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Development of an online-solid phase extraction-electrochemical method for the quantification of lead in water media

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ABSTRACT

In order to detect the lead in water sample with high sensitivity and selectivity, an automatic method based on a combined preconcentration setup and flow injection system was developed. A novel packed fiber solid phase extraction (PFSPE) cartridge packed with polystyrene nanofibers functionalized with dithizone (PS-DZ) was first designed to adsorb lead from water media in an online manner. Because the rapid adsorbtion/desorption equilibrium of lead ions on the nanofibers, the lead could be adsorbed on and liberated from the sorbent more fast and thoroughly compared with the conventional sorbent. The eluted lead in 0.1 mol L^{-1} HNO$_3$ was dispersed toward the electrolytic cell which was used for the quantification of the target ion. The anodic stripping voltammetry with glassy carbon electrode pre-coated by mercury film as working electrode was used in the detection part. Basing on the selective extraction of PS-DZ nanofibers, the interferential ions can be removed from the sample and the lead ion can be concentrated. The system was proved simple and convenient for quantification of lead in water samples with satisfactory results in an online and in site manner.

KEYWORDS

Electrospun nanofiber;
Packed fiber solid phase extraction (PFSPE);
Lead (II);
Anodic stripping voltammetry;
Online.

INTRODUCTION

Heavy metals, like lead, cadmium and copper are the cause of one of the most serious pollution problems of our time. They can threaten environment and human health even in small amounts, because they are not biodegradable and therefore retaine indefinitely in the ecological systems and accumulate in food chain[1]. Therefore monitoring of lead in the environment sample has become essential[2]. The direct determination of heavy metal ions in complex matrices is limited due to the low concentrations and matrix interferences[3]. Thus, to improve the sensitivity and selectivity of the determination of heavy metal ions, a preconcentration and separation procedure, such as liquid–liquid extraction, coprecipitation, and cloud point extraction[4-7] is essential and necessary.

There is a new technique called packed fiber solid phase extraction (PFSPE) [8], which is based on the use of electrospun nanofiber as the sorbent for the concentration of lead. Compared to the conventional SPE technique, the nanofiber sorbent possesses a large surface area which facilitates the attachment of target molecules, so that less amounts of sorbent, and less volume of sample and eluent are required[9]. Some successful applications of PFSPE have been reported in the extraction of target compounds, such as the cortisol in the saliva[9] vitamins in the plasma[10] and in the beverages[11], drugs in the plasma[12], and pollutants in the environmental water[13]. However, online automated PFSPE is rarely found to be reported.

In this work, an online-PFSPE method was developed. The concentrated lead eluated from the solid phase was impelled toward the electrolytic cell by the pump, and analyzed by anodic stripping voltammetry. Various experimental parameters were investigated, i.e., the condition of pre-coated mercury film, the enrichment time and voltage of lead etc.

EXPERIMENTAL

Reagents and solutions

All chemicals used in this work were of analytical reagent grade and were used without further purification. Doubly distilled deionized water was used throughout. The polystyrene (PS), Dithizone(DZ) were obtained from Shanghai Chemical Agents Institute. The standard labware and glassware used were cleaned with HNO3 and rinsed with double distilled water, according to Tuzen et al.[14]

Standard stock solutions (1mg.mL^{-1}) of lead were prepared by dissolving spectral pure grade chemical $Pb(NO_3)_2$ in double distilled water. Buffer solutions (NH_3/NH_4Cl) were prepared by mixing appropriate volumes of 1mol L^{-1} ammonium chloride and ammonia for pH 8–9. The elution reagent was 0.1 mol L^{-1} nitric acid. Mercury plating solution were prepared by dissolving 0.82 g of sodium acetate in 200 mg L^{-1} mercuric sulfate solution then diluted to 500 mL.

Instruments and apparatus

High-voltage power supply (DW-P403-1AC) was bought from Tianjin Dongwen High Voltage Power supply Co.,Ltd, syringe pump (WZ-50C6) was purchased from Smiths Medical Instrument (Zhejiang) Co., Ltd., electrochemical workstation (DL7021010001) and self-priming micropump (120SP1250-4EE) was supplied by Delin Enviromental Protection Technology Co., Ltd. Glassy carbon electrode, Ag/AgCl electrode, platinum electrode were all bought from Jiangsu Jiangfen Electroanalytical Instrument Co.,Ltd.

Fabrication of electrospun nanofiber and preparation of cartridge: Electrospun solution preparation: 1 g of PS was dissolved in 10 mL mixture of dimethylformamide and tetrahydrofuran (4/6, v/v). 0.1 g of dithizone was added into the polymer solution after PS was dissolved completely. The solution continued to be stirred at room temperature for more than 10 h before electrospinning.

PS-DZ Nanofiber electrospinning

electrospun solution was loaded into a glass syringe with a stainless steel tip. The electrospinning equipment was shown in Figure 1. The electrospun voltage was +17 kV, the feed rate was 1 mL h^{-1} for precursor solution. The nanofiber was collected on the collector which was covered by a piece of gauze pretreated by diluted HNO3 (1/9, v/v) and rinsed with distilled water.

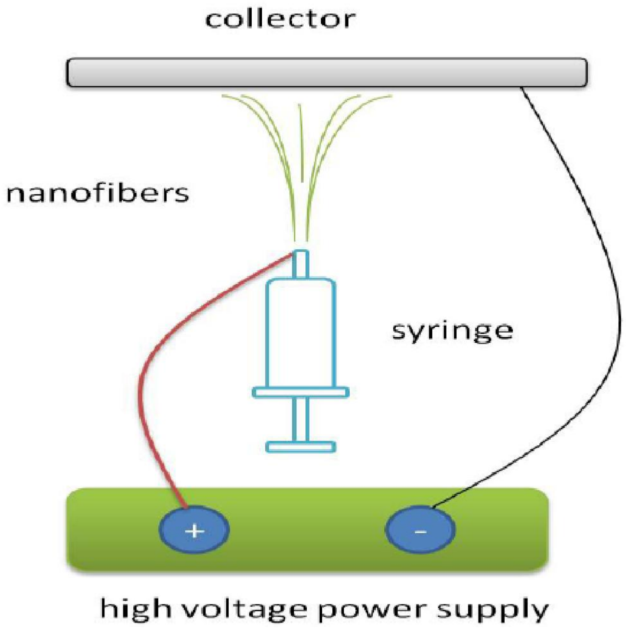
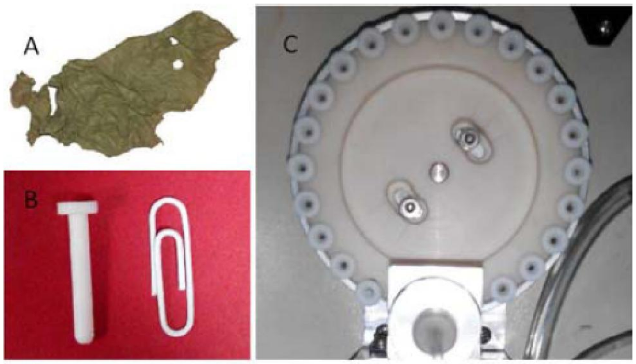


Figure 1 : The system of electrospinning

PFSPE cartridge preparation: A compact cartridge, as shown in Figure 2B, was designed for automatic online-PFSPE. 2 mg of PS-DZ nanofiber was packed in the cartridge. The cartridge was then inserted in the turntable designed specially, as shown in Figure 2C, in which 24 cartridges can be placed. After one sample was analyzed, the turntable would switch to other cartridges automatically.



A(PS-DZ nanofiber) B(PFSPE cartridge) C (Turntable)

Figure 2 : PFSEP devices

Flow injection system: The hyphenated flow injection-electrochemical system used is shown in Fig.3. The system consisted of two parts. Preconcentration setup was design for lead adsorption from water sample, and detection part was design for quantification of lead in the eluate obtained from preconcentration. Solenoid valves and nine-way valves ensured flowing into correct path for the solution. Syringe pump and peristaltic pump allowed the injection of a certain volume of reagent or sample. Electrolytic cell provided places for anodic stripping voltammetry. The turntable was used to switch the online PFSPE cartridges.

RESULTS AND DISCUSSION

Preconcentration setup

The preconcentration part is composed of optical control section, syringe pump, solenoid valves, turntable and connecting pipes, as show in Fig.3. At beginning, 0.4 mL of buffer solutions (NH_3/NH_4Cl) following with 2 mL of water sample is sampled in the syringe pump. The lead is absorbed by the PS-DZ nanofiber when the mixture is pushed through the PFSPE cartridge. The adsorption principle has been expounded in our previous research[3]. The elution reagent is pumped into the syringe and dispensed through the PS-DZ nanofiber to elute the lead absorbed. The eluate is pushed into the quantitative loop which is connected to the electrolytic cell. The preconcentration procedure ensures the satisfied purification and enrichment of lead in water sample. Once the determination of one sample is finished, the optical control section could make sure the turntable turn, and then the next PFSEP cartridge is loaded for the next sample analysis.

The pump parameters were optimized to obtain the high extraction recovery. An time interval was added between the two pump times. A pump time and an interval make a cycle operation. The cycle time period must be long enough when the pumping speed is determined. Several adjustable pump parameters are show in TABLE1. Experimental data show that the 3rd parameters could ensure the time conservation and smooth flow.

TABLE 1 : Summary of the pump parameters investigated

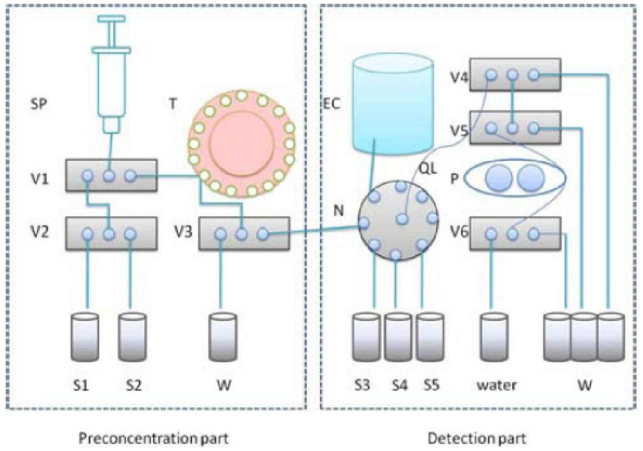
Number	Pumping speed	Pumping time(s)	Interval(s)	Cycle
1	300	20	15	6
2	300	15	10	8
3	100	30	20	12
4	100	20	10	18

Detection setup

The detection part is composed of optical control section, peristaltic pump, solenoid valves, nine-way valve, quantitative loop, electrolytic cell and connecting pipes, as show in Figure 3. The optical control section requests peristaltic pump pushed the eluate to the electrolytic cell when the quantitative loop is filled with eluate from the preconcentration part. Then the carrier fluid is dispensed in and the eluate is analyzed by anodic stripping voltammetry. The cleaning fluid is pumped in to clean the three electrodes after analysis, and then mercury pre-coated solution is introduced in to precoated mercury film on the surface of the electrode for the next detection. The dfferential pulse voltammogram of lead is shown in Figure 4.

The conditions pre-coating mercuty film were optimized to make sure the pulse perform well. The three electrode system was immersed into mercury precoated solution mixed by 200 mg L^{-1} HgSO4 and 0.01 mol L^{-1} of NaAc. The electric potential was set at -0.7

V, -0.8 V, -0.9 V, -1.0 V and -1.1 V respectively. The result was presented in Fig.5A, which showed that the peak area is largest at -1.0 V.



V1-V6(Solenoid valve); SP(Syringe Pump); P(Peristaltic pump); W(Waste); EC(Electrolytic cell); N(Nine-way valve); T(Turntable); QL(Quantitative loop); S1(sample or Standard solution); S2(Elution reagent); S3(Mercury pre-coated solution); S4(Carrier fluid); S5(Cleaning fluid)

Figure 3 : Flow injection analysis system

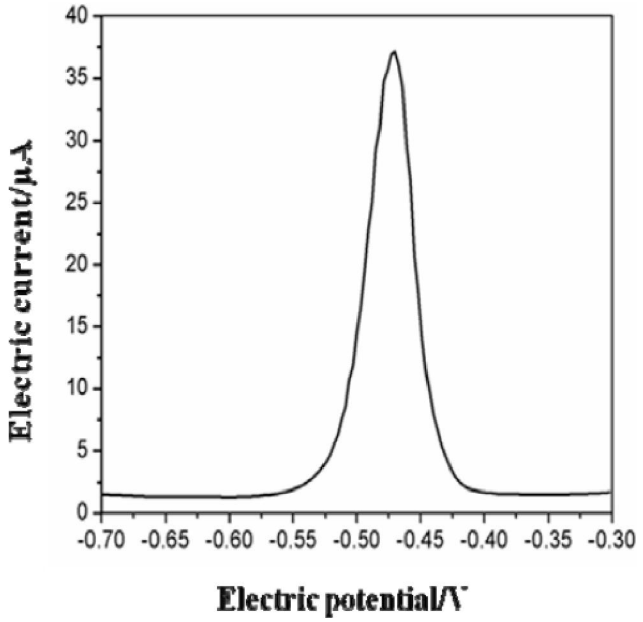


Figure 4 : The dfferential Pulse Voltammogram of lead

The enrichment electric potential and enrichment time were also investigated. The enrichment electric potential was set at -0.9 V, -1.0 V, -1.1 V, -1.2 V and -1.3V separately. The enrichment time was set at 130 s, 140 s, 150 s, 160 s and 170s. The results illustrated in Figure 5B and 5C revealed that a sharp pulse is achieved when enrichment condition is -1.1 V and 150 s.

Validation of assay

The standard calibration curves with water sample was linear in the range 5-100 μg L^{-1} and the liner regression equations were y=-0.0035+0.00178x (R=0.998). The LOD was 0.38 μg L^{-1}. The within-run and between-day precisions (RSD) were 4.7% and 5.4%, basically less than 10%.

Determination of real samples: The real samples, including lake water in a tourism area and tap water were used to examine how this method performed in the real samples. 100 μg L^{-1} of lead were added in the water samples to examine recovery of lead. As shown in TABLE 2, online-PFSPE electrochemical method performed well in the water samples with satisfactory recoveries.

CONCLUSIONS

A new online-PFSPE-electrochemical method was developed to determine lead in water sample. The procedure consisted of two parts. The preconcentration part which could reduce detection limit and improve sensitivity based on the PFSPE. The detection part designed for the quantification of lead depended on anodic stripping voltammetry. Experimental results indicated that this method was applicable to real water samples.

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REFERENCES

[1] I.Palchetti, C.Upjohn, A.P.F.Turner, M.Mascini; ANALYTICAL LETTERS, **33**, 1231-1246 **(2000)**.

[2] S.Anandhakumar, J.Mathiyarasu. Microchim Acta, **180**, 1065-1071 **(2013)**.

[3] J.Deng, X.Kang, L.Chen, Y.Wang, Z.Gu, Z.Lu; Journal of Hazardous Materials, 196: 187-193(2011).

[4] M.O.Luconi, M.F.Silva, R.A.Olsina, L.P.Fernandez; Talanta, **196(30)**, 187-193 **(2011)**.

[5] J.Liu, H.Chen, X.Mao, X.Jin; Inturn. J. Environ.

Anal. Chem, **76**, 267-282 **(2000)**.

[6] Y.Okamoto, Y.Nomura, H.Nakamura, K.Iwamaru, T.Fujiwara, T.Kumamaru; Microchemical Journal, **65**, 341-346 **(2000)**.

[7] J.Chen, K.C.Teo; Analytica Chimica Acta, **450**, 215-222 **(2001)**.

[8] X.Kang, C.Pan, Q.Xu, Y.Yao, Y.Wang, D.Qi, Z.Gu; Analytica Chimica Acta, **587**, 75-81 **(2007)**.

[9] L.Chen, X.Kang, J.Sun, J.Deng, Z.Gu, Z.Lu; J. Sep. Sci., **33**, 2369-2375 **(2010)**.

[10] Z.Liu, X.Kang, F.Fang; Microchim Acta, **168**, 59-64 **(2010)**.

[11] F.Fang, X.Kang, Z.Liu, Y.Ma, Z.Gu; Chinese Chemical Letters, **20**, 1491-1494 **(2009)**.

[12] X.Kang L.Chen, Y.Wang, Y.Zhang, Z.Gu; Biomed Microdevices, **11**, 723-729 **(2009)**.

[13] D.Qi, X.Kang, L.Chen, Y.Zhang, H.Wei, Z.Gu. Anal Bioanal Chem, **390**, 929-938 **(2008)**.

[14] M.Tuzen, K.O.Saygi, M.Soylak; Journal of Hazardous Materials, **156**, 591-595 **(2008)**.