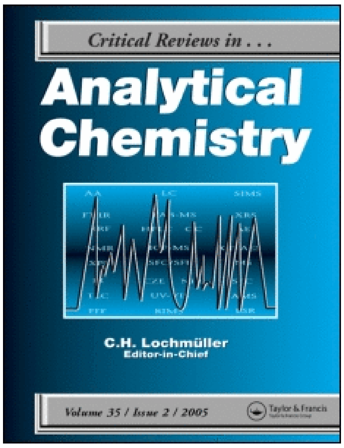

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Online Sample Pretreatment Systems for Determination of Cadmium by the ETAAS Method

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Online Sample Pretreatment Systems for Determination of Cadmium by the ETAAS Method

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Trace and ultratrace determinations of cadmium in environmental and biological samples have become of increasing interest due to the high toxicity of this metal and because electrothermal atomic absorption spectrometry is probably the method of choice for its determination. The measured signals are, however, inherently very susceptible to the composition of the sample matrix and notably to variation within it. The most effective way to avoid these problems is to perform appropriate sample pretreatment such as preconcentration and separation. Such procedures are most advantageously performed in flow systems where all unit operations can be executed online. This paper reviews selected systems, such as solid-phase extraction, liquid-liquid extraction, coprecipitation and chemical vapor generation using to improve sample pretreatment for cadmium determination.

Keywords cadmium, determination, sample pretreatment, preconcentration

INTRODUCTION

Cadmium (Cd) belongs to those trace heavy metals that are of major interest in environmental protection due to its cumulative toxicity. Its natural occurrence in the environment is due to volcanic emissions. The main contamination sources of this element are anthropogenic: industry wastewaters, mining operations, waste incineration as well as the combustion of some coals and oils. Sludge-based fertilizers and phosphate fertilizers are important sources of cadmium in agricultural soils. From the atmosphere, waters and soils, cadmium can go to the plants, to the marine organisms etc. and starting from here to arrive to being able to cause serious damages in human organs due to its toxicity (1, 2) Accumulation of cadmium in crop plants is of great concern due to the potential for food chain contamination through the soil-root interface. Although Cd uptake varies considerably with plant species, the processes that determine the accumulation of Cd in plant tissues are affected by soil factors (3). The increasing global emission of cadmium compounds into the atmosphere, together with aqueous and solid emission, lead to local contamination problems (1). An additional problem of Cd toxicity is its cumulative character (about 30 mg can be accumulated during a lifetime).

Increasing environmental awareness has resulted in ever-heightening pollution controls. As a result it has become necessary to monitor cadmium content in a variety of samples. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most sensitive techniques for the determination of cadmium, but the measured signals are inherently very susceptible to the composition of the sample matrix and notably to variation within it (4, 5). Due to the high volatility of cadmium, some difficulties are encountered for its determination, thus restricting the use of a high pyrolysis temperature and the production of concomitant background signals. These difficulties may be overcome to various degrees by applying a powerful background correction or by using chemical modifiers.

The most effective way to avoid these problems is to perform appropriate sample pretreatment, aimed at lowering the limits of detection, by both removal of interferences and increasing the concentration of the species of interest. Such procedures are most advantageously performed in flow injection (FI) or sequential injection (SI) systems where all unit operations can be executed online with high reproducibility and where risks of sample contamination are minimized (6–8). In addition to separation and preconcentration processes, online sample digestion using flow systems has been attracting considerable interest for some time, as it is often the most rate-limiting factor of the method (9). Recently a third generation of flow techniques has been introduced—sequential injection lab-on-valve (SI-LOV) has specific advantages and allows novel application in micro-miniaturization of online sample pretreatment (10, 11).

Various procedures for FI/SI online separation and preconcentration units coupled to ETAAS for cadmium determination

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have been proposed, including ion-exchange, adsorption, coprecipitation, liquid-liquid extraction and generation of volatile species. The methods based on sorbent extraction, from an online operational point of view, have proven to be most attractive, due to their high separation and preconcentration efficiency. Moreover, they can be easily implemented and controlled in the flow systems.

The aim of this overview is to highlight the current methods used for online sample pretreatment for cadmium determination by ETAAS method for improving the measurements. The reference list is focused primarily on papers from the most recent years.

ETAAS MEASUREMENTS

Due to the high volatility of cadmium, only a low pyrolysis temperature (up to 400°C) can be used in the heating cycle of the ETAAS measurements, which lead to high background absorption from organic matrices and salts. The volatility of cadmium can be reduced by the addition of suitable chemical modifiers. A large number of chemical compounds as well as different procedures for their introduction into the furnace have been investigated in order to obtain interference-free measurements conditions for determination of cadmium (12–16). However, reagent blanks, originating from modifiers, are pronounced and reduce the useful working range, impairing limits of detection and calling for additional purification of reagents, particularly with large sample aliquots and multiple injections.. The problem with reagent blank levels from several common modifiers used for determination of cadmium is illustrated in Figure 1 (17). Several blank contributions are higher than the characteristic mass despite of high-purity reagents employed.

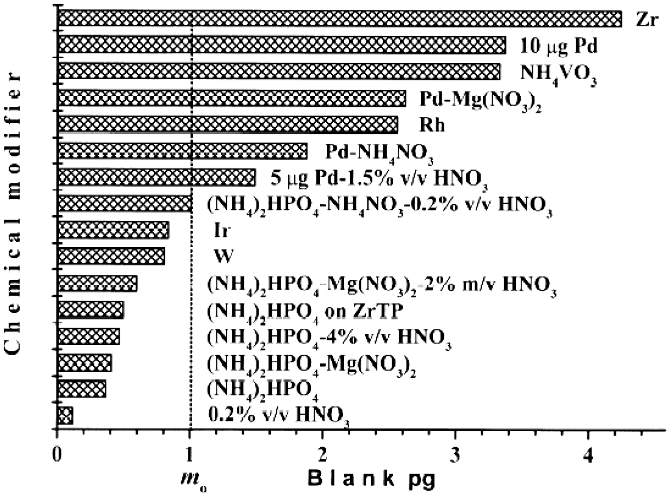

FIG. 1. Reagent blank levels for cadmium determination by ETAAS, originating from some typical chemical modifiers as compared with the characteristic mass (m_0) (17). (Reprinted with permission from Elsevier Science).

The modifier may be introduced together with a sample solution or injected separately into the furnace. This can be accomplished by chemical or thermal reduction of the metal as well as electrodeposition. Taking into account a significant simplification of the analysis procedure, improvement in the detection limit and increase in the atomizer lifetime, permanent modifiers are generally recommended. It has been shown that electrodeposited palladium exhibits lifetime up to 500 firings for the use in determination of selenium, with similar high volatility as Cd, without loss of sensitivity (18). Piaúcik and Bulska (19) demonstrated that all noble metals electrodeposited modifiers could stabilize cadmium up to 800°C in the presence of nitric acid and aqua regia.

Particularly, cadmium determination in biological materials poses several problems mainly due to incomplete atomization as well as both high background levels and build-up of carbonaceous residues inside the atomizer. Such residues in blood, serum or urine samples lead to irreproducible sample deposition, variable rates of atomization and even a partial occlusion of the light beam. These drawbacks can be avoided by including an oxygen or air-ashing step in the heating cycle. This, however, involves a risk of decreasing the useful lifetime of pyrolytic material. It has been demonstrated that the addition of both hydrogen peroxide and nitric acid to samples of a high organic content can also alleviate these problems (20). This is a simple way to produce an oxidizing environment inside the atomizer and an effective in situ mineralization of the sample. However, since the accumulation of residues inside the atomizer is not completely avoided, the inclusion in the heating program of the conventional ashing step is recommended for such samples.

ETAAS discontinuous operation poses some specific requirements on the design in FI/SI systems. The flow operations can be carried out in parallel with the furnace temperature program or sequentially, when the flow manifold is operated in stopped-flow mode during the furnace program. There are several different ways for connection of FI/SI systems and ETAAS detection (21, 22). The most frequently used is application of collecting vial or a flow-through cell located in the autosampler tray followed by the deposition of a suitable aliquot of sample into graphite furnace or sample introduction in the form of aerosol through conventional nebulization or thermospray. Automatic injection of small volumes retained in collecting tubes or valve loops, performed by air displacement as well as in situ trapping of volatile compounds in the preheated graphite furnace have been also used.

LIQUID-LIQUID EXTRACTION

Despite the various attempts at improving online solvent extraction systems in ETAAS applications, the number of publications remains rather low compared to similar flow systems based on sorption principles. Such a situation 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 (21, 23). Solvents often used in ETAAS applications, such as isobutyl ketone (IBMK), cannot be reliably propelled for extended periods even with solvent-resistant pump tubes.

With the aim of overcoming these limitations Fang and Tao (24) introduced a system characterized by organic solvent propulsion using PTFE tubing and a conical-cavity gravitational phase separator. For handling organic solvents, SI systems have shown significant advantages over FI systems, yielding simplicity of manifold design, robustness and versality as the former technique is based on aspirating and pumping all required solutions via a central selection valve to the manifold by means of one or several piston pumps, which themselves essentially might contain an inert liquid (7). Moreover, the limited capacities of the piston pump do not present a restriction in conjunction with the discontinuously operating ETAAS detector.

Flow injection online liquid-liquid extraction system was applied for ultra-trace cadmium determination using ammonium diethyldithiophosphate (DDPA) as chelating agent and IBMK as extractant (25). The ETAAS determination and solvent extraction were synchronized through a parallel-operated sequence. With a sampling frequency of 30 per hour, the limit of detection was 2.8 ng/L.

Organic solvents tend to distribute along the length of the graphite furnace because of their low surface tension and good wetting ability, thus resulting in loss of sensitivity and causing deterioration of precision in the detection step. To take advantage of the high surface tension of water, it is therefore beneficial to back-extract of analytes from the organic phase into an aqueous solution prior to ETAAS measurement. This approach was demonstrated by Wang and Hansen (26) for determination of cadmium via complexation with ammonium pyrrolidinedithiocarbamate (APDC). The Cd-APDC chelates were first extracted onto a small volume of IBMK (1080 μL) and then efficiently back-extracted into an aqueous phase (264 μL) containing dilute nitric acid with Hg(II).

Hg(II) ions were used as a stripping agent to accelerate the slow back-extraction process replacing cadmium from its complex with APDC. The aqueous solution was separated in a second separator and 30 μL of it was entrapped and metered in a sample loop and subsequently introduced via air segmentation into the graphite furnace for measurement. A low pyrolysis temperature of 400°C was used, which might be attributed to the fact that no chemical modifiers were applied. The detection limit of 2.7 ng/L, along with a sampling frequency of 13/h, was obtained.

SOLID-PHASE EXTRACTION

Undoubtedly, the systems based on sorption on principles, including microcolumns packed with chelating resins, reversed-phase silica gel sorbents (C_{18}) and those using open tube knotted reactors (KRs) made from PTFE tubing are most extensively used for online sample pretreatment in analysis of trace amounts of cadmium. In comparison with preconcentration/separation systems based on liquid-liquid extraction, the enrichment effects of sorption systems are not restricted by phase ratio, so that normally significant higher enrichment factors could be achieved.

Different types of manifold designs for FI/SI column sorption coupled to ETAAS detection have been proposed in the literature and are summarized in the monograph by Sanz-Medel (27). The main differences between them include the sample-loading mode (volume- or time-based system), kind of sorbent material, the position of sorption column in the manifold and the eluent delivery mode to the graphite furnace in ETAAS detection. Compared with sorption preconcentration systems for flame AAS, usually lower sample loading flow rates are used to obtain better recovery. This can be achieved without significantly deteriorating the sample throughput, due to the possibility of processing the preconcentration in parallel with the furnace temperature program.

The sample-loading mode is an important feature of this system. For pure separation purposes, as in the case of interference removal, where sensitivity is not of much concern, usually injection of a defined sample volume from a sample loop will be the method of choice, both due to simplicity and reliability. In FI/SI preconcentration system, the sample volume processed directly affects the achievable enrichment factor, thus, time-based loading is preferred. In this system the amount of sample processed is determined by the sampling flow rate and sampling time. For both systems, the loading flow rate is usually the main factor that determines the sample throughput, it means efficiency of the procedure. However, it should be taken into consideration that the maximum loading flow rates are limited by kinetic features of the retention system.

The two main types of design may be identified by the location of microcolumn in the flow systems. The column-in-loop designs incorporate the columns within the sample introduction probes of the graphite furnace, while in the column-in-tip designs, the columns are incorporated within the sample loop of the injector valve. Figure 2 shows the FI manifold for online preconcentration system, where the column is mounted in the tip of autosampler sampling probe, coupled to ETAAS detection. Column washing following sample loading is usually necessary due to interferences from the residual sample matrix. As the sample volume introduced into a graphite furnace is limited, various approaches for introducing the concentrated eluate have been proposed, including slow injection into a preheated tube, multiple injections with intermediate drying and zone sampling. The sample, rising and eluent solutions are segmented by air to prevent dispersion.

Column Packings

Among the chelating ion-exchangers used for online column preconcentration of cadmium, the well-known Chelex 100 (28–30) as well as Muromac A-1 (31) have been used. These two exchangers contain similar iminodiacetate functional groups, but Muromac A-1 does not swell and shrink with changes in acidity, which may create void volumes in online columns when ammonium form exchanger is eluted by a strong acid.

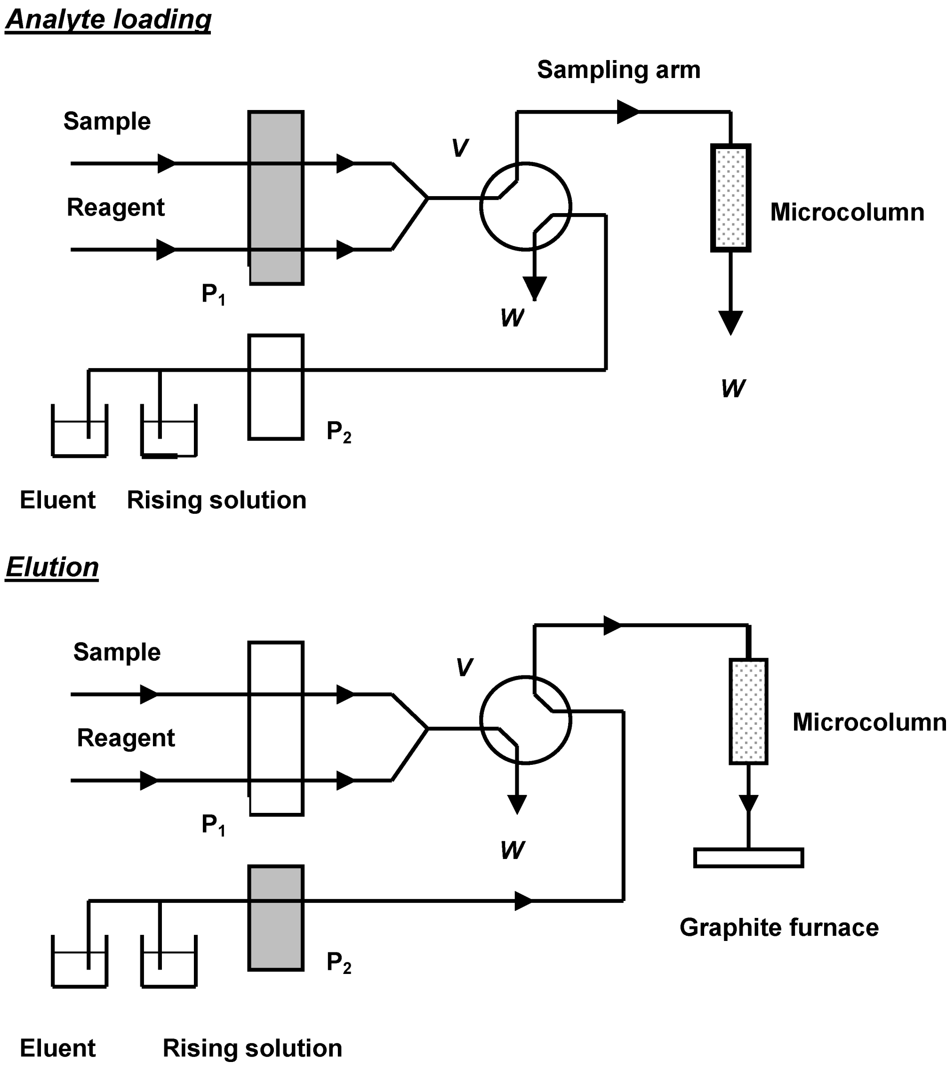

FIG. 2. FI manifold of column-in-tip sorption preconcentration system coupled to ETAAS. P_1 and P_2, peristaltic pumps; V, valve; W, waste.

The microcolumn packed with octadecyl-bonded silica gel (C_{18}) have been frequently used for sorption of cadmium non-polar complexes with sodium diethyldithiocarbamate (DDTC) (32, 33), APDC (34–36) and 4-(2-pyridylazo) resorcinol (37). Ma et al. (38) demonstrated outstanding selectivity for cadmium, lead and copper complexes with ammonium diethyldithiophosphate (DDPA) in strong acidic media.

Amberlite XAD-2 functionalized with 2–aminothiophenol (39) and macroporous anion exchanger AGMP-1 with 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron) (40) have been also applied. The advantage of these procedures is the use of polymeric sorbents, which has a wider operating pH range with respect to C_{18} packing and allows the use of an acidic eluent, more suitable than alcoholic eluents. However, most preconcentration/separation processes are not performed under extreme pH conditions.

Some of the proposed column packings can be used for the preconcentration/separation of a variety of metal ions, while others are fairly specific for a particular ion. Recently, there has been interest in developing more specific materials that can be use to remove one or a few particular ions from the mixtures containing high content of other ions that could otherwise swamp an unselective material and cause significant interferences. One such group of materials includes those with macrocyclic ligands such as crown ethers (41) or porphyrins (42) immobilized on a silica or polymer support. The binding characteristics of macrocyclic ligands can be varied by changing properties such as their cavity size, nature, number or the position of the donor atoms on the macrocycle. Another group of specific sorbents represents molecular imprinted polymers (MIPs) (44, 45). MIP materials are prepared by the copolymerization of functional and cross-linking monomers in the presence of the target analyte (the imprint molecule) that acts as a molecular template. Subsequent removal of the imprint molecule reveals binding sites that are complimentary in size and shape to the analyte. One of the advantages of such materials is that no complexing agent has to be added to the sample before column loading as it is necessary with C_{18} phase.

Hosten and Weltz (41) investigated such a macrocycling ligand immobilized on a silica gel support (Superlig, SL-Cd) which was claimed to be largely selective for preconcentration and separation of cadmium from samples of environmental and toxicological interest, such as sea water and urine. Both these matrices can cause considerable difficulties when they are analyzed directly by ETAAS. With acidified urine samples, good separation from the matrix components was obtained, but with unacidified samples there were still some interferences. Microwave-assisted digestion of the samples did not improve preconcentration, therefore it appeared that there must be constituents in the urine, such as anions, that affected the binding equilibria of cadmium onto the material ligand. Detection limit of 0.8 ng/L was obtained using elution with 40 μL of 2.5 mol/L nitric acid solution.

Knotted Reactors

The knotted reactor (KR) made of microline tubing interlaced knots was first used as the filterless collector of organic precipitates in online coprecipitation/dissolution technique to overcome the difficulty associated with the manipulation of a relatively large amount of precipitate in a continuous flow system. Because of the changes in the flow direction caused by the knots, the KR creates a secondary flow with some centrifugal force in the stream carrying particles towards the tubing walls.

During the development of online coprecipitation technique, a particular interaction between cadmium complex with diethyldithiocarbamate and hydrophobic tubing material of the KR was observed (46). The reactor produced from PTFE was shown to retain Cd-DDTC complex under appropriate experimental conditions through sorption. Since then, the KRs have been extensively investigated as sorption medium in online preconcentration systems as an attractive alternative to the C_{18} microcolumn sorption (47). The KRs produce significantly lower back-pressures then packed columns at similar flow rates, so that higher sample loading rates could be applied. Also, the KR is easily constructed in the laboratory with no need for packing materials and offers almost unlimited lifetime. However, it gives relatively weak retention of sorbed analyte complexes with typical efficiencies of 40–50%. Recently, another type of reactor, the serpentine reactor, having a figure-eight shape has been proposed (48), but its three-dimensional configuration created weaker secondary flow patterns than those observed in knotted reactor.

The complexing agents that have been applied for the formation of neutral hydrophobic metal complexes of cadmium include mostly DDTC, APDC and DDPA (46, 47, 49). These reagents are capable of forming complexes with several metal ions, but dithiocarbamates offer lower selectivity. DDTC solution should be prepared in basic buffer medium (pH$\sim$9) due to its instability in acid solution, whereas APDC can be simply prepared in deionized water. Because of its stability in acidic medium and high selectivity, the formation of diethyldithiophosphate cadmium complexes are preferred (49).

Lab-on-Valve System

In conventional FI/SI online preconcentration systems, the column or reactor are used as a permanent component. However, their long-term applicability is often hindered by the progressively tighter packing of the column material, which might result even in drastic increase of flow resistance. The properties of surface sorbent might be also irreversibly changed after having been subjected to a large number of samples, either due to contaminants, deactivation or even loss of its functional groups. Such problems can be solved if the packing material of microcolumn is renewed for each measuring cycle. This is possible by using the laboratory-on-valve (LOV) approach (10, 11), based on integrating a set of microchannels within a microfluidic system placed atop a conventional multiposition valve, as used in sequential injection assemblies. The SI-LOV coupling enhances the repeatability of many sample processing sequence at the μl-level including sample loading, reagent addition at specific mixing points as well as separation/preconcentration steps utilizing integrated microcolumn for cadmium determination by ETAAS (50–54).

The SI-LOV online preconcentration system incorporating a renewable ion-exchange microcolumn interfaced with ETAAS was used for determination of trace level of cadmium, nickel and bismuth in environmental samples (50, 53). This approach is schematically presented in Figure 3. The beads of hydrophilic SP Sephadex C-25 cation exchanger—whose material is a polysaccharide modified with sulfonic groups—were suspended in water. From the resulting slurry, a defined amount of beads was aspirated into the system. One introduced, the beads could readily be transferred back and forth between C_1 and C_2 microcolumn position for sample loading. After the beads have been rising by wash solution from the holding coil, they are eluted with a well-defined small volume of diluted nitric acid.

The whole solution was transported via air into the graphite tube or the leading volume of eluate was collected and introduced into the ICP via nebulizer. Finally the beads were discarded and the new microcolumn was aspirated for the next operation. Discarding of beads was done by changing the flow rate. At low flow rates ($<$1.2 mL/min) the beads are effectively entrapped in the microcolumn positions and can be transferred reproducibility in the LOV system, while at flow rates above 6 mL/min, they become squeezed and can pass out through the hole in the rods. With ETAAS detection, an alternative approach could be realized (10, 54). Instead of eluting the retained analyte from the microcolumn, the beads with a carrier solution are transported into the graphite tube, when they are ashed during the pyrolysis and atomization process.

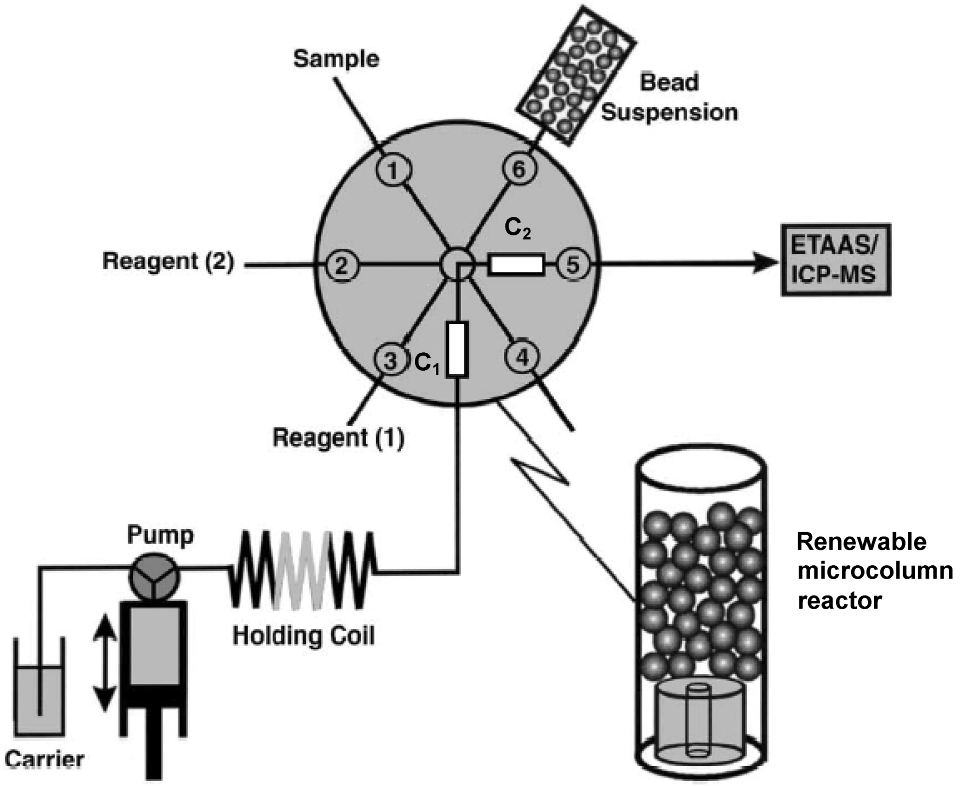

FIG. 3. The SI-LOV system with renewable column reactor (54). (Reprinted with permission from Elsevier Science).

Attempts have been also directed towards the investigation of online column sorption in the LOV format by using hydrophobic sorbent beads in the loading/elution mode. Two kinds of materials, poly(styrene-divinylbenzene)copolymer alkylated with octadecyl groups (C_{18}-PS/DVB) and poly(tetrafluoroethylene (PTFE), were investigated for the preconcentration of cadmium low levels after online analyte complexation with DDPA (51–53). These two reversed-phase sorbents were selected in view of their different morphology and physical properties. C_{18}-PS/DVB beads could be reproducibly handled in the LOV microconduit and transferred between the two column positions so the manipulation of the bead suspension was similar to that for the hydrophilic beads examined earlier.

In the case of PTFE, to keep them suspended and facilitate their manipulation, a slurry was maintained in an external, constantly stirred, reservoir due to much higher density that of the suspending liquid. Both hydrophobic sorbents are non-compressible, thus only beads elution approach could be realized using ethanol as an eluent. Manipulation of C_{18}-PS/DVB beads in comparison to PTFE is more straightforward, yielding better reproducibility values. However, this kind of sorbent is not really optimal from the analytical point of view to retain neutral chelates, as evidences by the lower sensitivity, narrower dynamic range and also in terms of enrichment factor. The major drawback of PTFE beads associated with their packing tendency were alleviated by precise flow-rate control during suspension aspiration into the LOV central port and the loading step; values as low as 0.24 ml/min being recommended for the first operation.

PRECIPITATION AND COPRECIPITATION

Preconcentration of cadmium by precipitation, and particularly by coprecipitation, using a batch operation, has been used for many years in combination with the ETAAS method. However, despite the capability of effectively separating interfering matrices and achieving high enrichment factors, these methods are usually tedious. The coupling of precipitation schemes with an automated FI/SI approach has changed the situation, and a number of efficient and relatively robust procedures for cadmium determination are now available (55–57). Fe(II)-hexamethylene dithiocarbamate (55) and Cu(II)-DDTC (56) were used for coprecipitation and IMBK for dissolution. Yebra et al. (57) proposed the method which involves cadmium precipitation as an ion pair formed between CdI_4^{2-} and quinine. The precipitate was then dissolved in ethanol.

For obvious reason, filters cannot be used to collect the precipitate in a continuous flow system because they would lead to increased back-pressure in the manifold. This problem was solved by employing knotted reactors. Although online coprecipitation systems are used much less frequently than online sorption systems, their higher tolerance to coexisting base metals can be an important benefit in applications when interferences from such origin are difficult to overcome.

Recently, an octadecyl-immobilized surface has been shown as a superb precipitate-collecting medium for ultratrace cadmium separation/preconcentration from complex matrix (58). The surface charge effect was assumed to dominate the adsorption of Cd(OH)$_2$ precipitate, facilitated by electrostatic interaction between the negatively charged C$_{18}$ bead surface and positively charged cadmium hydroxide clusters. It was found that the analytical performance of C$_{18}$ surface remained virtually constant in terms of retention efficiency, precision and flow resistance within about 100 cycles of successive sample

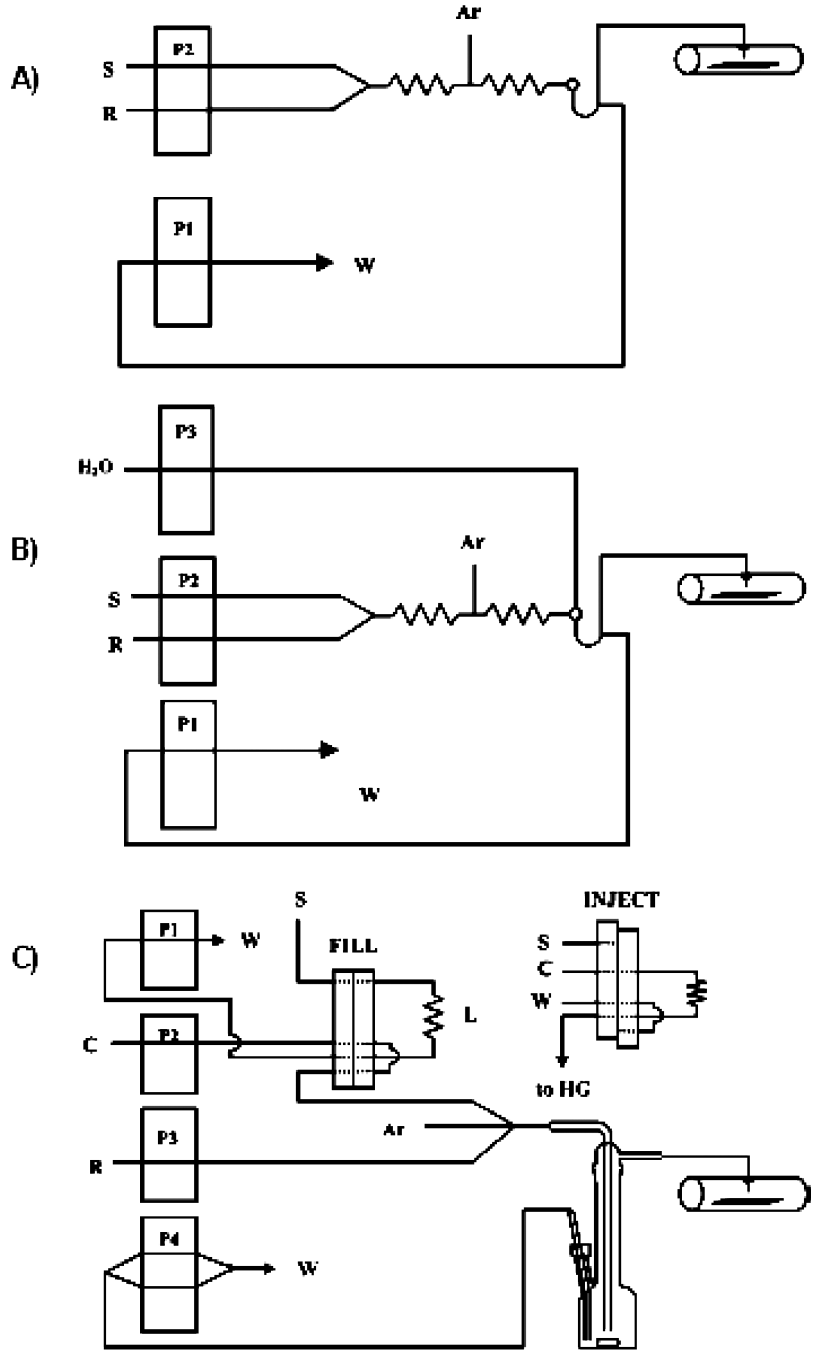

FIG. 4. Schematic diagrams of manifolds for VG and in situ collection in graphite furnace (64). (A) continuous flow system; (B) VG-ETAAS system with an additional external peristaltic pump for washing between samples; (C) semi-batch flow injection system. S, sample; C, carrier; R, reductant; W, waste; P, peristaltic pump, L, sample loop or reaction coil. (Reprinted with permission from Elsevier Science).

processing. For this reason, a renewable-surface approach was adopted by loading/discarding the microbeads in the sequential injection lab-on-valve system to avoid the deterioration of analytical performance.

CHEMICAL VAPOR GENERATION

For separation/preconcentration purposes, the vapor generation (VG) for cadmium volatile species could be used, although, analysis of recent literature indicates that these techniques are not so popular for Cd, in contrast to chelate extraction or solid-phase extraction. Literature data reveal much inconsistency and contradictory statements, probably because of the inherent instability of cadmium hydride and difficulties with generation, stripping of solution and transportation of volatile species (59–64).

Generation of cadmium hydride by the reaction of an acidified sample solution with sodium tetrahydroborate ($NaBH_4$) generally is used. CdH_2 is separated from the bulk solution with the hydrogen formed by the decomposition of the excess $NaBH_4$ and an added argon stream. Critical parameters of these assays are relatively narrow HCl range (0.2–0.6 mol/L) and high $NaBH_4$ levels (2–5% m/v) to provide some excess of reductant with a molar input ratio of $[BH_4^-]:[H^+] \geq 1.1$; high flow rates of argon purge gas and special attention to the construction of gas-liquid separator as well as transport lines because of vigorous reactions entailing aerosol formation (64). Analytical sensitivity and selectivity achieved with hydride generation could be improved by the use of surfactants (59–61). The most promising analytical results were obtained with diodecyldiemethylammonium bromide (DDAB) vesicles as the organized medium for Cd(II) reduction.

The coupling of VG separation and enrichment with in-atomizer trapping of hydrides or other vapors for ETAAS quantification has been presented in recent reviews (63, 64) (Fig. 4). Hydrides are best trapped on graphite surfaces which are chemically modified with Pd (59, 61) or thermally stabilized iridium on carbide-treated platforms, e.g., Ir-Zr and Ir-W [59, 64]. Temperatures of trapping, pyrolysis and atomization were 350, 500 and 1300°C, respectively. The best overall efficiency of VG, transportation and trapping was 41% (64). The addition of nickel(II) in the presence of thiourea provided improved tolerance to the interference of coexisting ions (62). However, the effect of Ni is highly dependent on its concentration; for concentration below 0.01 mg/L, its catalyzing affect is observed, while above this value, the presence of nickel significantly suppressed the production of the vapor species of cadmium. On the other hand, Lapmugnani et al. (64) reported that application of some additives with potential catalytic effect, such as Ga(II), Co(II), thiourea and vesicular media like DDAB, did not bring improvement in the efficiency of vapor generation. Increasing sample volume above 1–2 mL is inconvenient in the flow-injection mode, and a proportional improvement in the limit of detection may not be achieved (65). Larger samples could be processed in continuous flow approach or using batch-type generators (63).

CONCLUSIONS

Today, the greatest hindrances to coupling the continuous FI or SI systems to discrete ETAAS operations have been overcome at it is demonstrated by the great number of papers published in the last years. Online separation and preconcentration procedures can effectively eliminate the interfering effects from matrix components for determination of cadmium by ETAAS method. They also can offer improvements in sensitivity of measurements.

So far, online pretreatment of sample schemes for cadmium coupled to ETAAS have been predominantly focused on the determination of total metal content, while speciation studies have been conducted only in one paper (30). Two dissolved fractions of cadmium can be distinguished in natural waters; the weak Cd complexes, which are bioavailable, constitute the labile fraction, and the stable and inert complexes formed between cadmium and dissolved organic matter, which are not bio-accumulated. Fernadez et al. (30) presented an automatic FI system coupled to ETAAS for the sequential extraction of these two different fractions: a microcolumn packed with Chelex 100 resin was used for separation of "free" cadmium ions and its weak complexes, while a microcolumn with hydrophobic silica C_{18} retained cadmium-organic complexes.

The column sorption approach could be also employed for field-sampling techniques (66), where water samples are processed in flow systems at the sampling site and trace elements of interest are retained on a packing material. The microcolumns may then be returned to the laboratory and directly inserted into a FI/SI system for online elution and quantitative analysis. In addition to FI methodology, this technique achieves improvement in collection, transportation and storage of the samples as the conventional sample preservation methods could be omitted.

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