40]. Microcolumns of cellulose modified with oxime [41], 2,2'-diaminodiethylamine [41], or 8-hydroxyquinoline-5-sulphonic acid [42] have been applied to element separation and preconcentration. PTFE turnings packed in a mini-column have been used to retain DC complexes [43]. TiO_2 nanoparticles, modified with 1-(2-pyridilazo)-2-naphthol [44]; polyurethane foam [45, 46], modified with 2-(2-benzothiazolylazo)-*p*-cresol [47]; ion-exchangers with iminodiacetate functional groups such as Muromac A-1 [48–50], Chelex-100 [51, 52], Toyopearl AF-Chelate-650 M [6, 53], as well as cation-exchange – Type 732 [54], AG50W-X8 [55] and anion-exchange – Dowex 1-X8 [56, 57] resins have also been used for separation and preconcentration purposes.

Solid phase extraction in a knotted reactor. In 1994 Fang and co-workers [58] have found out that metal complexes could be retained on the inner walls of a PTFE KR (Fig. 3) without precipitate formation. Scanning electron microscopic observations of the KR wall surface were made [58] 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 (Fig. 4).

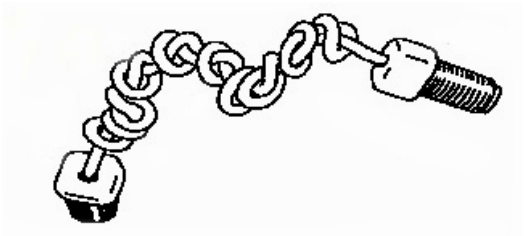

Fig. 3. Knotted reactor.

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 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.

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 [59, 60]. A disadvantage is the lower capacity of the KR.

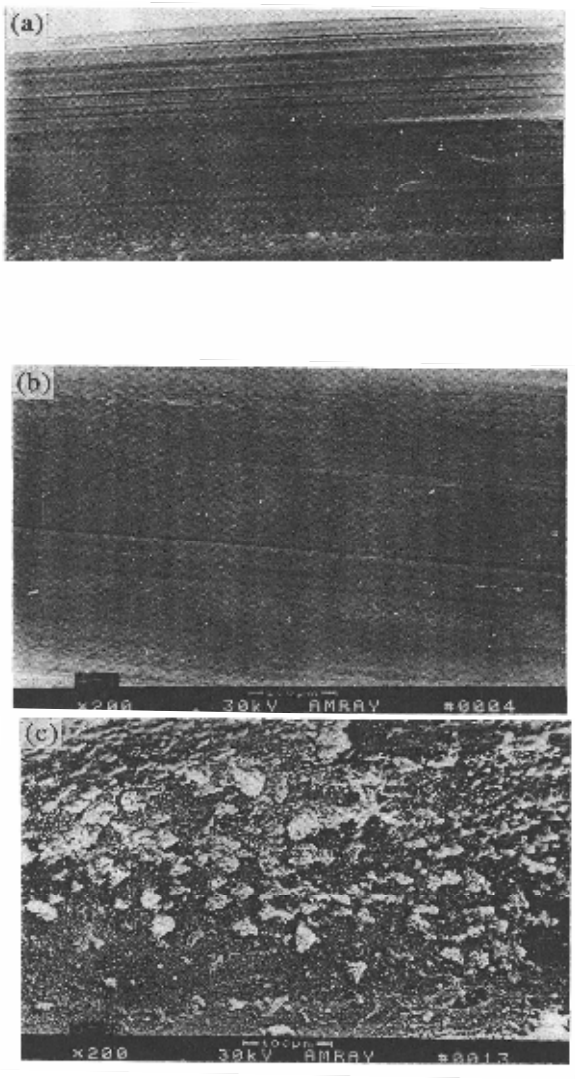

Fig. 4. Scanning electron micrograph of the inner walls of a PTFE KR (200-fold magnification).
(a) Untreated walls; (b) Cd-DDC sorbed on the walls for 50 s; (c) Cd-DDC - Fe(II)-HMDC coprecipitate collected on the walls [58].

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 further 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 [58]. Later on, Chen *et al*. [61] modified the system by sandwiching the eluted sample zone with air segments, thereby avoiding mixing of the neighboring phases of eluate and eluent at fast elution rates. Further, other developments in the FI manifold were introduced such as rinsing with a suitable liquid [62, 63] or blowing air through the KR and connecting tubing before elution [64].

An improvement in the scheme of FI on-line separation and preconcentration using a KR was proposed in 1999 by Ivanova *et al*. [68]. 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 an analyte complex with the immobilized reagent. The new scheme offers several advantages in comparison with the conventional preconcentration scheme of on-line merging of sample and reagent solution: (i) higher sensitivity owing to 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-filling step between samples of different analyte concentrations [68].

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 [58], Cu [61, 69], Pb [65], Pb [70]), APDC (Pb [64], Sb [66], As [67], Co [71], Tl [72], Cr [73,74], Pt [75], Fe [76], Cu, Ni [77], Co [78], Ag, Cd, Co, Cu, In, Mo, Ni, Pb, Sb [79]), DDPA (Pb [60], Bi [80], Cd, Pb [81]), HQ (Cu, Mn, Ni [77], Co [78], Co [84]), 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) (Co [78], Cu, Mn [68], rare earth elements [83]), 2-nitroso-1-naphthol-4-sulphonic acid (Co [78]), nitroso-R-salt/ tetrabutyl ammonium bromide (Co [84]) and dithione (Cd, Co, Cu, Zn [62]). Methods for speciation of Sb [66], As [67], Tl [72], Fe [76], and Cr [73, 74, 85] were also developed.

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 using 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.

FIA coupled with FAAS and ETAAS

Coupling a flame atomic absorption spectrometer to a flow injection system is not technically problematic, as both systems operate 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 feature of 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 introducing 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 are due to the discontinuous operation of ETAAS and the small volume of the graphite tube. The continuous flow techniques are now successfully combined with ETAAS by synchronization by parallel computerized systems. For introducing the concentrate, obtained by FI pretreatment into the graphite tube, various approaches have been proposed, e.g., eluate zone sampling, use of a preheated graphite tube, multiple injection of eluate with intermediate drying, and others [128–133]. 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 were introduced before elution [66]. 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 [86–88], foods [87, 89–92], medicines [41, 61, 93, 94], environmental samples, such as water [63, 86, 95–102], soils and sediments [86, 97, 103, 104] and plants [64, 69, 104]. Two reviews on FI-ETAAS appeared recently [105, 106].

FIA coupled with ICP MS

Like FAAS, ICP MS operates in continuous mode. This is the reason for its easy coupling to the continuously operating 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 an analyst must take into account and modify the FI manifold according to them. To avoid blocking of the sampling cone, drift of sensitivity, high interferences and poor precision, when solutions with high content of dissolved solids (over 0.2%) are introduced into the plasma, a rinsing step of the FI system is introduced before the elution. To reduce or eliminate the effect of organic solvents, which lead to instability or even extinction of the plasma, as well as to carbide polyatomic ion interferences [134], microlitre volumes of organic solvent [32], cooling spray chamber [135] or ultrasonic nebulizer with membrane desolvation [79, 136] are used.

FI-ICP MS has been widely used for trace and ultra-trace analysis of clinical samples [87, 110–117], foods and beverages [87, 114, 118–120], plants [121–123], soils and sediments [122–126], medicines [94, 127], biological samples [137, 138], waters [19, 107–109, 139], *etc*.

It may hence be concluded that FIA is a technique offering 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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ПОТОЧНО-ИНЖЕКЦИОНЕН АНАЛИЗ СЪЧЕТАН С АТОМНА СПЕКТРОМЕТРИЯ

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(Резюме)

Представени са основите на поточно-инжекционния анализ и компонентите на поточно-инжекционното устройство. Специално внимание е отделено на използването на плетен реактор. Описани са поточно-инжекционни методи за подготовка на пробите за анализ (разтваряне, разделяне и концентриране), съчетани с последваща атомно спектрометрична детекция – пламъков и електротермичен атомноабсорбционен анализ и масспектрометрия с индуктивно свързана плазма. Дадени са примери за определяне на голям брой елементи-примеси в обекти със сложен матричен състав.