Determination of Cd, Co, Ni and Pb in biological samples by microcolumn packed with black stone (Pierre noire) online coupled with ICP-OES

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Abstract

A simple and sensitive method using microcolumn (20-mm length × 2.0-mm i.d.) packed with black stone (Pierre noire) for the separation/preconcentration of Cd, Co, Ni and Pb in biological samples prior to their online determination by inductively coupled plasma optical emission spectrometry (ICP-OES) has been developed. Optimal experimental conditions including pH, eluent concentration and volume, sample volume and sample flow rate were investigated and established. The adsorption capacity of black stone for Cd, Co, Ni and Pb were found to be 23.4, 21.2, 18.1 and 22.2 mg g^{-1}, respectively. With a preconcentration time of 72 s and an elution time of 4 s, an enrichment factor of 20 and a sampling frequency of 25 h^{-1} were obtained. The detection limits corresponding to three times the standard deviations of the blank for Cd, Co, Ni and Pb were found to be 0.3, 0.4, 0.4 and 1.1 ng mL^{-1}. The precision for seven replicate determinations of Cd, Co, Ni and Pb gave relative standard deviations (RSDs) of 5.9, 4.8, 2.7 and 1.1%, respectively ($n = 7$, $C = 10$ ng mL^{-1}). The method was validated with certified reference material GBW09103 human urine and the results obtained were in good agreement with the certified values. The method was also applied to the determination of the target analytes in biological samples with satisfactory results.
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Keywords: Online microcolumn separation/preconcentration; Heavy metals; Black stone (Pierre noire); Biological samples; ICP-OES

1. Introduction

The potential sources of heavy metals pollution are various effluents emanating out of industries, domestic activities and erosion of natural deposits. However, if these metals are continuously released into the biosphere, they may inevitably affect the terrestrial and aquatic organisms. Cobalt and nickel are essential trace elements, having an important role in many body functions. These elements are required in small amounts; while they are toxic in large amounts [1]. Chronic ingestion of Co in daily diet can cause some toxicological effects [2–4]. Cadmium and lead are well recognized to be highly toxic and hazardous elements to human health [5–7].

In view of the above toxicological effects, the quantification of heavy metal ions in human body fluids at trace levels is important, especially in the assessment of occupational and environmental exposure to toxic metals [5]. Hence, the development of sensitive, precise and reproducible method for the determination of Cd, Co, Ni and Pb in biological samples is of paramount importance.

Various detection techniques including inductively coupled plasma mass spectrometry (ICP-MS) [1,8], flame atomic absorption spectrometry (FAAS) [9,10] electrothermal atomic absorption spectrometry (ETAAS) [11–13] and inductively coupled plasma optical emission spectrometry (ICP-OES) [14,15] have been reported for the determination of heavy metals.

Of all theses detection techniques, ICP-OES has gained strong recognition in trace heavy metals analysis due to the following advantages: multi-elemental analysis capability; large dynamic linear range; low detection limits; high productivity [16]. Despite the aforementioned advantages, direct determination of heavy metals ions in biological fluids is limited due to their low level of concentration and matrix interferences. Thus, preconcentration is required in order to bring the concentration of the analytes into the range of the detector, while separation is called for to eliminate potentially interfering matrix constituents.

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It is well documented that, flow injection (FI) microcolumn separation and preconcentration techniques online coupled to ICP-OES is a very efficient analytical techniques for trace heavy metals in environmental and biological samples [6,17,18]. This combination does not only provide an improvement in detection limits and reduces interference from the matrix, but also has significantly enhanced the analytical performance of the methods [19–21]. In comparison to their offline batch counterparts, these systems have a number of significant advantages for trace element determination including higher efficiency, lower consumption of sample and reagent, improved precision, possibility of working in a closed system with a significant reduction of airborne contamination, and increased sampling frequency. Online column preconcentration systems coupled with ICP-OES are based on the retention of the analytes in a microcolumn packed with an adsorbent that determines the sensitivity and selectivity of the analytical method. A great deal of research has been performed to explore the applicability and potentiality of various solid phase adsorbents including mesoporous alumina [1], nanometer-sized alumina [8], modified silica gel [10], activated carbon [9], PAN impregnated ambersorb 563 resin [22] impregnated amberlite XAD-4 [23] and amberlite XAD-1180 [24] for the preconcentration of some metal ions. Some promising natural and cheap materials such as clay minerals [25,26], zeolites [27] and expanded perlite [28] were also successfully employed as adsorbent.

Black stone is a natural stone which can be found easily in West Africa, the North eastern part of Nigeria. And it possesses the following amazing characteristics which attracted our attention to explore its potentiality as an adsorbent.

(i) Commonly used by rural dwellers as anti-snake or scorpion bite;
(ii) Ability to adhere firmly to the surface of the wounded or bitten area when brought into contact with the surface of the skin;
(iii) Ability to remain attached to the surface of the bitten area, sucks out the poison and then, falls down by itself;
(iv) It could be reused by boiling with hot water for 1 h and soaking in milk for thirty minutes;
(v) When placed on the inner surface of the lips it sticks firmly to it but, if placed on the outer surface of the lips or skin(dry or wet) with out wound it falls dawn immediately without adhering.

In this manuscript, the potentiality of utilizing black stone as an adsorbent was intensively explored. To the best of our knowledge, no research has in the past been conducted on the possibility of employing black stone as an adsorbent.

Sequel to the above-mentioned information, an online preconcentration/separation of Cd, Co, Ni and Pb in biological samples using microcolumn packed with black stone prior to their determination by ICP-OES has been explored. Experimental conditions including pH, eluent concentration and volume, sample and eluent flow rate, sample volume and coexisting ions, have been investigated and optimized. The developed method was applied to the determination of heavy metals in serum, whole

Table 1
Percentage composition of some major elements found in black stone

C (%)	6.43
H (%)	0.58
N (%)	0.58
Ca (%)	2.23
Si (%)	7.55
Na (%)	4.50
K (%)	1.24
Al (%)	3.88
Zn (%)	2.52
Mg (%)	0.42
Se (%)	0.16
Ti (%)	0.10
Fe (%)	0.17
As (%)	1.21
Ba (%)	0.04
Mn (%)	0.11
Cd (%)	nd
Ni (%)	nd
Co (%)	nd
Pb (%)	nd

nd = not detected.

blood and certified reference material (GBW09103) of human urine.

2. Experimental

2.1. Instrumentation

ICP-OES determination was performed with an Intrepid XP Radial ICP-OES (Thermo, Waltham, MA, USA) with a concentric nebulizer and a Cinnabar spray chamber. The operating conditions and wavelengths of the emission lines used are summarized in Table 1. The analytical lines of the analytes were selected on the basis of their net and background intensities and their freedom from spectral interference overlaps. The pH adjustment was conducted by means of a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, P.R. China) supplied with a combined electrode. The separation/preconcentration process was performed by means of an HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, P.R. China). A self-made PTFE microcolumn (20-mm length × 2.0-mm i.d.), packed with black stone (Pierre noire), was used for the separation/preconcentration of the analytes. In order to minimize dead volume, PTFE tubing with an i.d. of 0.5 mm was used for all connections.

2.2. Standard solutions and reagents

Standard stock solutions containing ($1 g L^{-1}$) Co, Cd, Ni and Pb were prepared separately by dissolving appropriate amounts of high purity Co $(NO_3)_2 \cdot 6H_2O$, Cd $(NO_3)_2$, $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, and $Pb(NO_3)_2$ (The First Reagent Factory, Shanghai, P.R. China) in 2% HCl. Diluted standard solutions and model solutions were prepared daily from the stock standard solutions. High purity de-ionized water and high purity
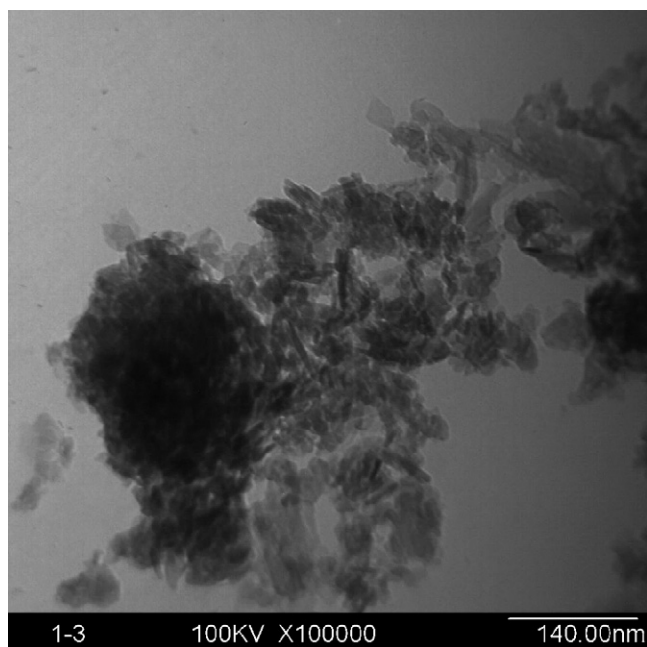
Fig. 1. TEM micrograph of black stone.

analytical grade reagents were used throughout for preparation of the standard and sample solutions.

2.3. Characterization of black stone

A transmission electron microscope (TEM) pattern of black stone as depicted in Fig. 1, was obtained by using a JEM-100CX II transmission electron microscope (JEOL, Tokyo, Japan). As can be seen, the particle size of the black stone was ∼50 nm.

The nitrogen adsorption–desorption isotherms of black stone were measured by micrometrics ASAP 2010 system. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The result showed that the BET surface area of black stone was $86.6 \, m^2 \, g^{-1}$ and the total pore volume was $0.24 \, cm^3 \, g^{-1}$ with an average pore width of 11.09712 nm.

Furthermore, elemental composition of black stone was determined by Vario EL III Elemental Analyzer (Elementar Co. Ltd., German) and Intrepid XP Radial ICP-OES (Thermo, Waltham, MA, USA) with a concentric nebulizer and a Cinnabar spray chamber. The results obtained were presented in Table 1.

IR spectrometry of black stone was also examined by DRFTIR (FTIR, NEXUS 870 FI-IR, Thermo Nicolet, USA). From the spectra obtained in Fig. 2, it could be seen that the spectral band at $3423 \, cm^{-1}$ corresponds to –OH stretching frequency, while 2978 and $2918 \, cm^{-1}$ correspond to C–H stretching frequencies. 1464 and $1382 \, cm^{-1}$ are typical C–H bending absorption bands.1042 and $960 \, cm^{-1}$ corresponds to Si–O–Si and Si–O–C stretching frequencies. The spectral band at $874 \, cm^{-1}$ corresponds to S–H group.

2.4. Sorbent preparation

Black stone was obtained from West Africa, the North Eastern part of Nigeria (Borno State). 10 g of the black stone was crushed and grounded to powdered form by mortar and pestle. The powder was placed in 50 mL of $2 \, mol \, L^{-1}$ HCl and allowed to stay overnight. After then, it was filtered and washed thoroughly with high purity de-ionized water. The residue was dried at 60 °C in vacuum, grounded and sieved to a fraction of 180 mesh, with corresponding particle size of 0.088 mm and then stored for future use as a packing material.
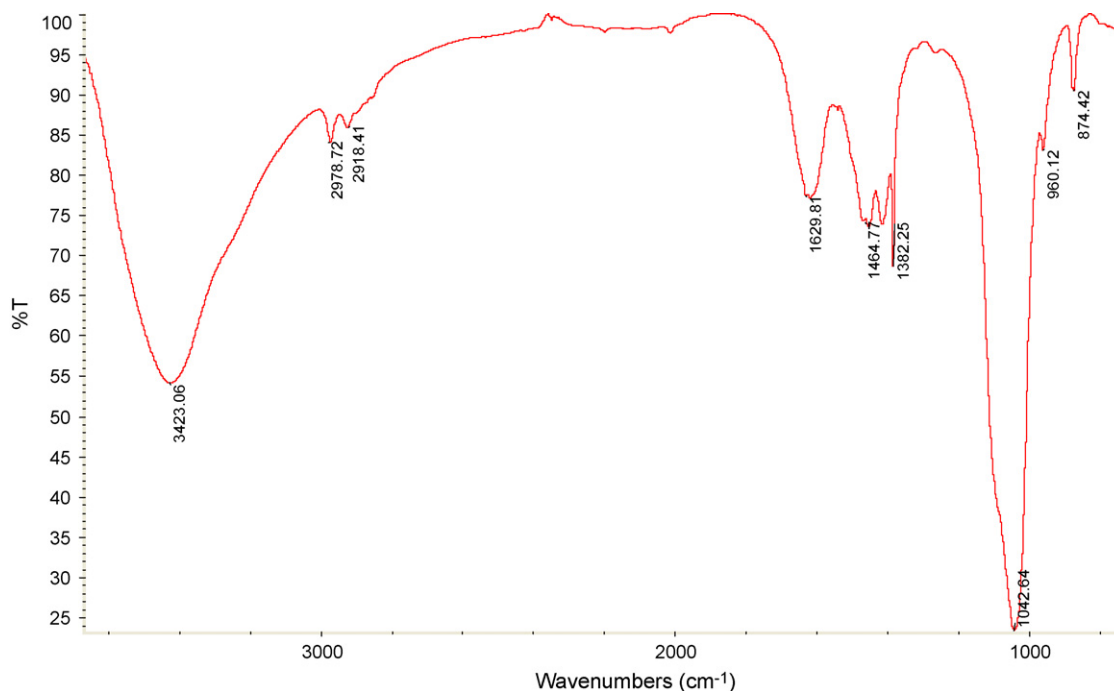

Fig. 2. IR spectra of black stone.

2.5. Column preparation

20 mg of black stone adsorbent was filled into a PTFE microcolumn (20-mm length × 2.0-mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 1.0 mol L^{-1} HCl solution and high purity de-ionized water were passed through the column in order to clean and condition it.

2.6. Sample digestion

4.0 mL of human urine (GBW09103) was put into the PTFE vessels. Then, 5 mL of concentrated HNO$_3$ was added. The PTFE vessels were kept open for about 5 min to allow vigorous reaction and the evolution of gas to reduce. The vessels were then closed and positioned inside the microwave oven, and subjected to the following digestion program: (5 min at 8 atm, 130 °C and 500 W). After digestion, the vessels were removed and allowed to cool down. A clear solution was observed. It was then heated to a very small volume on a hot plate, and diluted to the required volume.

Pooled human whole blood and serum samples collected from healthy adults were supplied by Wuhan University Hospital. The sample digestions for human whole blood and serum were conducted by putting 3.5 mL of sample into the PTFE vessels. Then, 5 mL of concentrated HNO$_3$ was added. The PTFE vessels were kept open for about 5 min to allow vigorous reaction and the evolution of gas to reduce. The vessels were then closed and positioned inside the microwave oven, and subjected to the following digestion program: (5 min at 8 atm, 100 °C and 500 W). After digestion, the vessels were removed and allowed to cool down. A clear solution was observed. To the clear solution, 0.5 mL H$_2$O$_2$ was added and then heated to a very small volume on a hot plate, and diluted to the required volume.

Blank for human urine was prepared by adding 5 mL of concentrated HNO$_3$ in to a PTFE vessel and then subjected to the same digestion procedure above. While the blanks for whole blood and serum were prepared by rinsing the test tubes containing the same amount of anticoagulant (obtained from Wuhan university Hospital) with 5 mL of concentrated HNO$_3$ and then transferred into the PTFE vessels and subjected to same digestion procedure above. During the process of data analysis, all values obtained were corrected by subtracting the blank values.

2.7. General procedure

Sample solutions containing the analytes Cd, Co, Ni and Pb were prepared by appropriate dilution of their stock solutions and then adjusted to the desired pH value with 0.1 mol L^{-1} HCl and NH$_3$·H$_2$O before use.

The operation sequence of the FI online column preconcentration and determination is shown in Fig. 3. In the preconcentration step, (a) pump P1 was activated, so that the sample was drawn through the column. And in the elution step, (b) pump P2 was activated, so that the eluent was propelled through the column reversibly. In this instance, the continuous impact on the sorbent could be avoided. Then, the eluting solution was introduced into the ICP-OES for analysis.
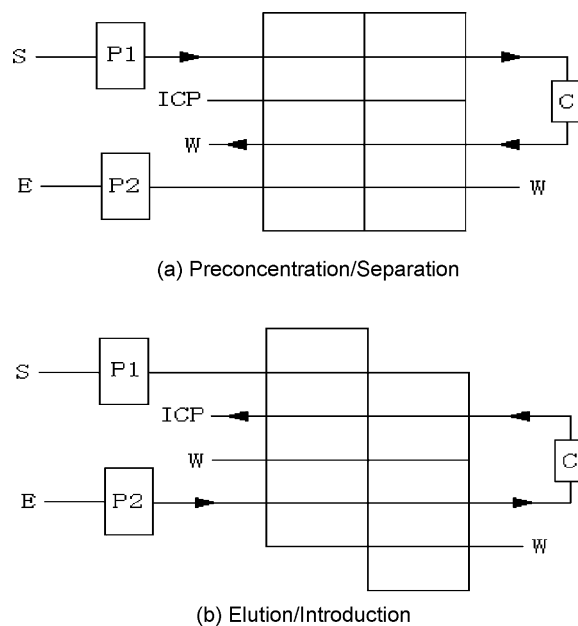

(a) Preconcentration/Separation

(b) Elution/Introduction

Fig. 3. Operation sequence for online column preconcentration and ICP-OES determination of Cd, Co, Ni and Pb.

High purity de-ionized water was used as the blank solution and subjected to SPE, and the blank values were determined. The determined values for the analytes were obtained by subtracting the blank values.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the retention of the analytes on microcolumn packed with black stone was studied. For this purpose, the pH of the sample solutions containing 0.05 μg mL^{-1} of the analytes were adjusted to a pH range of 1–9 by adding 1.0 mol L^{-1} NH$_3$·H$_2$O or HCl and passed through the column. The adsorption percentage (%) could be obtained by using the following equation: adsorption percentage (%) = $C_i - C_f/C_i \times 100$. Where C_i = initial concentration of target analytes before preconcentration and determination; C_f = final concentration of target analytes in the effluent after preconcentration and determination.

Fig. 4 shows the effect of pH on the adsorption of target heavy metals on the black stone packed microcolumn. As can be seen, quantitative adsorption (>90%) could be obtained at pH 6–8 for all studied metals. Hence, a sample solution of pH 7 was adopted for all subsequent studies as a compromise with respect to the effective separation/preconcentration of the analytes.

3.2. Effect of eluent concentration

In order to determine the optimum eluent concentration required for the quantitative recovery or desorption of the analytes at a concentration of 0.05 μg mL^{-1} from the adsorbent, various concentrations of HCl (0.1–3 mol L^{-1}) were studied. It was found that, with 0.5 mol L^{-1} HCl, quantitative recoveries
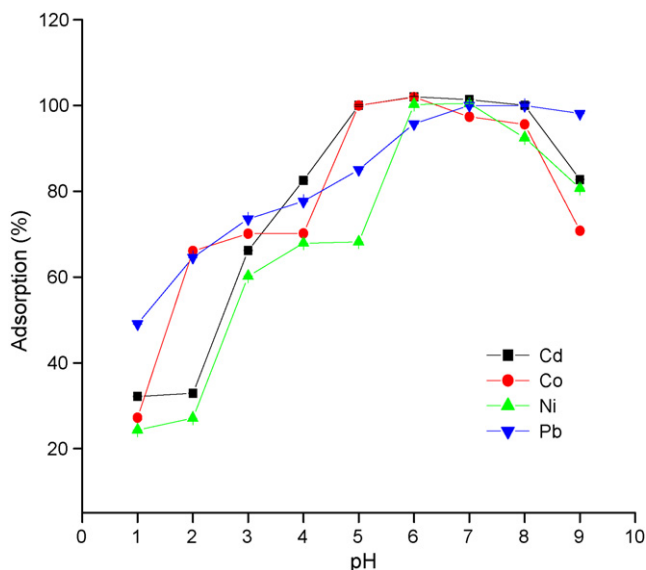
Fig. 4. Effect of pH on adsorption (%) of Cd, Co, Ni and Pb. Concentration of Cd, Co, Ni and Pb: 0.05 µg mL^{-1}; sample volume: 3 mL; sample flow rate: 2.5 mL min^{-1}; eluent volume: 0.15 mL; eluent concentration: 0.5 mol L^{-1} HCl; elution flow rate: 2.5 mL min^{-1}.

(>97%) for the studied analytes could be obtained. Therefore, 0.5 mol L^{-1} HCl was selected for further experiments.

3.3. Effect of eluent volume

The effect of eluent volume on desorption of the analytes at a concentration of 0.05 µg mL^{-1} has been studied by keeping eluent concentration of 0.5 mol L^{-1} and varying it volumes from 0.1 to 1.0 mL. The experimental results indicated that with 0.15 mL HCl, quantitative recoveries (>98%) for the target analytes could be obtained. Therefore, 0.15 mL of eluent volume was selected for subsequent experiments.

3.4. Effect of elution flow rate

The effect of elution flow rate on the recovery of the analytes was investigated by keeping the volume of 0.15 mL containing 0.5 mol L^{-1} HCl. The results indicated that the analytes could be recovered quantitatively at flow rate range of 1.0–3 mL min^{-1}. Hence, an elution flow rate of 2.5 mL min^{-1} was selected for this study.

3.5. Effect of sample flow rate

The effect of sample solution flow rate on the retention of analytes on black stone was investigated by passing 3 mL of sample solution through the microcolumn with the sample flow rate ranging from 0.5 to 3 mL min^{-1}. Fig. 5 illustrates the effect of sample flow rate on the retention of the studied analytes. As can be seen, the retention of analytes remained unchanged from 1.0 mL min^{-1} up to 3 mL min^{-1} and a quantitative recovery of 90% was obtained. Hence, the sample flow rate of 2.5 mL min^{-1} was selected as the optimum condition for all further experiments.
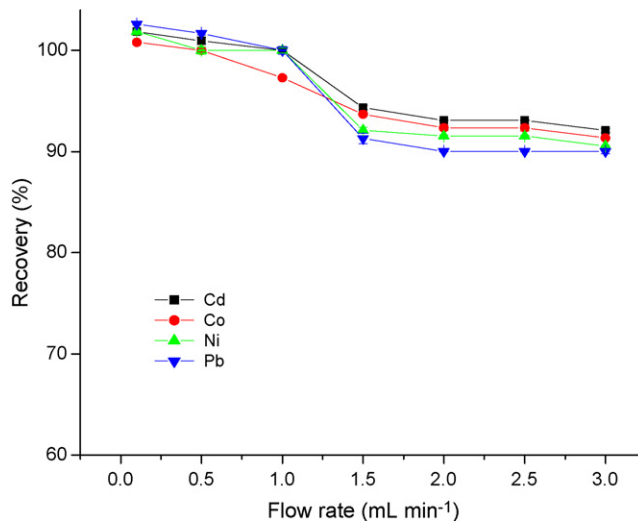

Fig. 5. Effect of sample flow rate. Concentration of Cd, Co, Ni and Pb: 0.05 µg mL^{-1}; sample pH: 7.0; sample volume: 3 mL; eluent concentration: 0.5 mol L^{-1} HCl; eluent volume: 0.15 mL; elution flow rate: 2.5 mL min^{-1}.

3.6. Effect of sample volume

In order to achieve a high preconcentration factor from a sample with very low analyte concentration, a large volume of samples solution is required. Therefore, it is important to study the effect of sample volume on the retention of analytes on black stone. The effect of the sample volume on the recovery of analytes was investigated by passing 1, 2, 3, 5, 10, 20 and 50 mL sample solutions containing 0.15 µg of analytes through the microcolumn according to the above-mentioned general procedure. Fig. 6 presents the effect of sample volume on the recovery of the target analytes. As can be seen, the recovery of the analytes was approximately quantitative (>95%) up to 50 mL of sample. In this work, for online purposes, a sample volume of 3 mL was employed for real sample analysis.

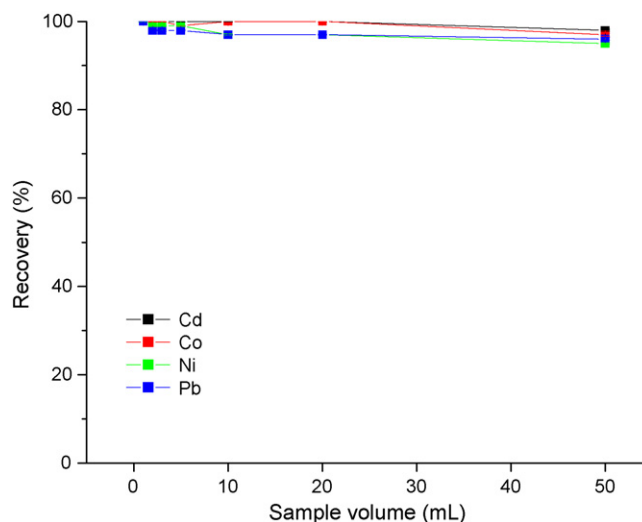

Fig. 6. Effect of sample volume on recovery (%). Amount of Cd, Co, Ni and Pb: 0.15 µg; sample pH: 7.0; sample flow rate: 2.5 mL min^{-1}; eluent concentration: 0.5 mol L^{-1} HCl; eluent volume: 0.15 mL; elution flow rate: 2.5 mL min^{-1}.

3.7. Effect of coexisting ions

The effect of some coexisting ions on the preconcentration and determination of Cd, Co, Ni and Pb were studied. To study the effect of coexisting ions, a series of sample solutions with varying concentrations of the coexisting ions and the fixed concentrations of analytes of 0.05 μg mL^{-1} were prepared and treated according to the recommended procedure. The tolerance limit of the coexisting ions is defined as the largest amount making the recovery of the studied elements less than 90% [29]. The tolerance limits of the coexisting ions were Na$^+$, K$^+$, Ca^{2+} 10,000 mg L^{-1}; Mg^{2+}, Al^{3+} 500 mg L^{-1}; Fe^{3+} 100 mg L^{-1}; SO$_4$$^{2-}$; Cl$^-$ 10,000 mg L^{-1}; NO$_3$$^-$ 1000 mg L^{-1}; PO$_4$$^{3-}$ 500 mg L^{-1}. It can be seen that the presence of the studied coexisting ions has no obvious effect on the determination of the target analytes in biological samples under the optimal experimental conditions.

3.8. Column reuse

The regenerability and stability of the column was investigated by passing the analytes through the column packed with 20 mg o f black stone and then followed by passing through 2 mL 1.0 mol L^{-1} HCl and 5 mL of high purity de-ionized water. It was observed that the column could be reused more than 50 runs without decrease in the recoveries of the studied analytes.

3.9. Adsorption capacity

In order to evaluate the amount of black stone required to quantitatively concentrate the analytes from a given solution, the adsorption capacity of black stone has been studied. The method used was adapted from that recommended by Maquieira et al. [30]. The adsorption capacities of Cd, Co, Ni and Pb were found to be 23.4, 21.2, 18.1 and 22.2 mg g^{-1}, respectively. A comparison of adsorption capacity of black stone with some other adsorption materials reported in literatures [19,31–34] indicated that, the adsorption capacity of black stone for Cd, Co, Ni and Pb is higher than those in the reported literatures.

3.10. Analytical performance

Under the optimal experimental conditions described above, a sampling frequency of about 25 h^{-1} and an enrichment factor of 20 were obtained. According to the IUPAC definition, the detection limits (3σ) of this method for Cd, Co, Ni and

Table 2
Results of analytes determined in certified reference material of human urine

Material	Elements	Found[a] (μg L^{-1})	Certified (μg L^{-1})
GBW	Cd	51 ± 2	53 ± 3
09103	Co	ND	–
human	Ni	288 ± 20	310 ± 30
urine	Pb	123 ± 10	112 ± 9

ND: Not detected.
[a] Mean ± S.D. ($n = 3$).

Table 3
Results of analytes determined in human whole blood (sample volume: 3 mL; $n = 3$)

Element	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)	Concentration [36] (ng mL^{-1})
Cd	0	1.2 ± 0.1	–	0.1–2
	5	6.3 ± 0.5	102	
Co	0	5.1 ± 0.5	–	0.1–20
	5	10.5 ± 0.5	96	
Ni	0	3.1 ± 0.2	–	1.1–4
	5	7.1 ± 0.4	88	
Pb	0	5.4 ± 0.2	–	40–290
	5	11.1 ± 0.4	106	

[a] Mean ± S.D. ($n = 3$).

Pb were 0.30, 0.41, 0.41 and 1.13 ng mL^{-1}, and the relative standard deviations (RSDs) were 5.9, 4.8, 2.7 and 1.1% ($n = 7$, $C = 10$ ng mL^{-1}), respectively. The comparison of detection limit of this method with other literatures [31,32,35] was made. It was found that, the detection limits of the developed method are comparable with that reported in literatures.

3.11. Real sample analysis

For real sample analysis, the standard calibration curve was employed. In order to validate the proposed method, a certified reference material (GBW09103) of human urine was analyzed, and the analytical results were depicted in Table 2. As could be seen, with the exception of Co, which was not detected, a good agreement was obtained between the values determined by the proposed method and the certified values for Cd, Ni and Pb, respectively. The method was also applied to the determination of target heavy metals in human blood and serum samples, and the analytical results along with the recovery for the spiked samples were listed in Tables 3 and 4, respectively. As could be seen, the concentration of Cd, Co, Ni, Pb in whole blood for none spiked samples were 1.2, 5.1, 3.1 and 5.4 ng mL^{-1}, respectively. Although, Cd and Ni were not detected in human serum which could be attributed to their detection limits, the concentrations for Co and Pb in human serum for none spiked sample are 1.20 and 3.80 ng mL^{-1}. The values obtained for the target metals in none spiked human blood and serum samples were within the range reported by Coroli et al. [36] for normal human

Table 4
Results of analytes determined in human serum (sample volume: 3 mL; $n = 3$)

Element	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)	Concentration [36] (ng mL^{-1})
Cd	0	ND	–	0.04–0.4
	5	4.85 ± 0.21	97	
Co	0	1.20 ± 0.14	–	0.08–0.45
	5	6.01 ± 0.10	97	
Ni	0	ND	–	0.05–1.3
	5	5.25 ± 0.21	105	
Pb	0	3.80 ± 0.57	–	0.08–40
	5	8.35 ± 0.64	94	

ND: Not detected.
[a] Mean ± S.D. ($n = 3$).

whole blood and serum with the exception of the detected value of Pb in whole blood which corresponded to the range provided by Bárány et al. (3.5–170 ng mL^{-1}) [37]. The recoveries for the target analytes in spiked serum and whole blood ranged from 88 to 106%.

4. Conclusion

A new method using a microcolumn packed with black stone for the preconcentration of Cd, Co, Ni and Pb has been developed. The method possesses some attractive features including simple, cost effective, environmentally friendly and good sensitivity. As an adsorbent for solid phase extraction, black stone possesses the following amazing characteristics: (1) it is a natural stone which can be found easily in West Africa, the North eastern part of Nigeria; (2) the functional groups are –OH and –SH; (3) larger adsorption capacity compared with other adsorption materials reported in literatures [19,31–34]; (4) it could be reused more than 50 runs without decrease in the recoveries of the studied analytes. The proposed method has been applied to the preconcentration of the target analytes in certified reference material (GBW09103) of human urine, human blood and serum samples with satisfactory results.

Acknowledgements

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