

Imidazole functionalized organic monoliths for capillary microextraction of Co(II), Ni(II) and Cd(II) from urine prior to on-line ICP-MS detection

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Abstract Monoliths composed of poly(1-vinylimidazole-ethylene glycol dimethacrylate), referred to as poly(VI-EGDMA), were modified with imidazole groups and used in capillary microextraction (CME) of trace levels of Co(II), Ni(II) and Cd(II) ions from human urine samples. The effects of sample pH, sample flow rate, sample volume, elution conditions and potentially interfering ions were investigated. Under the optimized conditions, the limits of detection (3σ) are 0.6 ng L^{-1} for Co(II), 6.4 ng L^{-1} for Ni(II) and 0.7 ng L^{-1} for Cd(II), with the relative standard deviations of 1.8 (Co), 4.2 (Ni) and 2.2% (Cd). A Certified Reference Material (ZK018–2, lyophilized human urine) was analyzed to validate the method, and the values found were in good agreement with the certified ones. The method was successfully applied to the analysis of trace Co, Ni and Cd in human urine samples, and the recoveries for spiked samples were in the range from 89% to 105%. The one-step preparation of monolithic material in our perception is an attractive feature for this material which also excels by good extraction performance in that it possesses abundant adsorption sites, good stability and a long lifetime.

Keywords Transition metal ion · Poly(1-vinylimidazole-ethylene glycol dimethacrylate) · Monolithic capillary microextraction · Imidazole groups · One-step preparation · Scanning electron microscopy · Ft-IR · ICP-MS · Certified reference material · Urine analysis

Introduction

Heavy metals have been widely used in different areas such as plating, steel, electronics and so on. As a result of these applications, they can inevitably accumulate in environment and then in human body [1]. Some metals are essential in the human body, such as Co and Ni, which played very important role in many metabolic processes in the organism, while excess accumulation of these metals may undoubtedly result in some side effects such as disorder of physiological functions and variety of diseases for human beings [2]. Other metals like Cd has been classified as extremely toxic elements even with low concentrations [3]. To estimate human exposure to these elements and evaluate the health risk, the development of a rapid, sensitive and accurate method for the detection of heavy metals in human fluids is of great significance.

Among different elemental detection techniques, ICP-MS is considered to be one of the most powerful analytical techniques for trace Co, Ni and Cd analysis because of its low limits of detection, multielement detection capability over a wide linear range. However, due to extremely low concentration of target elements and very complex matrix in the real samples, the direct analysis of trace Co, Ni and Cd in human fluids is quite difficult. Therefore, an appropriate sample pretreatment technique was highly needed before ICP-MS detection to concentrate the targets and remove the matrix in real samples. However, some conventional sample pretreatment techniques including liquid-liquid extraction (LLE) [4], cloud point

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extraction (CPE) [5, 6] and solid phase extraction (SPE) [7, 8] are generally quite complicated, time consuming and often need large volumes of sample or reagents. When faced with a small amount of sample such as biological samples, novel miniaturized sample preparation methods are needed urgently.

Capillary microextraction (CME), also termed as in-tube solid phase microextraction (in-tube SPME), as a special operation mode of SPME, featured with the merits of low sample consumption, fast speed, high selectivity, and easy automation [9, 10], which has been widely applied for the analysis of various polar and nonpolar compounds in environmental, biological, food and pharmaceutical samples. However, the application of CME for trace metals is relatively less than that for the organic substances due to the lack of proper CME materials [11].

CME materials play a key role in improving the selectivity and extraction efficiency towards trace metals. Commercially available capillary (such as Supel-Q PLOT [12]), home-made capillary coated with alumina [13], and amino group modified silica [14] have already been used in the extraction of trace metals. Open tubular capillary is easy to prepare, but possesses a relatively low phase ratio leading to low sample capacity. Monolithic capillary provides an alternative for open tubular CME with many unique advantages. In situ prepared monolithic column with through-pores and mesoporous exhibits high adsorption capacity and fast mass transport, and demonstrates a good application potential for the preconcentration of trace elements and their species. Silica-based monolithic capillaries modified with amino and mercapto groups [15–17] were synthesized for the analysis of trace heavy metals and their species. Besides, organic polymer-based monolithic capillary with better pH stability has also been used for trace metal analysis. Iminodiacetic acid modified polymer monolithic capillary was used for the extraction of trace elements in biological samples [18] and water samples [19]; Mercapto groups functionalized monolithic column was prepared for the extraction of Au and Pd [20]. All these above mentioned approaches, modification of the monolithic capillary with functional groups to improve the extraction selectivity towards trace elements was required. To facilitate the preparation procedure and improve the extraction performance, one step preparation of monolithic column containing proper functional group is highly expected.

Imidazole group is a suitable functional group for efficient extraction of transition metals due to its strong coordination interaction with transition metal ions. As the carbon-carbon double bond in vinylimidazole can be used for the free radical initiated polymerization, vinylimidazole can be used as monomer in polymerization. Therefore, the purpose of this work is to prepare an imidazole group containing monolithic column (poly(1-vinylimidazole-ethylene glycol dimethacrylate), poly(VI-EGDMA)) without any further modification and to

establish a new method for the determination of trace Co, Ni and Cd in human urine. The structure of the monolith was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The adsorption of Co, Ni and Cd on the poly(VI-EGDMA) monolithic column was investigated in detail. The method was applied for the determination of trace Co, Ni and Cd in human urine samples.

Materials and methods

Instrumentation

The determination of Co, Ni and Cd was carried out on an Agilent 7500a Quadrupole (Q) ICP-MS (Tokyo, Japan, <http://www.agilent.com/home>) with a Babington nebulizer. The detailed operation conditions are listed in the Table S1 (Supporting Information). An FIA-3110 flow injection system (Jitian Instruments Co. Ltd., Beijing, China, <http://www.bjtitanco.com/>) was used for the whole extraction process. The pH values were measured by a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China, <http://www.mt.com/us/en/home.html>) supplied with a combined electrode. The SEM of the monolithic capillary was obtained by a Quanta 200 scanning electron microscope (FEL, Netherlands, <https://www.fei.com/locations/fei-netherlands/>). The functional groups on the monolithic column were characterized by Thermo Nicolet iS10 FT-IR (Waltham, USA, <http://corporate.thermofisher.com/en/home.html>). Fused silica capillary (530 μm i.d. \times 680 μm o.d.) was obtained from Hebei Yongnian Optical Fiber Factory (Yongnian, China, <http://www.rui-feng.com/>). A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China, <http://www.preekem.com/>) was used for sample digestion.

Standard solutions and reagents

The stock standard solutions (1.0 g L⁻¹) of Co, Ni and Cd were prepared by dissolving appropriate amounts of Co(NO₃)₂·6H₂O, NiSO₄·(NH₄)₂SO₄·6H₂O and Cd(NO₃)₂ (all of analytical grade, The First Reagent Factory, Shanghai, China, <http://2064257.atobo.com.cn/>) in 1% (v/v) diluted HNO₃, respectively. γ -Methacryloxypropyl trimethoxysilane (γ -MAPS) was purchased from Chemical Plant of Wuhan University (Wuhan, China, <http://www.wdsilicone.cn/index.asp>). 1-Vinylimidazole (VI), ethylene glycol dimethacrylate (EGDMA) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Aladdin (Shanghai, China, <http://www.aladdin-e.com/>). *n*-propanol and 1,4-butanediol were purchased from Sinopharm (Beijing, China, <http://www.sinoreagent.com/>). All other chemicals were of analytical grade or better. High

purity water (18.2 M Ω cm) obtained from Milli-Q Element system (Millipore, <http://www.merckmillipore.com/CN/en>) was used throughout this study. All stock standard solutions were stored in polyethylene bottles in a refrigerator held at 4 °C. All glassware was kept in 10% nitric acid for at least 24 h and washed three times with high purity water before use.

Preparation of imidazole group functionalized poly(VI-EGDMA) monolith

Firstly, the fused silica capillary (530 μm i.d. \times 680 μm o.d.) was activated according to the procedure reported in our previous work [20]. The inner wall of the capillary was vinylized with γ -MAPS to anchor the polymer monolith on the inner wall of the capillary. Then the imidazole group functionalized monolithic column was prepared in one-step without any further modification. Briefly, 45 mg VI (as monomer) and 105 mg EGDMA (as crosslinker) were dissolved in the mixture of 140 mg *n*-propanol (as porogen) and 210 mg 1,4-butanediol (also as porogen), and then 1.5 mg AIBN were added into the above mixture (as initiator). The prepolymerization solution was mixed and homogenized by sonication for 15 min, and then filled in the above vinylized capillary. The capillary was sealed at both ends with a rubber septum and immersed in a water bath at 60 °C for 12 h. The capillary was washed with ethanol to remove the unreacted components and the imidazole groups on the VI were exposed on the porous surface. Finally, the monolithic capillary was cut into 2.5 cm length for further use.

Analytical procedures

The system employed was similar to our previous work [21]. Briefly, two polymer monolithic capillaries were on-line and in parallel combined with ICP-MS to improve the analytical speed. As shown in Fig. S1, an FI system, consisting of two pumps and an eight-way valve (Position 0 and 1), was used for on-line coupling CME and ICP-MS, two polymer monolithic capillaries were placed in parallel to the FI system, and the eluents from these two monolithic capillaries were injected sequentially into the ICP-MS through a Y-junction. Briefly, the aqueous sample solution containing Co, Ni and Cd was prepared in 0.01 mol L⁻¹ phosphate buffer at pH 6. Initially when the valve was at Position 0, two portions of aqueous sample solution was passed through two monolithic capillaries at the same time. Then the valve was switched to Position 1, one portion of 20 μL 0.5 mol L⁻¹ HNO₃ was passed through one of the monolithic capillaries for the elution of the analytes retained on the capillary followed by on-line ICP-MS determination, after that the other portion of 20 μL 0.5 mol L⁻¹ HNO₃ was used for the elution of the other monolithic capillary and on-line ICP-MS determination. The whole

procedure for each aqueous sample solution was carried out in triplicate. The standard solutions of Co, Ni and Cd with series concentrations were conducted with the same analytical procedure, and the obtained external calibration curve was used for quantification analysis.

Sample preparation

Human urine samples were collected from the Zhongnan Hospital of Wuhan University (Wuhan, China). The ethics committee reviewed and approved the informed consent forms provided by all participants according to ethics requirements. Certified Reference Material of ZK018–2 human urine purchased from Tanmo Reference Material (Beijing, China) was used to validate the method. Urine samples were digested according to the following procedure. 5 mL of human urine was placed in a 50 mL PTFE vessel, and 3 mL of concentrated HNO₃ was added, then the human urine was subjected to microwave digestion procedure. The heating programs were described as follows: 150 °C at 20 atm for 8 min, 180 °C at 25 atm for 8 min and then 200 °C at 25 atm for 3 min. Then, the PTFE vessels were withdrawn from the oven and maintained at 120 °C on a hot plate to evaporate the excess acid to near dryness. The residue was then dissolved with high pure water and adjusted to pH 6 with a volume of 5 mL, and finally subjected to the CME-ICP-MS analysis. High purity water was used as the blank sample and subjected to the same procedure described above.

Results and discussion

Choice of materials

According to the Lewis acid-base theory, there is a high affinity between transition metal ions as Lewis acid and ligands containing N as Lewis base. Therefore, monolithic material with N-containing functional group has high adsorption efficiency towards transition metal ions [15]. Imidazole group is a suitable functional group for efficient extraction of transition metals, and the carbon-carbon double bond in VI can be used for the free radical initiated polymerization to fix the imidazole groups on the polymer materials. With EGDMA as a classical and relatively hydrophilic crosslinker, one step preparation of poly(VI-EDMA) monolithic column with imidazole functional group is feasible for the extraction of transition metal ions.

The extraction feasibility of the prepared poly(VI-EDMA) monolithic column towards the transition metal ions Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) was investigated, and the results are shown in Fig. 1. As can be seen, all the studied metal ions can be quantitatively adsorbed (adsorption efficiency >85%) on the monolith when

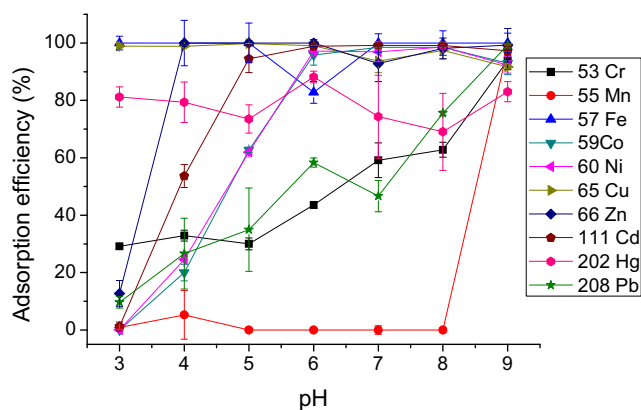


Fig. 1 The effect of sample pH value on the adsorption efficiency of different transition metal ions. Experimental conditions: $c = 10 \mu\text{g L}^{-1}$; sample volume: 1 mL, sample flow rate: 0.1 mL min^{-1}

pH reached 9 probably due to the hydrolysis of transition metal ions under the basic pH environment. In weakly acidic condition ($\text{pH} < 7$), the ions Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) can be quantitatively adsorbed due to their affinity to imidazole group on the monolith. In normal human urine samples, the concentration of Fe(II), Cu(II) and Zn(II) in human urine is at the $\mu\text{g L}^{-1}$ level [22] which can be detected

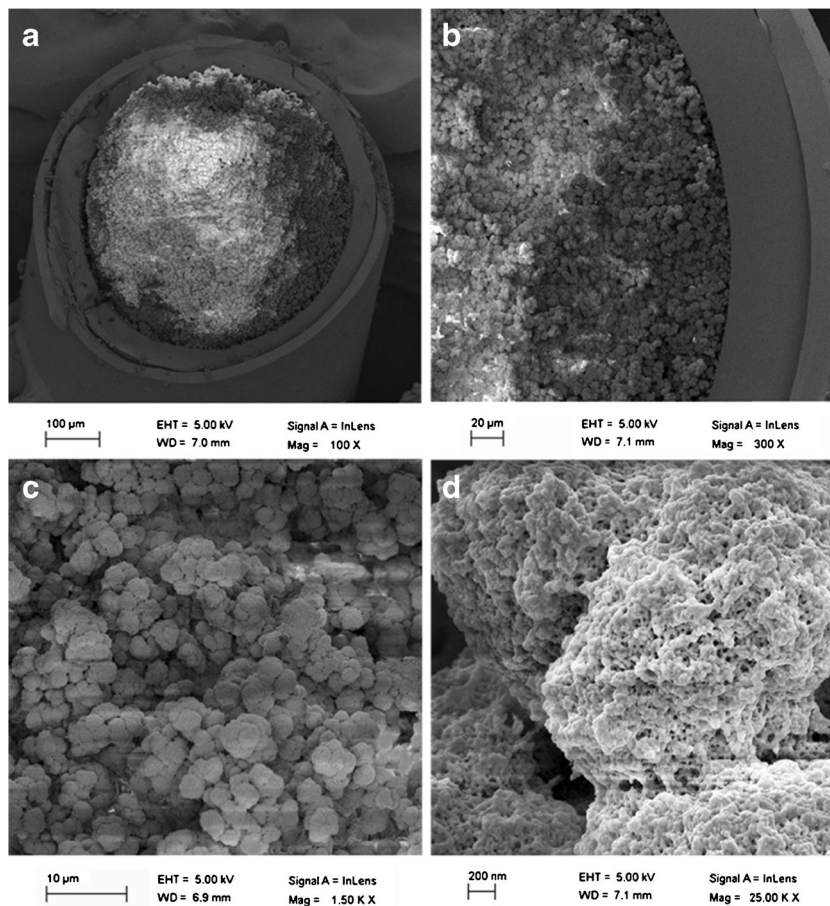
by ICP-MS without preconcentration. The concentration of Co(II), Ni(II) and Cd(II) in human urine is relatively low, and Co(II), Ni(II) and Cd(II) were selected as model metal ions to validate the analytical performance of the method.

Characterization of the polymer monolithic capillary

The cross section of the monolithic column was characterized by SEM, and the results are shown in Fig. 2. With the magnification of $100\times$ (Fig. 2a), it can be seen that the monolithic column possess a continuous skeleton. When the magnification was $300\times$ (Fig. 2b), it shows that the framework of the monolith is attached tightly to the inner-wall of the capillary. From Fig. 2c with the magnification of $1500\times$, it can be seen that the structure of the monolith is uniform and compact, and the monolith exhibits well-controlled skeleton and continuous macroporous. With the magnification of $25,000\times$ (Fig. 2d) of the cross section, aggregated microsphere and ordered mesoporous can be observed clearly which offers porous surface and provides the adsorption sites for the targets.

FT-IR was also used to characterize the poly(VI-EGDMA) materials. From the FT-IR spectrum shown in Fig. S2, a characteristic feature of C-N bond around 1626 cm^{-1} was observed. The peak around 1148 cm^{-1} belongs to the deformation

Fig. 2 SEM of the cross section of poly(VI-EGDMA) with different magnifications (A $\times 100$, B $\times 300$, C $\times 1500$, D $\times 25,000$)



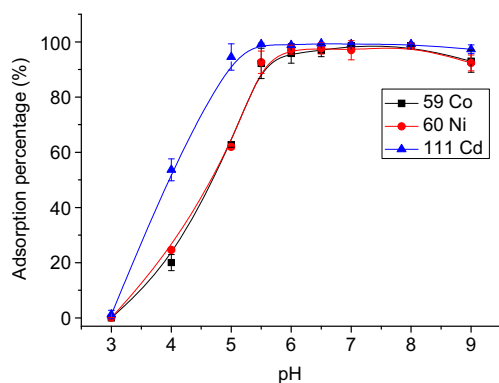


Fig. 3 The effect of sample solution pH value on the adsorption percentage of Co, Ni and Cd. Experimental conditions: $c = 10 \mu\text{g L}^{-1}$; sample volume: 1 mL, sample flow rate: 0.1 mL min^{-1}

vibration of imidazole ring and the peak around 1731 cm^{-1} belongs to ester carbonyl groups in EGDMA. These characteristic peaks indicated that the poly(VI-EGDMA) monolithic column was successfully prepared and it contains massive imidazole groups for the adsorption of targets.

Optimization of the method

The following parameters were optimized: (a) sample pH value; (b) sample flow rate; (c) eluent concentration; (d) eluent volume; (e) sample volume.

The adsorption behavior of Co, Ni and Cd in the range of pH 3–9 was investigated in detail, and the results are presented in Fig. 3. It can be seen that the adsorption percentage of the targets was increased with the increase of pH in the range of pH 3–5.5 and quantitative adsorption was achieved when the pH was higher than 5.5. In order to achieve a high adsorption percentage of Co, Ni and Cd, and avoid the hydrolysis of them in higher pH, pH 6 was selected as the final pH for the following experiments. Respective data and Figures of other conditions (Fig. S3–S6) are given in the Electronic Supporting Material. It was found that the following experimental conditions to give

best results: (a) a sample pH value of 6; (b) sample flow rate of $0.125 \text{ mL min}^{-1}$; (c) HNO_3 concentration of 0.5 mol L^{-1} ; (d) eluent volume of 0.02 mL; (e) sample volume of 1 mL.

Interference of potentially interfering ions

In order to study the anti-interference capability of the method, the effect of potentially interfering ions prevailing in biological samples such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Cl^- , Br^- , NO_3^- and SO_4^{2-} was explored. For this purpose, 1 mL sample solution containing target metal ions each at $1 \mu\text{g L}^{-1}$ and a certain amount of interfering ions were subjected to the CME-ICP-MS procedure. When the recoveries of the target metal ions were kept in the range of 85–115%, the effect of the interfering ions were considered to be negligible. Table 1 lists the tolerance limits of different potentially interfering ions along with the concentration ranges in human urine samples [22]. From the obtained results, it can be concluded that the column has an excellent selectivity for the adsorption of Co, Ni and Cd under the selected conditions and shows great potential in the analysis of Co, Ni and Cd in complicated biological samples.

Preparation reproducibility, regeneration and adsorption capacity

In order to evaluate the preparation reproducibility of the monolithic column, the extraction efficiencies of seven segments of monolithic capillary prepared in the same beach and among different beaches were investigated under the optimized conditions. It was found that the relative standard deviations (RSDs, $n = 7$) were 2.6% (Co), 2.6% (Ni) and 2.8% (Cd) in one beach, and 3.1% (Co), 4.6% (Ni) and 4.2% (Cd) among different beaches. These results indicate that the prepared monolithic column featured with good reproducibility.

Table 1 Effect of potentially interfering ions on the determination of Co, Ni and Cd

Potentially interfering ions	Tolerance limit (mg L^{-1})	Concentration range in urine (mg L^{-1}) [22]
Na^+	16,000	~2200
K^+	10,000	~1.9
Ca^{2+}	2000	~120
Mg^{2+}	2000	~90
Fe^{3+}	10	~0.17
Cu^{2+}	10	4×10^{-5} – 5×10^{-2}
Zn^{2+}	10	0.27–0.85
Cl^-	25,000	–
Br^-	2000	–
NO_3^-	15,000	–
SO_4^{2-}	2000	–

Table 2 Analytical performance of on-line CME-ICP-MS for the determination of Co, Ni and Cd

Elements	Co	Ni	Cd
Linear range ($\mu\text{g L}^{-1}$)	0.002–20	0.02–20	0.002–20
Linear equations	$y = 2840201x + 52176$	$y = 551628x + 180758$	$y = 380573x - 25831$
Correlation coefficient (R^2)	0.995	0.997	0.998
Detection limits (ng L^{-1})	0.6	6.4	0.7
RSD (%; $C = 0.05 \mu\text{g L}^{-1}$, $n = 7$)	1.8	4.2	2.2
Sample throughput (h^{-1})	13		
Enrichment factor	50		

The regenerability of the column was also investigated. The monolithic column can be easily regenerated by flushing with 20 μL 0.5 mol L^{-1} HNO_3 and 40 μL pH 6 phosphate buffer after an elution process. After regeneration, the prepared monolith can be reused at least 50 times without obvious decrease of extraction efficiency. Under the optimized conditions and the above mentioned on-line CME-ICP-MS procedure, two segments of monolithic column were in parallel on the FI system for the CME and as a result the analysis of two samples can be completed in 9 min (8 min for adsorption, 0.32 min for sequential elution, and 0.48 min for regeneration). Therefore, the sample throughput can be as high as 13 h^{-1} , which greatly improved the analysis speed.

Adsorption capacity is one of the key factors for evaluating the performance of adsorption materials. The method used in the study of the adsorption capacity was adapted from the procedure recommended by Hu et al. [10]. Briefly, 100 $\mu\text{g L}^{-1}$ of each target metal ion was passed through the 2.5 cm of self-prepared poly(VI-EGDMA) monolith and the raffinate was determined by ICP-MS. The maximal adsorbed amounts (μg) of target

analytes on 1 m monolithic column were 13.3 (Co), 56.0 (Ni) and 41.6 (Cd) $\mu\text{g m}^{-1}$.

Analytical performance of the on-line CME-ICP-MS method

The limits of detections (LODs, 3σ) of the method, defined as three times the standard deviation of blank signal intensity, were calculated to be 0.6, 6.4 and 0.7 ng L^{-1} for Co, Ni and Cd, respectively. The RSDs for seven replicate determinations of 0.05 $\mu\text{g L}^{-1}$ of target metal ions were 1.8, 4.2 and 2.2% for Co, Ni and Cd, respectively. Figures of merit are summarized in Table 2.

For comparison, the analytical performance of the method and other related approaches reported in the literature for Co, Ni and Cd analysis is listed in Table 3. As can be seen, the method has relatively lower LODs than those methods with ICP-MS as detectors. Besides, the method is an on-line one with relatively high sample throughput, high EF and consumes much less sample/ reagents. The one-step preparation of imidazole group functionalized monolithic capillary not

Table 3 Comparisons of analytical performance

Analytical procedure	Sorbents/coatings	Sampling frequency (h^{-1})	EF	On/off-line	LOD (ng L^{-1})			Ref.
					Co	Ni	Cd	
SPE-ETAAS	Polymer gel	-	25–75	off-line	10	20	5	[23]
CME-ICP-MS	Al_2O_3	8	10	on-line	0.33	1.5	1.4	[12]
CME-ICP-MS	APTES-Silica	-	20	off-line	1.5	5.2	1.2	[15]
Hollow fiber SPME-ICP-MS	Graphene oxide-silica	8	10	on-line	0.39	20	6.7	[24]
Hollow fiber SPME-ICP-MS	Sol-gel with Dowex50W- $\times 8$	-	30	off-line	-	-	100	[25]
SPE-ICP-MS	β -Cyclodextrin-crosslinked polymer	-	10	off-line	5.84	-	-	[26]
MSPE-FAAS	Fe_3O_4 -MOF-199	-	200	off-line	-	400	150	[27]
MSPE-ICP-MS	Mercaptobenzothiazole- Fe_3O_4 @ SiO_2 @C	-	40	off-line	-	2	-	[28]
MSPE-FAAS	Fe_3O_4 @ SiO_2 @poly(4-vinylpyridine)	-	50	off-line	-	600	30	[29]
MSPE-FAAS	Fe_3O_4 -polythionine	-	50	off-line	300	-	-	[7]
DESs extraction	Fe_3O_4 nanoparticles	-	100	off-line	-	-	100	[30]
DMSPE-EDXRF	graphene oxide nanoparticles	-	-	off-line	-	90	70	[31]
MSPE	Fe_3O_4 @tannic acid	-	113, 118	off-line	200	-	200	[32]
CME-ICP-MS	poly(VI-EDMA) monolithic capillary	13	50	on-line	0.6	6.4	0.7	This work

MSPE magnetic solid phase extraction, FAAS flame atomic absorption spectrometry, MOF metal organic framework, DESs Deep eutectic solvents, DMSPE Dispersive micro solid-phase extraction, EDXRF energy dispersive X-ray fluorescence spectrometric

Table 4 Analytical results of Co, Ni and Cd in human urine sample (means \pm s.d., $n = 3$)

Samples	Element	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Urine 1	Co	0	0.053 \pm 0.023	101
		1	1.07 \pm 0.05	
	Ni	0	3.26 \pm 0.08	98
		1	4.16 \pm 0.38	
	Cd	0	0.361 \pm 0.041	94
		1	1.28 \pm 0.05	
Urine 2	Co	0	0.321 \pm 0.002	101
		1	1.33 \pm 0.01	
	Ni	0	1.08 \pm 0.06	98
		1	2.05 \pm 0.09	
	Cd	0	0.489 \pm 0.010	89
		1	1.33 \pm 0.03	
Urine 3	Co	0	0.047 \pm 0.005	89
		1	0.934 \pm 0.066	
	Ni	0	4.54 \pm 0.09	105
		1	5.82 \pm 0.32	
	Cd	0	0.137 \pm 0.029	94
		1	1.07 \pm 0.01	

only makes the preparation quite simple, but also results in good stability of the extraction material.

As the poly(VI-EDMA) monolithic column was prepared in situ with only one step, the good preparation reproducibility (RSDs were 2.6%–2.8% in one beach, 3.1%–4.6% among different beaches) of the monolith may attribute to the simple preparation procedure. Compared with those monolith modified with functional groups after preparation, the one-step prepared monolith contains the functional groups (imidazole groups) among the whole structure instead of the small part of the pore surface. It may result in the relatively higher adsorption capacity compared with our previous work [21] (56.0 $\mu\text{g m}^{-1}$ vs 17.1 $\mu\text{g m}^{-1}$ for Ni and 41.6 $\mu\text{g m}^{-1}$ vs 17.7 $\mu\text{g m}^{-1}$ for Cd).

Sample analysis

In order to verify the accuracy of the method, the method was applied to the determination of Cd in ZK018–2 lyophilized human urine. The measured result of Cd was $14.4 \pm 1.1 \mu\text{g L}^{-1}$, and the certified result was $15.0 \pm 2.6 \mu\text{g L}^{-1}$. The t -test value is 0.96 ($t_{0.05, 2} = 4.30$). As can be seen, the determined values were in good agreement with the certified values, which indicates the good accuracy of the method.

The method was also applied to the analysis of real human urine samples. The analytical results and the recoveries for the spiked samples are summarized in Table 4. It can be seen that the recoveries for the spiked samples were between 89% and 105%.

Conclusions

An imidazole group functionalized poly(VI-EGDMA) monolithic column was prepared through in-situ free radical initiated polymerization without any further modification. The prepared monolithic capillary featured with merits of high mass transfer rate, high adsorption capacity and long lifetime. With the poly(VI-EGDMA) monolithic capillary as the extraction column, an on-line CME-ICP-MS was developed for the determination of trace Co, Ni and Cd in urine samples. The method is simple, selective, accurate and applicable for the analysis of Co, Ni, Cd in complex biological samples. The monolithic CME with higher sample throughput is still to be established.

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Compliance with ethical standards The authors declare that they have no competing interests.

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