P76: FIBER FABRIC SORBENT EXTRACTION FOR ON-LINE TOXIC METAL DETERMINATION IN ENERGY BEVERAGES

Kazantzi V., Anthemidis A.

Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece.- vkazantzi@chem.auth.gr

Abstract – In the present study, a novel flow injection on-line fiber fabric sorptive extraction (FI-FFSE) platform was developed, in order to take advantage of the benefits of FPSE technique in automatic mode. For this purpose, a microcolumn packed with a sol-gel coated fiber fabric medium, the poly-dimethylsiloxane (PDMS), incorporated into a FI-SPE system, was presented for the first time. This configuration provides insignificant backpressure, resulting in high loading flow rates and shorter analytical cycles. The on-line formed complex of metal with sodium diethyl dithiocarbamate (DDTC) was retained onto the fabric surface, while methyl isobutyl ketone (MIBK) was used to elute the analytes prior to atomization. For 90 s preconcentration time, enrichment factors of 165 and 43 and detection limits (3s) of 1.6 and 0.3 μg L^{-1} were achieved for lead and cadmium determination, respectively, with a sampling frequency of 30 h^{-1}. The developed method has been successfully demonstrated for on-line lead and cadmium determination by FAAS in commercially available energy and refreshment drinks.

Keywords: automatic; fabric phase sorptive extraction; atomic absorption spectrometry; energy beverages; toxic metals

1. INTRODUCTION

Marketing of energy beverages is grown rapidly with global consumption nearly doubling during the last years. These types of drinks are mostly referred to young adults aged 18-34, something that leads to a high concern for the research community about the risks and the potentially harmful effects of their consumption on consumers' health, due to their often high content of caffeine, sugar and other ingredients such as taurine, guarana, vitamins, and herbal ingredients. Much work on energy beverages has focused on various negative physiological effects related to their consumption, including agitation, elevated blood pressure, sleep disturbance, increased susceptibility to addiction, dental caries, miscarriage, arrhythmia and even death [1].

Among other harmful ingredients, energy beverages are likely to contain traces of heavy metals such as cadmium, lead, mercury arsenic, zinc, etc. which may be present due to the environmental pollution from surface and underground water, food and fruits utilized during production. Generally, heavy metals have been proved harmful and toxic to the human body and constitute a major topic of public health concern. These metals have the potential of causing acute and chronic toxicity by various modes of action in both children and adults [2].

Up to date, numerous extraction methodologies either in batch or automatic mode have been developed and applied for the determination of heavy metals in different types of samples. Despite the fact that solid phase extraction (SPE) has become the technique of choice as well as other techniques followed by the trend of miniaturization like solid phase micro extraction (SPME), stir bar sorptive extraction (SBSE) and thin film micro extraction (TFME), there is always a growing demand for greener procedures as well as high concern for more sensitive and reliable pretreatment techniques. In this context, fabric phase sorptive extraction (FPSE) introduced by Kabir and Furton [3], achieved to overcome drawbacks of most used sample preparation techniques like multiple time consuming steps, high consumption of organic solvents and small sorbent loading.

Till now, FPSE has been applied to extract several analytes from different types of matrices taking advantage of the principles of sol-gel technology and the rich surface chemistry of various commercially available natural and synthetic fabrics used as FPSE substrates including cellulose, polyester, nylon, fiber glass and polyamide [4]. Our research group evaluated the FPSE technique in a new mode for automatic systems, called fabric disk sorptive extraction (FDSE) [5] and applied for the extraction of trace metals in environmental water samples followed by flame atomic absorption spectrometry (FAAS) with satisfactory results.

In the present work, sol-gel coated fibers were fashioned and used for the first time in an automatic SPE microcolumn preconcentration system. The proposed fiber fabric sorbent extraction (FFSE) method is based on the reformation of the FPSE media as fibers packed into a microcolumn as an alternative approach for automation of the FPSE technique. The performance of the packed microcolumn with sol-gel poly-dimethylsiloxane (PDMS) coated fibers was demonstrated for ultra-trace amount of Pb(II) and Cd(II) determination using sodium diethyl dithiocarbamate (DDTC) as chelating reagent and methyl isobutyl ketone (MIBK) as eluent. The proposed method was thoroughly optimized and evaluated by analyzing energy and refreshment drink samples.

2. EXPERIMENTAL

2.1 Instrumentation

A Perkin-Elmer (Norwalk, CT, USA) Model 5100 PC flame atomic absorption spectrometer with deuterium lamp background corrector was used as detector system. Lead and cadmium hollow cathode lamps (HCL) operated at 10 mA and 4 mA respectively, were used as light sources. The wavelength was set at 283.3 nm and 228.8 nm for Pb(II) and Cd(II) 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, methyl isobutyl ketone (MIBK), which serves as an additional fuel during elution steps. The air flow rate was set at 10.0 L min^{-1} and acetylene flow rate at 1.0 L 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, operated in preconcentration mode, was coupled to the nebulizer system of the spectrometer. The FIAS-400 manifold consisted of two peristaltic pumps with Tygon tubing and a 5-port 2-position injection valve (IV). Only one peristaltic pump was used for the propulsion of the sample and chelating reagent. Due to the incompatibility of organic solvents used in this study: MIBK, methanol and ethanol with the pumping tube, a syringe pump (MicroCSP-3000, FIAlab instruments, Bellevue, WA) with a 2.5 mL glass barrel was used for eluent delivery. The entire flow system was controlled by a personal computer using the AA Lab. Benchtop version 7.2 application software. 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. All the tubing of the flow system was made of poly-tetrafluoroethylene (PTFE).

2.2 Materials, reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water, produced by a Milli-Q system (Millipore, Bedford. USA, http://www.millipore.com) was used throughout the study. Working standard solutions of Pb(II) and Cd(II) were prepared by appropriate stepwise dilution of a 1000 mg L^{-1} Pb(II) and Cd(II) stock standard solutions (Merck Titrisol) to the required μg L^{-1} levels prior to use. The standard solutions and samples were acidified to 0.01 mol L^{-1} HNO_3 (pH~2.0). The chelating reagent 0.05% (m/v) sodium diethyl dithiocarbamate (DDTC) was freshly prepared daily by dissolving the appropriate amount in water. MIBK was used after saturation with water, without any other purification. Laboratory glassware was rinsed with water and decontaminated overnight in 10% (v/v) nitric acid solution.

An FPSE sorbent medium, the sol-gel PDMS coated on a polyester substrate, was studied in the proposed fiber fabric sorbent extraction (FFSE) method. A detailed procedure of sol-gel coatings on various substrates is described elsewhere [6].

The developed method was applied to the analysis of energy and refreshment drink samples. Three brands of canned energy drink samples (ED1, ED2, ED3) as well as two refreshment ones (RD1, RD2) were randomly purchased from the market and evaluated for lead and cadmium determination.

All samples were directly analyzed by the proposed FI-FFSE-FAAS method after completely degassed using a magnetic stirrer.

3. RESULTS AND DISCUSSION

3.1 Preparation of the FFSE microcolumn

The microcolumn used in the present study, was constructed using a glass syringe tube with 4.0 mm i.d. and an active length of 50.0 mm. The sol-gel coated fiber fabric medium was reformatted in fibers with the help of a blade. The resulted fibers were packed and fixed into the microcolumn. No frits or glass wool were necessary at the two ends of the microcolumn. The amount of the sorbent packing material was 75 mg.

This novel column configuration presents low flow resistance, high extraction efficiency with excellent reproducibility and satisfactory sensitivity. The FFSE microcolumn was proven to operate reliably for at least 600 analytical cycles.

3.2 Optimization of the experimental parameters

All chemical and manifold parameters were studied and optimized using standard aqueous solutions of Pb(II) at 100 μg L^{-1} and Cd(II) at 20 μg L^{-1}. The optimum and selected ones for both metals are: sample acidity, 0.01 mol L^{-1} HNO_3; chelating reagent, DDTC; [DDTC]= 0.05% m/v; sorbent amount= 75 mg; eluent, MIBK; loading flow rate= 10.4 mL min^{-1}, elution flow rate= 4.8 mL min^{-1}, preconcentration time= 90 s.

3.3 Analytical performance characteristics

For a preconcentration time of 90 s, the linear range for Pb(II) was 5.5 - 300 μg L^{-1}, the detection limit (3*s*) was 1.6 μg L^{-1} and the precision as relative standard deviation (RSD) was s_r=2.9% (n=10), at the 50.0 μg L^{-1} concentration level. The regression equation was A = 0.0034 + 0.0014[Pb(II)] and the correlation coefficient was 0.9985.

For a preconcentration time of 90 s, the linear range for Cd(II) was 1.2- 60 μg L^{-1}, the detection limit (3*s*) was 0.3 μg L^{-1} and the precision as relative standard deviation (RSD) was s_r=2.8 % (n=10), at the 10.0 μg L^{-1} concentration level. The regression equation was A = 0.0028 + 0.0065[Cd(II)] and the correlation coefficient was 0.9987. The enhancement factors, were 165 and 43 for Pb(II) and Cd(II) respectively and the sampling frequency was 30 h^{-1} for both metals.

3.4 Analysis of energy and refreshment drink samples

The obtained results for the analysis of real samples are given in Table 1.

Table 1. Analytical results of lead and cadmium determination in energy and refreshment drink samples.

	Added*	Found*	Recovery (%)
Lead			
ED1	-	N.D.	-
	10.0	9.5 ± 0.5	95.0
ED2	-	N.D.	-
	10.0	9.7 ± 0.4	97.0
ED3	-	N.D.	-
	10.0	10.5 ± 0.9	105.0
RD1	-	6.4 ± 0.4	-
	10.0	16.2 ± 0.8	98.0
RD2	-	N.D.	
	10.0	10.6 ± 0.6	106.0
Cadmium			
ED1	-	N.D.	-
	5.0	4.8 ± 0.2	96.0
ED2	-	N.D.	-
	5.0	4.7 ± 0.3	94.0
ED3	-	3.3 ± 0.2	-
	5.0	8.2 ± 0.4	98.0
RD1	-	N.D.	-
	5.0	5.3 ± 0.4	106.0
RD2	-	5.6 ± 0.4	-
	5.0	10.4 ± 0.5	96.0

*concentration in μg L-1; N.D.: not detected.

The recorded recoveries ranged from 94 to 106 % which were considered as satisfactory, indicating the applicability of the developed method for lead and cadmium determination in similar type of samples.

3. CONCLUSIONS

The use of the FFSE microcolumn packed with sol-gel coated fibers, in flow systems, produces high contact between the target analytes and the sorbent material, resulting in better extraction efficiency. The proposed automated FI-FFSE-FAAS method proved to be simple, rapid and accurate for lead and cadmium determination in energy and refreshment drink samples.

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