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Thermo-responsive polymer coated fiber-in-tube capillary microextraction and its application to on-line determination of Co, Ni and Cd by inductively coupled plasma mass spectrometry (ICP-MS)

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ABSTRACT

The poly(N-isopropylacrylamide) (PNIPA) gel is a widely studied thermo-responsive material that exhibits discontinuous change in volume when the external temperature is increased. In this paper, PNIPA gel was prepared and applied as a novel polymer coating for fiber-in-tube capillary microextraction of trace Co, Ni and Cd followed by on-line ICP-MS detection. The PNIPA coating was synthesized by using ethylene triethoxysilane (ETEOS) as the cross-linking agent under acidic conditions. This siloxane incorporated PNIPA gel achieves a dramatically rapid response rate when the external temperature is changed. The micro-structure of PNIPA coating was examined by scanning electron micrograph (SEM). Various experimental parameters including pH, temperature, sample flow rate and volume, elution solution and interfering ions affecting the extraction of the target analytes have been carefully investigated and optimized. Under the optimized conditions, the limits of detection were 0.45, 4.6 and 6.9 ng L^{-1} for Co, Ni and Cd, respectively. With a sampling frequency of 13 h^{-1}, the relative standard deviations (RSDs) for Co, Ni and Cd were 4.8, 5.1 and 6.4% ($C = 1$ μg L^{-1}, $n = 7$), respectively. The proposed method had been successfully applied to the determination of Co, Ni and Cd in human urine. To validate the proposed method, certified reference materials of NIES No. 10-b rice flour and GBW07601 (GSH-1) human hair were analyzed and the determined values were in a good agreement with the certified values. The PNIPA coated fiber-in-tube capillary can be reused for more than 150 times without decreasing the extraction efficiency.

1. Introduction

Cobalt and nickel are essential trace elements, which are required for the implementation of multiple functions in the organism but can be harmful at high concentrations [1]. Cadmium is one of the most toxic heavy metal elements for animals and humans even at low concentrations with long biological half-life (10–40 years). Cd was listed as the sixth most poisonous substance jeopardizing human's health [2]. Consequently, the development of sensitive, reproducible and accurate analytical method for determination of trace cobalt, nickel and cadmium in environmental and biological samples is of particular significance.

Inductively coupled plasma mass spectrometry (ICP-MS) [3–5] was one of the most powerful techniques for trace/ultratrace elements analysis due to its super high sensitivity, low limits of detection, high sample throughput, wide linear dynamic range and multi-element detection capability. Nevertheless, direct and accurate determination of trace metals in biological samples (e.g. human serum and human urine) by ICP-MS is still challenging because of their extremely low concentrations and very complicated sample matrix. Therefore, a sample pretreatment step is required to separate the analytes from the matrix and preconcentrate them before their measurements. The conventional techniques for the separation/preconcentration of trace metals, including liquid–liquid extraction (LLE) [6], solid phase extraction (SPE) [7] and cloud point extraction (CPE) [8], are time consuming and labor intensive, which require large volumes of sample and reagents. This is especially the case when limited sample amount is available for forensic, biological and clinical fields. Therefore, a novel miniaturized sample preparation method is needed urgently to overcome these disadvantages.

Capillary microextraction (CME, also termed as in-tube solid phase microextraction), developed from solid phase microextraction (SPME) [9], was first introduced by Bigham et al. [10] as a viable solvent-free extraction technique. CME utilizes an open tubular capillary column as extraction device, and a sorptive coating on the inner surface of capillary as the extraction medium in which the analyte in aqueous sample is directly extracted and concen-

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trated. Similar to SPME, CME is also based on the distribution of analytes between the sample matrix and the extracting phase coated on the inner surface of a capillary. Utilizing a silica-fused capillary with stationary phase coating on the inner surface to perform extraction, CME overcomes the inherent shortcomings of fiber SPME such as fiber breakage and mechanical damage of the coating. As a simple, sensitive, time-effective, solvent-free, easy-to-automate and miniaturized sample preparation technique, CME has been widely used for analysis of trace organic and inorganic analytes by on-line coupling with different detection instrumentations such as gas chromatography (GC) [11], high-performance liquid chromatography (HPLC) [9], capillary electrophoresis (CE) [12], electrospray mass spectrometry (ES-MS) [13], ICP-MS [14,15] and liquid chromatography–mass spectrometry (LC–MS) [16].

The extraction coating and its stability play a fundamentally important role in the CME sample preparation technique which determines its efficiency, selectivity and sensitivity, therefore, further development of CME will mainly depend upon the new breakthroughs in adsorbent development and coating technology [11]. Besides the conventional organic poly(dimethyl siloxane) (PDMS) and poly(ethylene glycol) (PEG) coatings [10], a large number of new capillary coatings have been increasingly developed and investigated. Due to its abilities to form inclusion complexes with certain analytes, β-cyclodextrin coated capillary [17] was prepared by sol–gel method and applied to in-tube SPME–HPLC determination of non-steroidal anti-inflammatory drugs (ketoprofen, fenbufen and ibuprofen) in urine samples with satisfactory limits of detection and good precision. Moreover, the β-cyclodextrin coated capillary was proved to be reusable and the extraction efficiency did not decrease after 250 extractions. Silica-fused capillary modified by 2-acrylamido-2-methyl-1-propanesulfonic acid (which was a strong cation exchanger) had been tested for its stability over a wide pH range of 2–9. The results show that the interaction of Et_3Pb^+ with the capillary coating was negligible while Pb^{2+} could be selectively retained at pH > 7 [18]. In our previous works, metal oxides coated capillaries, such as ordered mesoporous Al_2O_3 [19], ZrO_2 [20] and TiO_2 [21] coated capillaries, were synthesized and on-line coupled with ICP-MS for analysis of Co, Ni, Cd Cr, Cu, Cd, Pb and V, respectively. Besides the open tubular CME, other forms of CME such as fiber-in-tube CME [22,23] had also been developed for on-line separation/preconcentration of trace analytes. Generally, in fiber-in-tube CME, several hundreds of fine filaments of polymeric material were packed longitudinally into a short capillary or polyether ether ketone (PEEK) tube. Compared to open tubular CME, the preparation process of fiber-in-tube CME is labor-saving and both internal volume and phase ratio are dramatically reduced and therefore the extraction is more effective.

Recently, considerable attention has been drawn to the so-called smart hydrogels, which can undergo a reversible and yet discontinuous volume phase change in response to various external physicochemical factors, such as pH, temperature, electrical potential and metabolites and ionic factors [24]. It has been recognized that such smart gels could be potentially used in the biomedical and pharmaceutical fields [24–26]. Among them, temperature- and pH-responsive hydrogels have been most widely studied, because these two factors have a physiological significance [24]. Thermosensitive hydrogels are of great interest in therapeutic delivery systems and in tissue engineering as injectable depot systems. The cross-linked poly(N-isopropylacrylamide) (PNIPA) gel was a widely studied thermo-responsive material, which exhibited a phase transition temperature (Ttr) or lower critical solution temperature (LCST) around 32 °C [25]. At temperatures below the LCST, the PNIPA gel was soluble in water; as the temperature was increased above LCST, it underwent abrupt changes in volume and precipitated suddenly from solution. Therefore, PNIPA gel with LCST below human body temperature (36–37 °C) had shown tremendous promise in targeted delivery in the body [26]. However, the report on the application of PNIPA to inorganic analysis is really scarce [27]. Tanaka et al. [27] proposed a simple preconcentration method for the determination of trace metals (Co, Ni, Cu, Pb) in water samples by electrothermal vaporization (ETV)-ICP-MS. The method is based on the thermoresponsive precipitation of PNIPA, from the aqueous sample solution and the simultaneous incorporation of hydrophobic metal chelates (metal-APDC (ammonium pyrrolidinedithiocarbamate) chelates) into the precipitate.

The aim of this work was to prepare cross-linked PNIPA coating by polymerization and to develop a system of PNIPA coated fiber-in-tube capillary microextraction of trace Co, Ni and Cd followed by on-line ICP-MS determination. Experimental parameters affecting fiber-in-tube capillary microextraction of target analytes were studied in detail and the optimal experimental conditions were established. The developed method was applied to the analysis of trace Co, Ni and Cd in human serum and urine with satisfactory results.

2. Experimental

2.1. Instrumentations

An Agilent 7500a ICP-MS (Agilent, Tokyo, Japan) with Babington nebulizer was used for determination. The optimal operation conditions were summarized in Table 1. The isotopes of interest were ^{59}Co, ^{60}Ni and ^{111}Cd.

The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China) was used for sample digesting. An IFIS-C flow injection system (Ruimai Tech. Co. Ltd., Xi'an, China) was used for online coupling CME with ICP-MS. Optical fiber (240 μm o.d.) with protective polyimide coating and fused silica capillary (530 μm i.d. × 680 μm o.d.) were provided by Hebei Yongnian Optical Fiber Factory, China. PTFE tubing with 0.5 mm i.d. was used for all connections. These connections were kept as short as possible to minimize the dead volume. The structure of PNIPA coated fiber was characterized by 170SX FI-IR (NICOL ET, USA). Differential scanning calorimetry (DSC) experiments were performed from 20 to 35 °C (heating rate: 5 °C/min) on the swollen gels using a DSC calorimeter (DSC-Pyris 1, Perkin-Elmer) under a helium atmosphere. The SEM of the coating was obtained using an X-650 scanning electron microscope (Hitachi, Tokyo, Japan) at an acceleration voltage of 25 kV.

Table 1
Operating parameters of ICP-MS.

ICP-MS	
RF power	1200 W
RF matching	1.6 V
Outer gas flow rate	15 L min^{-1}
Intermediate gas flow rate	0.9 L min^{-1}
Nebulizer gas flow rate	1.08 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	20 ms
Integration mode	Peak area
Points per spectral peak	1
Isotopes and potential interference species	^{59}Co: $^{24}Mg^{35}Cl$, $^{40}Ca^{19}F$, $^{43}Ca^{16}O$, $^{42}Ca^{16}O^{1}H$, $^{40}Ar^{19}F$ ^{60}Ni: $^{25}Mg^{35}Cl$, $^{23}Na^{37}Cl$, $^{43}Ca^{16}O^{1}H$, $^{44}Ca^{16}O$, $^{40}Ar^{20}Ne$, $^{46}Ti^{14}N$ ^{111}Cd: $^{95}Mo^{16}O$, $^{94}Zr^{16}O^{1}H$, $^{71}Ga^{40}Ar$, $^{97}Mo^{14}N$

2.2. Standard solutions and reagents

The stock solutions (1 g L^{-1}) of Co, Ni, Cd, Cr, Cu, Zn and As were obtained by dissolving appropriate amounts of $Co(NO_3)_2{\cdot}6H_2O$, $NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$, $CdCl_2{\cdot}2.5HO_2$, $CuSO_4{\cdot}5H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $NaAsO_2{\cdot}12H_2O$ (all of analytical reagent grade, The First Reagent Factory, Shanghai, China) in 1% (v/v) diluted HNO_3 and diluted to 100 mL with high purity deionized water, respectively. The stock solutions of interfering elements were prepared from their salts by a conventional method. All other chemicals were of analytical reagent grade or specpure grade.

The monomer of N-isopropylacrylamide (NIPA, 97%) was purchased from Aldrich Chemical Corp. (Milwaukee, WI, USA) and recrystallized with hexane. Ethylene triethoxysilane (ETEOS) (analytical reagent grade) was purchased from Chemical Plant of Wuhan University (Wuhan, China). Ammonium persulfate (APS), sodium bisulfite (SBS) and glacial acetic acid (HAc) were of analytical reagent grade and supplied by Wuhan Shenshi Chemical Company (Wuhan, China). The high purity deionized water (18.2 MΩ cm) obtained from Milli-Q Element purification system (Millipore, Massachusetts, USA) was used throughout this work.

Certified reference material of NIES No. 10-b rice flour was obtained from National Institute for Environmental Studies (NIES, Ibaraki-ken, Japan). Certified reference material of human hair GBW 07601(GSH-1) was purchased from National Research Centre for Certified Reference Material (GBW, Beijing, China).

2.3. Analytical procedure

The schematic diagram of on-line CME–ICP-MS employed in this work was illustrated in Fig. 1 as well as the amplification of the PNIPA coated fiber-in-tube capillary. Generally, 1 mL of sample solution (pH 8) containing Co(II), Ni(II) and Cd(II) was passed through PNIPA coated fiber-in-tube capillary at a flow rate of 0.3 mL min^{-1} with the flow injection system. Afterwards, the analytes retained on the capillary were on-line eluted with 50 μL of 0.1 mol L^{-1} HNO_3 for further ICP-MS detection. The blank solution and the series of standard solution were carried out with the same experimental procedure of on-line CME–ICP-MS.

2.4. Preparation of PNIPA coated fiber-in-tube capillary

The PNIPA coated fiber-in-tube capillary was illustrated in Fig. 1. As could be seen, two optical fibers (10 cm, 240 μm o.d.) with a thin layer of PNIPA coating were placed in a 10 cm capillary (530 μm i.d. × 680 μm o.d.) and utilized as the extraction device. Compared to conventional open-tubular capillary, the void was reduced greatly and the extraction efficiency could be improved.

2.4.1. Synthesis of PNIPA coating through polymerization

The synthesis of PNIPA was based on the procedure reported in literature [25] with minor modification. Briefly, 80 mg of monomer NIPA and 16 μL ETEOS were dissolved in 500 μL mixed solvent of HAc/distilled water (v/v = 1:4). APS and SBS were used as a pair of redox initiators (4.0 wt% based on NIPA). The polymerization/cross-linking reaction was first carried out at room temperature (18 °C) for 15 min and then the reaction was continued at 60 °C for 5 h. After the reaction, the obtained PNIPA solution was transferred to a clean glass tube (10 cm, 500 μm i.d.) and further used in the coating process.

2.4.2. Preparation of PNIPA coated fiber-in-tube capillary

Prior to coating, optical fiber (60 cm, 240 μm o.d.) with protective polyimide coating was pre-cleaned by immersing in high purity deionized water for 30 min and dried at 40 °C. Then the fiber was cut into 6 pieces (each 10 cm).

The coating procedure was performed as described previously [28]. The above pretreated fiber was inserted vertically into the PNIPA solution contained in a clean glass tube (10 cm, 500 μm i.d.) for a controlled period of time (10–15 min) to facilitate the formation of PNIPA coating and its chemical bonding to the fiber substrate. After that, the fiber was drawn out from the solution and dried for 30 min. For each fiber, this coating process was repeated four times until the desired thickness of the coating was obtained. The coated fiber was dried in a desiccator at room temperature for 6 h under nitrogen protection.

Finally, two PNIPA coated fibers (10 cm) were simultaneously inserted into one capillary (10 cm, 530 μm i.d. × 680 μm o.d.) and employed as the extraction media. Compared with the conventional coated capillary, this fiber-in-tube capillary is easy to be bent in extraction process.

2.5. Characterization of PNIPA coating

2.5.1. FT-IR characterization

The IR spectra of gel samples were measured on a Nicolet 170SX FT-IR spectrophotometer. Before the measurement, the originally swollen gel samples were kept at 48 °C for 2 h and then further dried in a vacuum for 48 h.

2.5.2. DSC characterization

DSC experiments were performed from 15 to 35 °C (heating rate: 5 °C/min) on the swollen gels using a DSC calorimeter (DSC-Pyris1, Perkin-Elmer) under a helium atmosphere. All samples were equilibrated in distilled water at 15 °C for at least 24 h prior to the experiments. During the thermal analyses, distilled water was used as a reference.

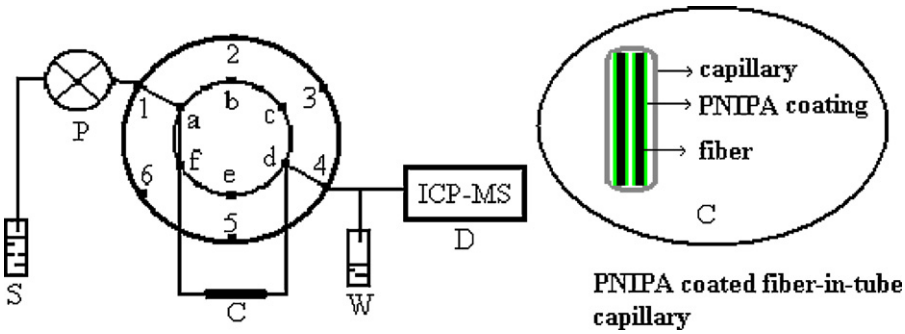

Fig. 1. Schematic diagram of on-line capillary microextraction (CME)-ICP-MS with PNIPA coated fiber-in-tube capillary as extraction device.

2.5.3. Surface morphology

After PNIPA coated fibers were prepared, they were dried in a vacuum at room temperature for 3 h. The surface morphology of PNIPA coated fiber was studied by using a scanning electron microscope (SEM, Hitachi-X650, Japan). Before SEM observation, the fibers were coated with gold in SEM coating equipment.

2.6. Sample preparation

2.6.1. Certified reference materials

50 mg of NIES No. 10-b rice flour and 50 mg of GBW07601 (GSH-1) human hair were weighed into 50 mL polytetrafluoroethylene (PTFE) vessels, and then 2.0 mL concentrated HNO_3 was added, respectively. The heating programs for microwave digestion were as follows: 3 atm for 1 min, 8 atm for 2 min and then 10 atm for 3 min. After digestion, clear solution could be observed. The solution was evaporated to a very small volume by a plate heater to remove the superfluous acid under a relatively low temperature to avoid loss of analytes. The residue was then dissolved with high purity deionized water and diluted to 3 mL. Prior to use, the solution was adjusted to pH 8.0 with 0.01 mol L^{-1} $NH_3{\cdot}H_2O$ and made up to 5 mL with high purity deionized water.

2.6.2. Human serum and urine

Pooled human serum collected from healthy adults was supplied by the Hospital of Wuhan University (Wuhan, China) and urine samples were collected from the healthy laboratory workers.

For microwave digestion of serum and urine samples, 4.0 mL of human serum and 4.0 mL human urine samples were transferred into 50 mL PTFE vessels, and 2.5 and 2.0 mL concentrated HNO_3 were added into the human serum and urine samples, respectively. After the same digestion procedure as described above, both of the solutions of human serum and urine were adjusted to pH 8.0 and diluted to 4 mL with high purity deionized water.

All of the blank samples with the same amount of acid were subjected to the same procedure except for adding no samples.

3. Results and discussion

3.1. Characterization of PNIPA coating

3.1.1. IR spectra of PNIPA coating

The IR spectra of the dried gel samples of PNIPA coating are shown in Fig. 2. A broad band in the wave number range of 3200–3600 cm^{-1} was observed, which belongs to N–H stretching vibration. The typical amide I band (1637.6 cm^{-1}) of C=O stretch

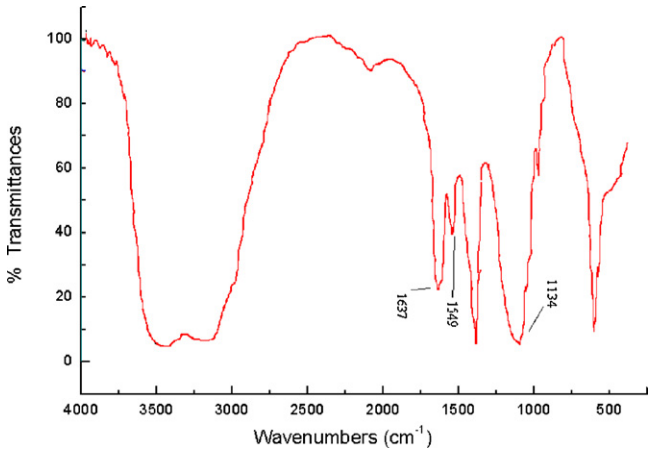

Fig. 2. Infrared spectra for PNIPA coating.

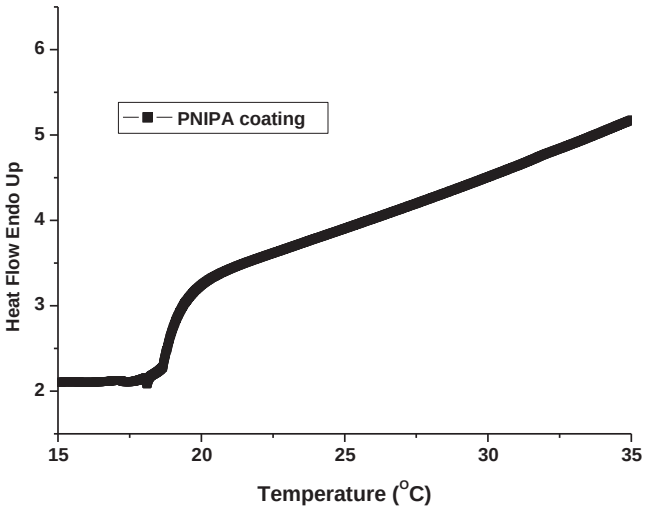

Fig. 3. DSC thermograms of PNIPA coating at a heating rate of 5 °C/min from 15 to 35 °C.

of PNIPA and an amide II band (1549.2 cm^{-1}) of N–H vibration were also found in each spectrum. Besides, a band at 1133.9 cm^{-1} that belongs to Si–O–Si stretching vibration could also be observed. These data suggest that the PNIPA gels are cross-linked through the Si–O–Si bond.

3.1.2. DSC behavior of PNIPA coating

DSC thermograms of gels are shown in Fig. 3. Here, the temperature at the maxima of the DSC endotherms was also referred to as the LCST of the gel. Based on the calculating method described in ref. [29] and the data given in Fig. 3, the LCST of the PNIPA gel prepared in this work was calculated to be 19.02 °C.

3.1.3. Surface morphology of PNIPA coating

The surface morphologies of bare fiber (240 μm o.d., 150×), PNIPA coated fiber (150×) and its amplification (300×) were given in Fig. 4(A)–(C), respectively. Compared to the surface of the bare fiber in Fig. 4(A), the surface of the coated fiber in Fig. 4(B) is very thin but very compacted. Furthermore, from the micrograph shown in Fig. 4(C), the thickness of the PNIPA coating on the fiber was estimated to be about 1.5 μm.

3.2. Optimization of CME parameters

3.2.1. Effect of pH value

The effect of pH on the adsorption of Co(II), Ni(II), Cd(II), Cu(II), Cr(III), Zn(II) and As(III) on PNIPA coated fiber-in-tube capillary was evaluated and the results were given in Fig. 5. As can be seen, above 80% of Cu(II) was adsorbed on PNIPA coating in a narrow pH range of 5–6, but a gradual decrease of adsorption percentage was observed at pH higher than 6; the adsorption percentage of Co(II), Ni(II) and Cd(II) was increased rapidly with the increase of pH and a quantitative adsorption was obtained in the pH range of 7.5–9; as for other metal ions such as Cr(III) and Zn(II), their adsorption on the PNIPA coated fiber were not quantitatively in the pH range of 1–9; As(III) was not retained by the PNIPA coated capillary in the whole pH range studied in this work. Therefore, it was difficult to achieve a simultaneous quantitative adsorption of all the tested metal ions at a certain pH value. Finally, pH 8.0 was selected to guarantee quantitative adsorption of Co(II), Ni(II) and Cd(II) for further experiments.

According to the theory of Pearson's concept of hard and soft acids and bases [30], the interaction force between soft acid and soft base, or hard acid and hard base, are stronger than the inter-

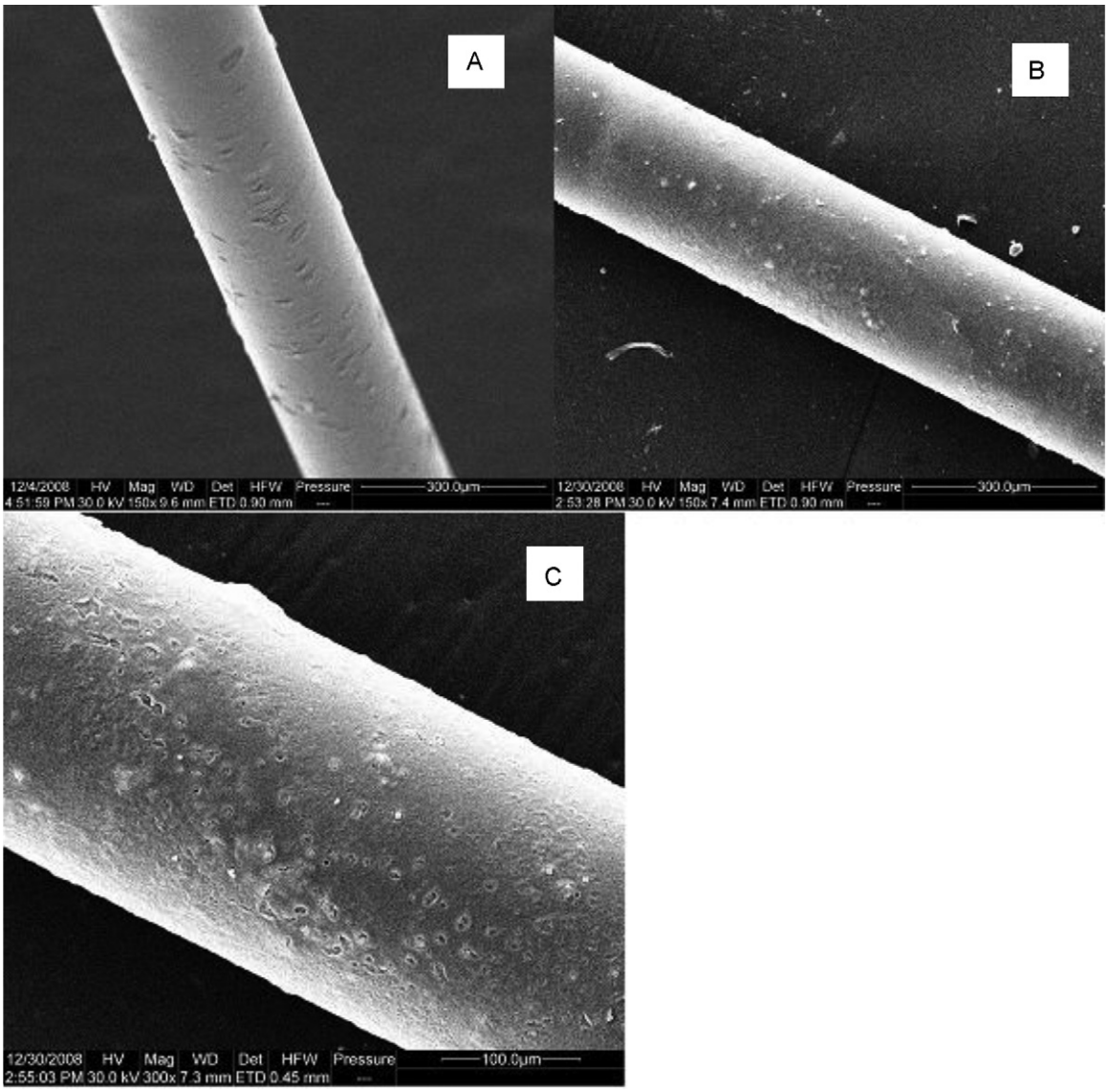

Fig. 4. SEM of bare fiber × 150 (A), PNIPA coated fiber × 150 (B) and PNIPA coated fiber × 300 (C).

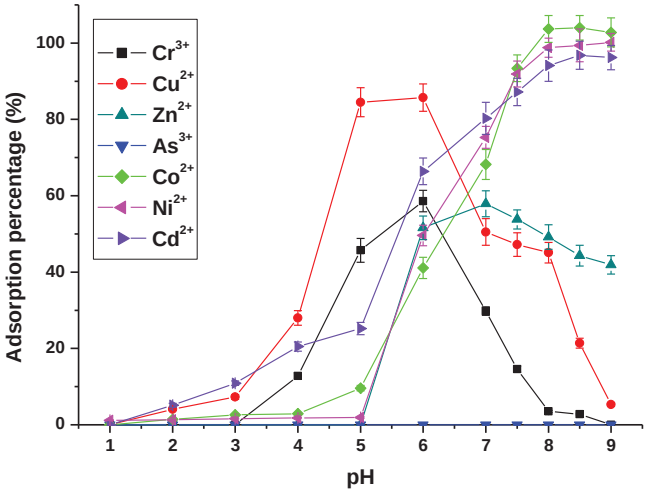

Fig. 5. Effect of pH on the adsorption percentage of Co(II), Ni(II), Cd(II), Cu(II), Cr(III), Zn(II) and As(III); sample volume: 1 mL; Co(II), Ni(II), Cd(II), Cu(II), Cr(III), Zn(II) and As(III): 10 μg L^{-1}.

action force between soft acid and hard base, or hard acid and soft base. Since the functional group of PNIPA coating (amide, $-CONH_2$) was nearly soft bases, it had preference towards soft acids such as transitional metal ions Co(II), Ni(II) and Cd(II); on the other hand, the amide had only a very weak interaction force with the hard acid metal ions such as As(III), which was coincident with the experimental results obtained above.

3.2.2. *Effect of temperature*

In this work, the effect of temperature on the adsorption was also explored in the range of 10–50 °C and the results were given in Fig. 6. As could be seen, the effect of the temperature on the adsorption behavior of Co(II), Ni(II) and Cd(II) on PNIPA coated fiber-in-tube capillary was negligible. Therefore, all the following experiments were performed at room temperature.

3.2.3. *Effect of sample flow rate*

The effect of sample flow rate was evaluated by passing 1 mL of sample solution through the capillary with the flow rate varying in the range of 0.1–0.7 mL min^{-1}. It was found that quantitative recoveries (>90%) of Co(II), Ni(II) and Cd(II) were obtained at flow

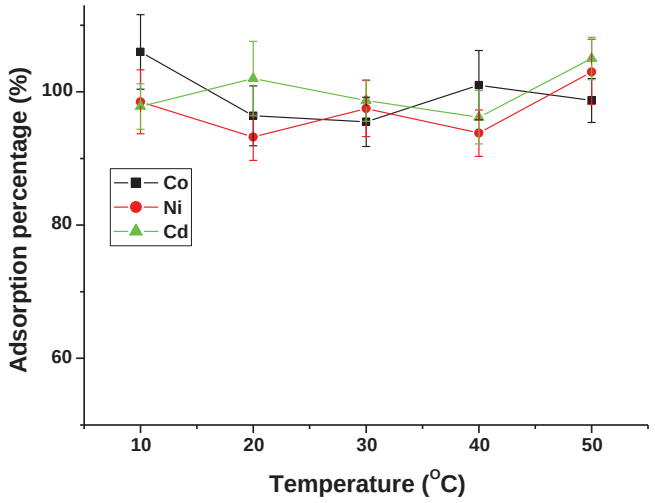

Fig. 6. Effect of temperature on the adsorption percentage of Co(II), Ni(II) and Cd(II), sample volume: 1 mL; Co(II), Ni(II) and Cd(II): 10 μg L^{-1}.

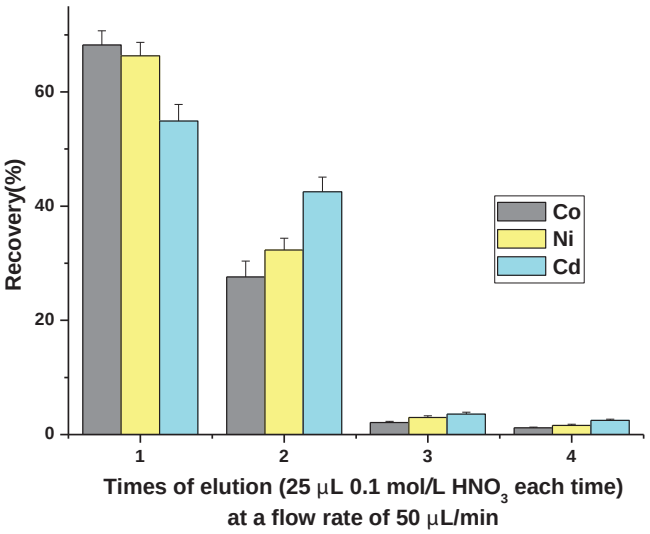

Fig. 7. Effect of eluent volume on the adsorption percentage of Co(II), Ni(II) and Cd(II), sample volume: 1 mL; Co(II), Ni(II) and Cd(II): 10 μg L^{-1}.

rates less than 0.4 mL min^{-1}. Accordingly, a sample flow rate of 0.3 mL min^{-1} was employed in this work.

3.2.4. Effect of elution

3.2.4.1. Eluent concentration. As illustrated previously in Fig. 5, at pH 2, the adsorption percentage of Co(II), Ni(II) and Cd(II) on PNIPA coated fiber-in-tube capillary was nearly to zero, therefore, the target metal ions retained on the fiber could be easily desorbed by changing the pH of the medium. Accordingly, HNO_3 was applied as the eluent to achieve simultaneous desorption of Co(II), Ni(II) and Cd(II) from PNIPA coated fiber-in-tube capillary and the results were given in Table 2. As could be seen, Co(II), Ni(II) and Cd(II) could be eluted easily and quantitatively (>90%) when the concentration of HNO_3 was higher than 0.05 mol L^{-1}. Accordingly, 0.1 mol L^{-1} HNO_3 was selected to guarantee a satisfactory recovery.

3.2.4.2. Eluent volume. To study the effect of the elution volume, 100 μL of 0.1 mol L^{-1} HNO_3 was used as eluent to continuously elute the target metal ions adsorbed on the PNIPA coated fiber-in-tube capillary at a flow rate of 50 μL min^{-1}, and the analytes in four effluents (each 25 μL) were determined by ICP-MS. The experimental results in Fig. 7 indicated that 50 μL of eluent was sufficient to elute quantitatively (>90%) all the analytes in 1 min. Finally, 50 μL of 0.1 mol L^{-1} HNO_3 with a flow rate of 50 μL min^{-1} was employed as the optimized elution conditions.

3.2.5. Effect of sample volume

In order to investigate the breakthrough volume of the method, sample solutions of 1, 2, 5, 10 and 12 mL containing Co(II), Ni(II) and Cd(II) (each of 10 ng) were passed through the PNIPA coated fiber-in-tube capillary and then subjected to the analytical procedure described above. It was found that the quantitative recoveries were obtained with sample volumes ranging from 1 to 10 mL for the target metal ions. Considering the analytical speed, a sample volume of 1.0 mL was chosen, which results in an enrichment factor of 20 and a sampling frequency of 13 h^{-1}.

Table 2
Recovery (%) of Co(II), Ni(II) and Cd(II) with different concentration of HNO_3.

Concentration of HNO_3 (mol L^{-1})	Recovery (%, mean ± SD, n = 3)		
	Co(II)	Ni(II)	Cd(II)
0.01	102.8 ± 4.6	98.6 ± 3.4	85.3 ± 5.0
0.05	106.4 ± 5.7	100.5 ± 7.2	98.4 ± 5.4
0.1	95.9 ± 3.8	104.8 ± 6.3	92.9 ± 4.7
0.3	97.7 ± 6.9	99.1 ± 5.1	91.5 ± 3.9
0.5	105.2 ± 5.8	93.5 ± 4.0	92.7 ± 4.2

3.2.6. Effect of capillary length

The influences of capillary length on the preconcentration/separation of Co(II), Ni(II) and Cd(II) were investigated under the optimum conditions, and the results were shown in Fig. 8. As can be seen, the recoveries of Co(II), Ni(II) and Cd(II) were increased with the increase in capillary length from 5 to 10 cm, and quantitative recoveries (over 90%) were obtained at a length of 10–20 cm. As a result, a two 10-cm PNIPA coated fibers were simultaneously inserted into one 10 cm capillary as the extraction device for further works.

3.2.7. Coexisting ions interference

The interference caused by coexisting ions prevailing in biological samples was explored with 1 mL sample containing each 10 μg L^{-1} of Co(II), Ni(II) and Cd(II), respectively, and the results were given in Table 3. The tolerance limits, which were defined as 10% decrease of the signal intensity, are 10,000 mg L^{-1} K^+, Na^+;

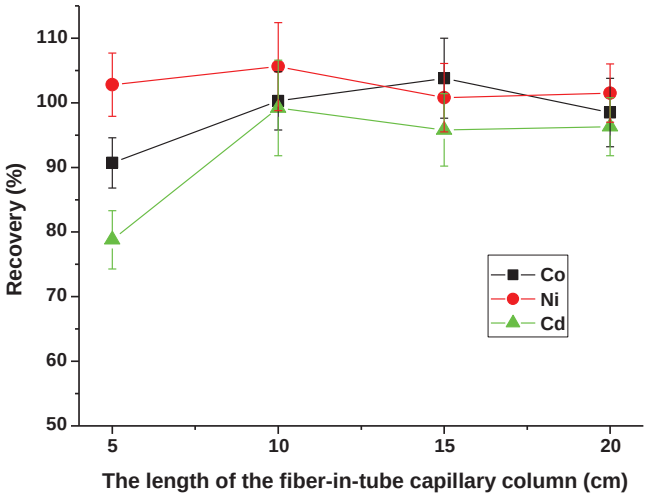

Fig. 8. Effect of capillary length on the adsorption percentage of Co(II), Ni(II) and Cd(II), sample volume: 1 mL; Co(II), Ni(II) and Cd(II): 10 μg L^{-1}.

Table 3
Tolerance of coexisting ions.

Coexisting ions	Tolerance limits (mg L^{-1})
K^+, Na^+	10000
Mg^{2+}	4000
Ca^{2+}	2000
Al^{3+}	10
Fe^{3+}	4
Zn^{2+}	2
SO_4^{2-}	8000
Cl^-	10000

Table 4
Reproducibility of thermo-responsive coated fiber-in-tube capillary ($n = 7$).

Capillaries prepared in one batch and three different batches	RSDs ($C = 1\ \mu g\ L^{-1}$, $n = 7$)		
	Co(II)	Ni(II)	Cd(II)
Capillaries prepared from the same batch	8.8%	6.4%	5.7%
Capillaries from three different batches	8.6%	9.0%	7.8%

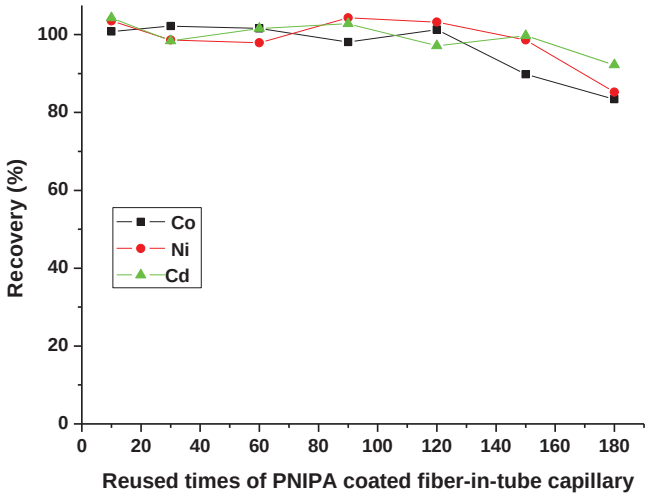

Fig. 9. Maximal used times of PNIPA coated fiber-in-tube capillary under optimized experimental conditions.

4000 mg L^{-1} Mg^{2+}; 2000 mg L^{-1} Ca^{2+}; 10 mg L^{-1} Al^{3+}; 4 mg L^{-1} Fe^{3+}; 2 mg L^{-1} Zn^{2+}; 10,000 mg mL^{-1} Cl^- and 8000 mg L^{-1} SO_4^{2-}. Based on the above results, it can be concluded that the PNIPA coating material had good selectivity towards Co(II), Ni(II) and Cd(II) under the optimized experimental conditions and could be employed for the extraction of Co(II), Ni(II) and Cd(II) from the biological samples.

3.2.8. Reproducibility of the preparation of PNIPA coated fiber-in-tube capillary

The extraction efficiencies of three PNIPA coated fiber-in-tube capillaries prepared in the same batch and different batches were tested under the optimized conditions, and the precisions were shown in Table 4. As could be seen, no distinct difference in recoveries for the target analytes was observed from fiber-in-tube capillaries prepared in the same batch or different batches. These results demonstrated that the preparation of PNIPA coated fiber-in-tube capillary had a good reproducibility.

3.2.9. Analytical performance

3.2.9.1. Regeneration of PNIPA coated fiber-in-tube capillary. The regeneration is one of the key factors in evaluating the performance of the adsorption material. Under the optimized experimental conditions, 250 mL of sample solution containing 10 μg L^{-1} Co(II), Ni(II) and Cd(II) was prepared. 1 mL above sample solution and 50 μL eluent were continuously passed through one PNIPA coated fiber-in-tube capillary (10 cm) and the analytes in the eluents were determined by ICP-MS. Fig. 9 is the evaluation of the reused times of the prepared PNIPA coated fiber-in-tube capillary. It was obvious that PNIPA coated fiber-in-tube capillary could be reused for more than 150 times while the recoveries of the target analytes was kept above 90%.

3.2.9.2. Adsorption capacity. The adsorption capacity is another important factor for evaluating the performance of the adsorption material. The capacity study used in this work was based on the method recommended by Hu et al. [19]. Briefly, 40 mL sample solution containing 50 μg L^{-1} analytes was passed through the PNIPA coated fiber-in-tube capillary (10 cm) and the analytes in the effluents were determined by ICP-MS. The maximal adsorption capacities evaluated from the breakthrough curve were 758 ng (Co), 965 ng (Ni) and 988 ng (Cd) for 10 cm PNIPA coated fiber-in-tube capillary.

3.2.9.3. Precision and limits of detection. According to the IUPAC definition, the limits of detection (3σ) of the method, defined as three times the standard deviation of blank signal intensity, were 0.45, 4.6 and 6.9 ng L^{-1} for Co, Ni and Cd, respectively. The relative standard deviations (RSDs) for seven replicate determinations of 1 μg L^{-1} of the target metals were in the range of 4.8–6.4%, with a sampling frequency of 13 h^{-1}. The analytical performance of on-line CME–ICP-MS was summarized in Table 5.

For comparison, the limits of detection of the proposed method and the other similar methods reported in the literatures for Co, Ni and Cd were listed in Table 6. As could be seen, the proposed

Table 6
A comparison of analytical performance with literatures.

Samples	Analytical procedure	Limits of detection (LOD, ng L^{-1})			
		Co(II)	Ni(II)	Cd(II)	Literatures
Human urine	CME–ICP-MS	0.45	4.6	6.9	This work
Human urine	CME–ICP-MS	0.33	1.5	1.4	[19]
Food samples	SPE–FAAS[a]	590	1290	270	[31]
Water samples	SPE–RP-HPLC[a]	2	3	3	[32]
Drinking waters	CPE–ETAAS[a]	10	–	–	[33]
Urine samples	ID-ETV-ICP[a]	–	–	20	[34]
Lake water	SPE–ICP-MS[a]	8.2	38	79	[35]

[a] ETV: electrothermal vaporization; SPE: solid phase microextraction; FAAS: flame atomic absorption spectrometry; RP-HPLC: reversed-phase high-performance liquid chromatography; CPE: cloud point extraction; ETAAS: electrothermal atomic absorption spectrometry; and ID: isotope dilution.

Table 5
Analytical performance of on-line fiber-in-tube CME–ICP-MS for trace analysis of Co(II), Ni(II) and Cd(II) (sample volume = 1 mL) under optimized experimental conditions.

Ions	Linear range (μg L^{-1})	Linear equations	Linear coefficient (R^2)	RSD ($C = 1\ \mu g\ L^{-1}$, $n = 7$)	Detection limits (ng L^{-1})	Enrichment factor
Co(II)	0.005–25	$y = 2442100x + 7988$	0.9979	4.8%	0.45	18.6
Ni(II)	0.01–20	$y = 82159x + 7015$	0.9972	5.1%	4.6	19.3
Cd(II)	0.02–25	$y = 21867x + 5403$	0.9924	6.4%	6.9	19.0

Enrichment factor is defined as the ratio of calibration slope obtained with and without CME.

Table 7
Analytical results of As(V), As(III), Se(IV) and Se(VI) in certified materials of environmental water samples of NIES No. 10-b rice flour and GBW07601 (GSH-1) human hair (mean ± SD, $n = 3$).

Samples	Element	Certified ($\mu g\,g^{-1}$)	Determined ($\mu g\,g^{-1}$)	t-test[b]
NIES No. 10-b rice flour	Co	(0.02)[a]	0.024 ± 0.003	2.31
	Ni	0.39 ± 0.04	0.36 ± 0.02	2.60
	Cd	0.32 ± 0.02	0.30 ± 0.03	1.15
GBW07601 (GSH-1) human hair	Co	0.071 ± 0.008	0.080 ± 0.007	2.23
	Ni	0.83 ± 0.15	0.76 ± 0.08	1.52
	Cd	0.11 ± 0.02	0.12 ± 0.01	1.73

[a] Information value.
[b] $t_{0.05,2} = 4.30$.

Table 8
Analytical results of Co, Ni and Cd in human serum and urine samples (Average ± S. D., $n = 3$).

Sample	Contents ($\mu g\,L^{-1}$)	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)
Human serum				
Co	0.43 ± 0.04	1.0	1.52 ± 0.08	106 ± 5
Ni	3.15 ± 0.27	1.0	3.82 ± 0.15	92 ± 4
Cd	0.21 ± 0.02	1.0	1.17 ± 0.07	97 ± 6
Human urine				
Co	1.09 ± 0.06	1.0	2.05 ± 0.10	98 ± 5
Ni	4.83 ± 0.29	1.0	5.54 ± 0.17	95 ± 3
Cd	0.57 ± 0.04	1.0	1.63 ± 0.06	104 ± 4

method not only offers the lowest limits of detection, but also consumes very small sample and reagents. Thus, the developed method was quite suitable for trace and ultratrace analysis of samples with limited volumes (≤1 mL) and complicated matrix.

3.2.10. Real sample analysis

The accuracy of the proposed method was validated by determining the contents of Co, Ni and Cd in certified reference material of NIES No. 10-b rice flour and GBW07601 (GSH-1) human hair, and the results with the value of the Student's t-test were listed in Table 7. As can be seen, the determined values are in good agreement with the certified values.

The proposed method was also applied to the analysis of Co, Ni and Cd in real human serum and urine samples. The analytical results, together with the recoveries for the spiked samples, are given in Table 8. As could be seen, satisfactory recoveries ranging from 91% to 104% were obtained.

4. Conclusion

In the present paper, a novel thermo-responsive PNIPA coating was prepared and applied as the fiber coating for fiber-in-tube CME of trace Co, Ni and Cd in human serum and urine followed by on-line ICP-MS detection. The experimental results have demonstrated that PNIPA coating could be used as CME material with high extraction efficiency, high adsorption capacity, good chemical stability and good regeneration capability. Compared to open tubular CME, the preparation process of fiber-in-tube CME is labor-saving and both internal volume and phase ratio are dramatically reduced and therefore the extraction is more effective. It is expected that developing new CME coating materials will extend its application in ultratrace elements and their species analysis in various samples with complicated matrix.

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References

[1] S. Caroli, A. Alimonti, E. Coni, F. Petrucci, O. Senofonte, N. Violante, Crit. Rev. Anal. Chem. 24 (1994) 363–398.
[2] IARC Monographs on the evaluation of carcinogenic risks to humans, vol. 58, International Agency for Research on Cancer, Lyon, France, 1993, pp. 41–117.
[3] D. Beauchemin, Anal. Chem. 80 (2008) 4455–4486.
[4] J.W. Olesik, Anal. Chem. 63 (1991) 12A–21A.
[5] M. Tanner, D. Gunther, Anal. Chim. Acta 633 (2009) 19–28.
[6] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta, Part B 64 (2009) 1–15.
[7] C.Z. Huang, B. Hu, Spectrochim. Acta, Part B 63 (2008) 437–444.
[8] N.N. Meeravali, S.J. Jiang, J. Anal. At. Spectrom. 23 (2008) 1693–11693.
[9] R. Eisert, J. Pawliszyn, Anal. Chem. 69 (1997) 3140–3147.
[10] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 (2002) 752–761.
[11] L. Fang, S. Kulkarni, K. Alhooshani, A. Malik, Anal. Chem. 79 (2007) 9441–9451.
[12] J.J. Chen, Y.C. Lee, H.C. Lin, R.L.C. Chen, J. Food Drug Anal. 12 (2004) 332–335.
[13] Z. Mester, J. Pawliszyn, Rapid Commun. Mass Spectrom. 13 (1999) 1999–2003.
[14] R. Garcia-Sanchez, R. Feldhaus, J. Bettmer, L. Ebdon, J. Anal. At. Spectrom. 16 (2001) 1028–1034.
[15] F. Zheng, B. Hu, Anal. Chim. Acta 605 (2007) 1–10.
[16] J.C. Wu, Z. Mester, J. Pawliszyn, Anal. Chim. Acta 424 (2000) 211–222.
[17] Y. Fan, Y.Q. Feng, S.L. Da, Z.H. Wang, Talanta 65 (2005) 111–117.
[18] Z. Mester, H. Lord, J. Pawliszyn, J. Anal. At. Spectrom. 15 (2000) 595–600.
[19] W.L. Hu, B. Hu, Z.C. Jiang, Anal. Chim. Acta 572 (2006) 55–62.
[20] Y.W. Wu, B. Hu, Z.C. Jiang, Y.Q. Feng, P. Lu, B.Y.Z. Li, Rapid Commun. Mass Spectrom. 20 (2006) 3527–3534.
[21] Y.W. Wu, B. Hu, W.L. Hu, Z.C. Jiang, B.Y.Z. Li, J. Mass Spectrom. 42 (2007) 467–475.
[22] K. Jinno, M. Kawazoe, Y. Saito, T. Takeichi, M. Hayashida, Electrophoresis 22 (2001) 3785–3790.
[23] G. Vas, K. Vekey, J. Mass Spectrom. 39 (2004) 233–254.
[24] S. Ganta, H. Devalapally, A. Shahiwala, M. Amiji, J. Controlled Release 126 (2008) 187–204.
[25] X.Z. Zhang, R.X. Zhuo, Langmuir 17 (2001) 12–16.
[26] M. Prabaharan, J.F. Mano, Macromol. Biosci. 6 (2006) 991–1008.
[27] T. Tanaka, Y. Ando, T. Saitoh, M. Hiraide, J. Anal. At. Spectrom. 17 (2002) 1556–1559.
[28] M.M. Liu, Y. Liu, Z.R. Zeng, T.Y. Peng, J. Chromatogr. A 1108 (2006) 149–157.
[29] X.D. Xu, X.Z. Zhang, J. Yang, S.X. Cheng, R.X. Zhuo, Y.Q. Huang, Langmuir 23 (2007) 4231–4236.
[30] R.G. Pearson, Coord. Chem. Rev. 100 (1990) 403–425.
[31] V.A. Lemos, E.M. Gama, A.S. Lima, Microchim. Acta 153 (2006) 179–186.
[32] Q.F. Hu, G.Y. Yang, Y.Y. Zhao, J.Y. Yin, Anal. Bioanal. Chem. 375 (2003) 831–835.
[33] R.A. Gil, J.A. Gasquez, R. Olsina, L.D. Martinez, S. Cerutti, Talanta 76 (2008) 669–673.
[34] K.H. Lee, S.H. Liu, S.J. Jiang, Analyst 123 (1998) 1557–1560.
[35] J. Yin, Z.C. Jiang, G. Chang, B. Hu, Anal. Chim. Acta 540 (2005) 333–339.