An automated flow injection system for metal determination by flame atomic absorption spectrometry involving on-line fabric disk sorptive extraction technique

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ABSTRACT

A novel flow injection-fabric disk sorptive extraction (FI-FDSE) system was developed for automated determination of trace metals. The platform was based on a minicolumn packed with sol-gel coated fabric media in the form of disks, incorporated into an on-line solid-phase extraction system, coupled with flame atomic absorption spectrometry (FAAS). This configuration provides minor backpressure, resulting in high loading flow rates and shorter analytical cycles. The potentials of this technique were demonstrated for trace lead and cadmium determination in environmental water samples. The applicability of different sol-gel coated FPSE media was investigated. The on-line formed complex of metal with ammonium pyrrolidine dithiocarbamate (APDC) was retained onto the fabric surface and methyl isobutyl ketone (MIBK) was used to elute the analytes prior to atomization. For 90 s preconcentration time, enrichment factors of 140 and 38 and detection limits (3σ) of 1.8 and 0.4 $\mu g\,L^{-1}$ were achieved for lead and cadmium determination, respectively, with a sampling frequency of 30 h^{-1}. The accuracy of the proposed method was estimated by analyzing standard reference materials and spiked water samples.

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1. Introduction

During the last couple of years, a remarkable progress has been made in regard to flow-based sample pretreatment methodologies hyphenated with atomic spectrometry for the determination of trace metals. Flow injection techniques, are used for fluidic manipulation and on-line sample processing, providing an effective alternative to the batch mode of sample preparation [1]. Combining flow techniques with flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) provide unique capabilities which can benefit as well as significantly enhance the performance of each method [2].

Solid-phase extraction (SPE) is a highly popular sample preconcentration technique and has become the focal point of improving and creating greener and more efficient approaches for sample pretreatment, resulting in the development of numerous microtechniques known as miniaturized solid-phase extraction techniques [3,4]. A wide variety of novel sorbent materials has

been developed and used for on-line column preconcentration and determination by FAAS of toxic trace metals like lead, in different types of sample matrices in order the traditional stationary phases to be replaced as well as improve extraction performance characteristics of the target analytes [5,6].

Sol-gel chemistry offers an efficient pathway to incorporate organic components into inorganic polymeric structures in solution phase under mild thermal conditions [7], allowing the development of new inherently porous sorbents in different forms including particles, monoliths, films and fibers for analytical sample preparation techniques [8]. The advantages of sol-gel technology, for example the use of relatively inexpensive chemicals for sol-gel synthesis, the unique ability to achieve molecular level uniformity in the synthesis of hybrid organic-inorganic advanced material systems and the creation of surface coatings on a substrate of practically any geometrical shape, have been exploited to achieve significant advances in micro/nano sample preparation [9].

Recently, Kabir and Furton [10] introduced a novel sample preparation technique known as fabric phase sorptive extraction (FPSE) in order to overcome the major shortcomings of the most commonly used sample preparation techniques, such as poor extraction performance for highly polar analytes, low sorbent

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loading that often results in poor extraction sensitivity, short lifetime of the physically held coatings and the limited range of pH stability (pH 2–11). The sorptive extraction technique FPSE, integrates the advantages of inherently porous sol-gel derived hybrid organic–inorganic sorbents with flexible and permeable fabric substrates, resulting in a highly efficient and sensitive extraction medium that can be introduced directly into any kind of fluidic matrix resulting in higher extraction sensitivity and shorter preparation time [11] or can be used as an extraction disk, through which the sample matrix containing the analytes of interest can be passed to facilitate the extraction [12].

Briefly, FPSE uses a combination of a porous surface (ca. 2.0 cm × 2.0 cm) as the substrate (cellulose/polyester/fiber glass) and a sol-gel derived hybrid organic-inorganic sorbent material system. The sol-gel coated FPSE medium is inserted into the sample vial along with a magnetic stirrer for about 30 min in order for the analyte to be extracted. After the extraction, an elution/back-extraction process is carried out for 5–10 min followed by centrifugation/filtration prior to the instrumental analysis [13].

To date, FPSE has been used for the determination of various organic compounds such as antibiotics in milk [13,14], triazine herbicides in environmental waters [15], non-steroidal anti-inflammatory drugs in environmental water samples [16], selected estrogens [11], benzodiazepines in blood serum [17], endocrine disruptors alkyl phenols from ground water, river water, sewage water, sludge and soil samples [18]. Lakade et al. [19] reported a comparative study of different FPSE sorbents for the extraction of pharmaceuticals and personal care products from environmental aqueous samples. Finally, the importance of the FPSE technique as well as its advantages and applications in pharmaceutical analysis, has been well demonstrated by Samanidou and Kabir [20]. Nevertheless, this technique has not been applied for metal determination coupled with AS.

Despite the significant advantages of the FPSE technique such as the direct use of the FPSE media into the original, unaltered sample matrix and the minimization of sample preparation steps [11], there is a necessity for automation in order to overcome drawbacks like high sample preparation time and repeatability of the batch-mode extraction procedure.

In the present study, a novel automated on-line flow injection-fabric disk sorptive extraction (FI-FDSE) platform was developed for metal preconcentration and determination by FAAS. For this purpose, minicolumns packed with sol-gel coated fabric media in the form of disks were prepared for the first time and incorporated into a FI system. To the best of our knowledge, the automation of the FPSE technique has not yet been reported. The developed FI-FDSE system was applied to on-line lead and cadmium determination in environmental water samples due to their high toxicity even at very low concentrations. The workability of four coated FPSE media: PTHF, PDMDPS, PEO-PPO–PEO triblock co-polymers and graphene as column fabric disk packing materials was investigated.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer (Norwalk, CT, USA) Model 5100 PC flame atomic absorption spectrometer with deuterium lamp background corrector was furnished with lead and cadmium hollow cathode lamps (HCL) operated at 10 mA and 4 mA respectively. The wavelength was set at 283.3 nm and 228.8 nm for lead and cadmium respectively and the monochromator spectral bandpass (slit) at 0.7 nm. The flame composition was adjusted properly to compensate for the effect of the used eluent, MIBK, served as an

additional fuel. The air flow rate was set at 10.0 mL min^{-1} and acetylene flow rate at 2.0 mL min^{-1}. The resulting nebulizer free uptake rate was 5.8 mL min^{-1}.

A Perkin-Elmer (Norwalk, CT, USA) Model FIAS-400 flow injection analysis system was coupled to the nebulizer system of the spectrometer operated in preconcentration mode. The FIAS-400 manifold consisted of two peristaltic pumps with Tygon tubing and a 5-port 2-position injection valve (IV). One peristaltic pump was used for the propulsion of the sample and the chelating reagent. Due to the incompatibility of organic solvents such as MIBK, methanol and acetonitrile with the pumping tube, a syringe pump (MicroCSP-3000, FIAlab instruments, Bellevue, WA) with a 2.5 mL glass barrel (TECAN) and a three-position Teflon/Kel-F valve on the top of it, was used for eluent propulsion. The syringe pump was controlled through a FIAlab®-3000 sequential injection system (FIAlab) using the combined FIAlab software. The entire flow system was controlled by a personal computer using the AA Lab. Benchtop version 7.2 application software. Both programs were synchronized. A «T» type mixing device was used just ahead of the inlet of FAAS for flow compensation (FC) between elution flow rate and nebulizer aspiration.

2.2. Preparation of fabric disk sorptive extraction media

A large number of commercially available natural and synthetic fabrics can be used as the potential candidates as substrate for FPSE which include cellulose, polyester, nylon, fiber glass and polyamide. Polyester and cellulose fabrics provide sol-gel active functional groups and therefore both fabrics have been widely used as FPSE substrates for sol-gel coating. Both the substrate and the sol-gel coating contribute to the final selectivity and polarity of the extraction media.

Four different FPSE sorbent media were studied through the developed fabric disk sorptive extraction (FDSE) platform (Table 1). A relatively non-polar organic polymer, sol-gel PDMDPS on a hydrophobic polyester substrate with a sorbent loading of 1.93 mg cm^{-2} was used as a non-polar extraction media, whereas sol-gel PTHF (with a sorbent loading of 3.96 mg cm^{-2}), sol-gel PEO–PPO–PEO (with a sorbent loading of 5.68 mg cm^{-2}) and sol-gel graphene (with a sorbent loading of 7.57 mg cm^{-2}) coated on hydrophilic cellulose fabric substrate were used as polar extraction media.

Sol-gel coating on the selected substrates involves a number of sequential steps including (1) surface treatment of cellulose and polyester substrates; (ii) design and preparation of sol solution incorporating all necessary sol-gel reaction ingredients; (iii) conditioning and ageing of sol-gel coated FPSE media; (iv) postcoating cleaning of the FPSE media.

A detailed account of the aforementioned steps, their significance, and the composition of sol solutions prepared for sol-gel PDMDPS, sol-gel PTHF, sol-gel PEO-PPO–PEO triblock co-polymers coatings were described elsewhere [9,13–17,19]. Sol-gel graphene is new sorbent and was prepared by mixing 40 mg of graphene oxide, 10 mL sol-gel precursor methyltrimethoxysilane, 20 mL methylene chloride: acetone (50:50; v/v) mixture as the solvent,

Table 1
Characteristics of the fabric phase sorptive extraction media used in the proposed FI-FDSE-FAAS method.

Fabric media	Substrate	Sorbent loading (mg cm^{-2})	Polarity
Sol-gel PDMDPS	Polyester	1.93	Non-polar
Sol-gel PTHF	Cellulose	3.96	Medium polar
Sol-gel PEO-PPO-PEO	Cellulose	5.68	Polar
Sol-gel graphene	Cellulose	7.57	Polar