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Suspended nanoparticles in surfactant media as a microextraction technique for simultaneous separation and preconcentration of cobalt, nickel and copper ions for electrothermal atomic absorption spectrometry determination

Shayessteh Dadfarnia*, Farid Shakerian, Ali Mohammad Haji Shabani

Department of Chemistry, Faculty of Science, Yazd University, Yazd 89195-741, Iran

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ABSTRACT

The aim of this study was to describe a new method of microextraction based on the suspension of alumina nanoparticles in the surfactant media for simultaneous separation and preconcentration of the ultra-traces of cobalt, nickel and copper ions. In this technique, the alumina nanoparticles were suspended in the non-ionic surfactant solution of Triton X-114. The analytes in the sample solution were adsorbed onto the nanoparticles. After the phase separation based on the cloud point of the mixture at 40 °C, the nanoparticles settled down in the surfactant rich phase. Then 120 μL of nitric acid (3.0 mol L^{-1}) was added to the surfactant rich phase which caused desorption of the analytes. Finally, the liquid phase was separated by centrifugation from the nanoparticles and was used for the quantification of the analytes by the electrothermal atomic absorption spectrometry (ETAAS). The parameters affecting the extraction and detection processes were optimized. Under the optimized experimental conditions (i.e. pH ~ 8, Triton X-114, 0.05% (v/v); temperature 40 °C), a sample volume of 25 mL resulted in the enhancement factors of 198, 205 and 206 and detection limits (defined as $3S_b/m$) of 2.5, 2.8 and 2.6 ng L^{-1} for Co(II), Ni(II) and Cu(II) respectively. The sorbent showed high capacity for these metal ions (30–40 mg g^{-1} sorbent). The method was successfully applied to the determination of the analytes in natural water samples.

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1. Introduction

The sample preparation step in an analytical process has been recognized as the main bottleneck of the analysis, especially when trace determination is the purpose [1,2]. Despite the invaluable advances in the separation and quantification methods of the analysis, the conventional liquid–liquid extraction (LLE) is still the most widely used sample preparation technique [3,4]. However, it requires a large amount of organic solvent and is time consuming. To overcome the disadvantages, researches have been directed toward the development of the techniques that are environment friendly, and reduce the costs of analysis through reduction or complete elimination of the organic solvent as well as miniaturized sample preparation method [5]. As a result, a high proportion of the recent analytical publications deals with the novelties in microextraction techniques, such as cloud point extraction (CPE) [6–9], stir bar sorptive extraction (SBSE) [10–12], solid phase microextraction (SPME) [13–15], and liquid phase microextraction (LLME) [16–18]. The SPME was introduced by Pawliszyn in the early 1990s [19,20] which was widely used in sample preparation. The SPME methods have the advantages of rapidity, simplicity, being solvent free and compatibility with most detection systems. However, it has the drawbacks of fiber breakage, stripping of coating, bending of the needle and limited suitability for the extraction of trace metal ions.

One important demand shared by the fundamental research on solid phase extraction and microextraction is the development and characterization of the new sorbents. The main goals of the researchers on this field are improvement of the capacity, sensitivity and detection limit attainable, and enhancement of the thermal, chemical and mechanical stability of the sorbents [21,22].

The nanosized materials can be considered as promising sorbents due to their special properties such as high sorption capacity, simplicity and rapidity of the sorption/desorption process. Alumina nanoparticles are one of the most important metal oxide materials widely used for structural, microelectronic, and membrane applications as well as water and wastewater

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* Corresponding author. Tel.: +98 35 1821 2667; fax: +98 35 1821 0644.
E-mail address: sdadfarnia@yazduni.ac.ir (S. Dadfarnia).

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treatment purposes [23]. Unmodified and modified alumina nanoparticles with different organic ligands have been used for the separation and preconcentration of the metal ions [24–30]. However, one of the limitations of the use of the nanosized materials as sorbents is the slow flow rate of the sample through the column packed with these particles. The flow rate can be facilitated by using a pump, but pumping the sample through the column makes the nanoparticle dislodged by passing through the foam which is used to retain the sorbent in the column. Consequently, most of the reports concerning the use of the nanoparticles as sorbents are based on the modification of the nanoparticles with different ligands, which cluster them together and retain them in the column. Also, some glass particles are added to these sorbents to prevent them from packing the column too tight [31]. On the other hand, the use of the nanoparticles in the batch mode extraction is not attractive since the rate of their settlement is very slow, and the separation of the sorbent from the large aqueous sample volume is difficult. In order to overcome the above mentioned problems, we introduced a new microextraction method named suspended nanoparticles in the surfactant media. Co(II), Ni(II) and Cu(II) were used as the model inorganic ions in the development and evaluation of the method. In this procedure 10 mg of the alumina nanoparticles was added to the sample solution containing 0.05% (v/v) of Triton X-114 as the nonionic surfactant. The mixture was put in an ultrasonic bath for about a few minutes, causing further dispersion and suspension of the nano-alumina. The analytes were quickly adsorbed on the alumina nanoparticles at this point. The phase separation was based on the cloud point of the mixture followed by centrifugation. The nanoparticles easily settled down in the surfactant rich phase and the aqueous phase was decanted. Then, 120 μL of nitric acid (3.0 mol L^{-1}) was added to the surfactant rich phase and the analytes were desorbed. Finally, the mixture was centrifuged and the liquid phase was used for the determination of the analytes by ETAAS.

2. Experimental

2.1. Reagents and chemicals

The reagents used throughout this study were of the analytical reagent grade obtained from Merck Company (Darmstadt, Germany). The standard stock solutions of nickel (II) (1000 mg L^{-1}), cobalt (II) (1000 mg L^{-1}) and copper (II) (1000 mg L^{-1}) were prepared separately by dissolving the proper amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in 1% nitric acid solution. Working solutions were prepared daily by serial dilution of the stock solutions. Deionized water was used throughout the sample preparation process and all the solutions were stored in clean polypropylene (Nalgene, Lima, OH, USA) containers. Aluminum oxide nanopowder, < 50 nm particle size (TEM), was purchased from the Sigma-Aldrich company. All glasswares were kept in 10% nitric acid overnight and subsequently rinsed several times in deionized water before use. A Pd/Mg modifier was prepared from the palladium modifier solution for ETAAS and $Mg(NO_3)_2 \cdot 6H_2O$ according to the method given in the literature[32].

2.2. Instrumentation

A Varian Zeeman spectra atomic absorption spectrometer (model 220Z) was used for all metal measurements. The Varian hollow cathode lamps of cobalt, nickel and copper were used as the light sources, and were operated at currents of 4, 7 and 4 mA, wavelengths of 232.0, 242.5 and 327.4 nm and spectra bandwidths of 0.2, 0.2 and 0.5 nm, respectively. The furnace tube was a standard platform tube with a pyrolytic coating. The Zeeman background correction was used for all measurements. The furnace temperature programs applied were as recommended by the manufacturer (Table 1). Peak height measurement was used for all the quantifications. The pH measurements were carried out with a Metrohm pH meter (model 827, Switzerland) using a combined glass calomel electrode. The sample injection volume was 10 μL in all the experiments.

Table 1
Temperature program of electrothermal atomic absorption for determination of analytes.

Steps	Co(II) temperature (°C)	Ni(II) temperature (°C)	Cu(II) temperature (°C)	Time (s)	Gas flow (L min^{-1})
Drying	85	85	85	5	3.0
	95	95	95	40	3.0
	120	120	120	10	3.0
Ashing	750	800	800	8	3.0
Atomization	2300	2400	2300	3.1	0
Tube cleaning	2300	2400	2300	2	3.0

2.3. Procedure

10 mg of alumina nanoparticles was added to 25 mL of a standard or sample solution containing cobalt, nickel and copper. It was made 0.05% with respect to Triton X-114 and the pH was adjusted to 8 using diluted ammonia solution. The mixture was then put in an ultrasonic bath for a few minutes (~2 min), causing further dispersion and suspension of the alumina nanoparticles. At this stage, the analytes were adsorbed onto the alumina nanoparticles. The mixture was heated in a thermostated water bath at 40 °C until the solution became cloudy (~5 min). The phases were separated by centrifuging the solution for 6 min at 4000 rpm. At this stage, the aqueous and the surfactant rich phase were separated and the nanoparticles containing the analytes were settled in the surfactant rich phase. The phases were further cooled in an ice-water bath, causing increase in the viscosity of the surfactant rich phase, and the aqueous phase was easily decanted. Then, 120 μL of nitric acid (3.0 mol L^{-1}) was added to the tube which caused desorption of the analytes into the surfactant rich phase. The mixture was centrifuged and finally, the supernatant solution was transferred into an electrothermal cup, and 10 μL of it along with 10 μL of the modifier was injected into the graphite tube of ETAAS for the quantification of each analyte.

2.4. Preparation of water samples

The water samples were filtered through a 0.45 μm Millipore filter. The pH was adjusted to ~8 using dilute ammonia solutions and treatments according to the given procedure

3. Results and discussion

Initial experiments indicated that the alumina nanoparticles suspended in the aqueous phase can easily settle down in the surfactant rich phase. On this basis, a microextraction method was designed and the possibility of simultaneous extraction of the Co(II), Ni(II) and Cu(II) as a model component was examined. In order to obtain high enrichment factors, the effects of different parameters affecting the extraction were optimized using a univariable approach.

3.1. *Effect of pH*

The effect of the sample pH in deposition of analytes on the suspended alumina nanoparticles in the aqueous phase is presented in Fig. 1, illustrating that the alumina nanoparticles are most effective in the retention of the analytes at $\mathrm{pH}>7$. Therefore, a pH of ~8 was used in the subsequent work; the solubility product of the analytes hydroxide did not exceed this pH. The progressive decrease in the extraction at pH less than 7 is due to the positive charge of the alumina surface in the acidic media which repels the positively charged analytes.

3.2. *Effects of type, concentration and volume of desorbing solution*

The nature of the desorbing solution was found to have a significant effect on the recovery and measurement process. Different solutions such as nitric, hydrochloric and sulfuric acids (at concentration of 2 mol L^{-1}) were examined. 200 μL of the above mentioned solution was added to the alumina nanoparticles containing the analytes in the surfactant rich phase and the amounts of analytes released in the solution were measured by ETAAS. The results implied that nitric acid is the most suitable eluent for this purpose. The concentration of the nitric acid was then varied from 0.5 to 5 mol L^{-1}. Consequently, the recovery of the analytes increased with an increase in nitric acid concentration up to 3.0 mol L^{-1} and then remained constant at a higher concentration. Therefore, for the subsequent work, nitric acid with a concentration of 3.0 mol L^{-1} was chosen. Furthermore, the effect of the volume of the desorbing solution was studied in the range of 50–350 μL. The results demonstrated that the recovery of the analytes increased slowly by increasing the volume of the desorbing solution in the range of 50–120 μL, and then it became constant when the volume of the desorbing solution was increased to 350 μL. Thus, 120 μL of the desorbing solution was chosen as the optimum volume of desorbing solution in further studies.

3.3. *Effect of Triton X-114 concentration*

Triton X-114 was chosen for the formation of surfactant rich phase due to its low cloud point temperature, commercial availability in a highly purified homogeneous form, low toxicological properties and cost as well as high density of the surfactant rich phase which facilitate the phase separation through centrifugation. The influence of Triton X-114 concentration in the range of 0.01–0.5% (v/v) on the extraction efficiency and the ease of the suspension and sedimentation of the alumina nanoparticles from 25 mL sample were studied. It was observed that when the surfactant concentration was above 0.04%, the extraction of the analytes was quantitative in a single step process. In order to have a high enrichment factor, the minimum amount of Triton X-114 concentration which provides a quantitative extraction (0.05% (v/v)) was selected for the subsequent work. At lower concentrations, the extraction efficiency was low presumably due to the inadequacy of assemblies in order to entrap the alumina nanoparticles quantitatively.

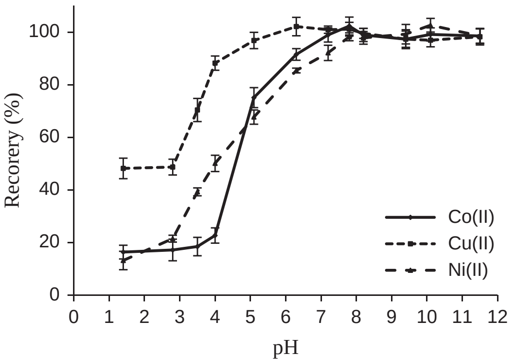

Fig. 1. Effect of pH of the sample solution on the retention of metal ions; conditions: sample volume; 25 mL; Triton X-114 concentration; 0.05% (v/v); extraction time; 4 min, amount of sorbent; 0.01 g; amount of cobalt, nickel and copper; 2.4, 2.4 and 3.0 ng, respectively.

3.4. *Sorption and desorption time*

In order to have a good precision, sensitivity and speed, it is necessary to find an extraction time that guarantees the complete adsorption of the analytes onto the nanoparticles. The effect of adsorption time was examined by varying the extraction time from 0 to 15 min at constant experimental conditions. The adsorption of the Co(II), Ni(II) and Cu(II) was found to be very fast and the extraction was completed in about 2 min. This revealed the existence of a very high surface area between the suspended nanoparticles and the aqueous phase, thereby the fast achievement of the equilibrium state. The effect of time on desorption of the analytes from the adsorbent was studied by varying desorption time ranging from 0 to 5 min. It was found that desorption of analytes was very fast and the absorbance signals of the metal ions were maximum and independent of desorption time. An adsorption and desorption time of 2 min and 30 s was selected for subsequent work, respectively. The short extraction time can be referred to as one of the advantages of the proposed method.

3.5. *Effect of salt*

In order to investigate the effect of the ionic strength on the extraction of the analytes, several experiments were performed with different NaCl concentrations (0.02–1.0 mol L^{-1}) while keeping other experimental parameters constant. The results confirmed that the salt addition has no significant effect on the extraction process and the recoveries of metal ions were quantitative. These observations suggest the possibility of the application of the method to the simultaneous separation of Co(II), Ni(II) and Cu(II) from saline solution such as the sea water.

3.6. *Effect of sample volume*

An important aspect of the method development is demonstration of the capability of the system in enrichment of low concentration of the analytes from a large sample volume. An increase in the sample volume will increase the enrichment factor; however, it may reduce the extraction efficiency. In order to study the effect of the sample volume on the extraction efficiency, some experiments were carried out for the extraction of 2.4, 2.4 and 3.0 ng of Co(II), Ni(II) and Cu(II) respectively from a different sample volume (5–40 mL). The results showed (Fig. 2) that the quantitative recoveries ($>95\%$) were obtained for the sample volume up to 25 mL. Thus, a sample volume of 25 mL was selected for further studies.

3.7. *Effect of mass of sorbent*

The efficiency of the analytes deposition was dependent on the mass of the sorbent as shown in Fig. 3. When mass of the sorbent was greater than 7 mg, the extraction was quantitative and independent of the amount of the sorbent. A mass of 10 mg of the alumina nanoparticles was selected as the optimum amount of the sorbent for further studies.

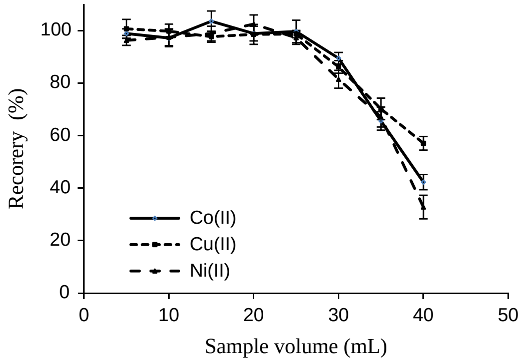

Fig. 2. Effect of sample volume on the recovery of metal ions; conditions: pH~8, Triton X-114 concentration=0.05% (v/v), extraction time=4 min, amount of sorbent=0.01 g, amount of cobalt, nickel and copper is 2.4, 2.4 and 3.0 ng, respectively.

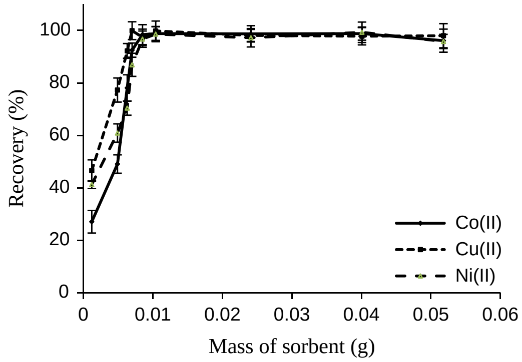

Fig. 3. Effect of mass of sorbent on the recovery of metal ions;conditions: pH~8, Triton X-114 concentration=0.05% (v/v), extraction time=4 min, sample volume=25 mL, amount of cobalt, nickel and copper is 2.4, 2.4 and 3.0 ng, respectively.

3.8. *Interferences study*

The potential interference ions in the determination of the analytes were studied. A relative error of less than 5% was considered to be within the range of experimental error. For this purpose, the effect of the diverse ions, at an initial mole ratio of 1000 (ion/copper), on the recovery of 2.4, 2.4 and 3.0 ng of cobalt, nickel and copper, respectively from 25 mL aqueous solution was studied. When the interference was observed the concentration of the foreign ions was lowered. The results indicated that there is no significant interference with the extraction and determination of the analytes at the given mole ratio (Table 2). Thus, the system has high selectivity for the analyte ions.

3.9. *Sorbent capacity*

100 mL of the solution at the concentrations of 90 mg L^{-1} of each analyte was mixed with 0.2 g alumina nanoparticles and was stirred for 120 min under optimum conditions. The concentrations of the analytes remaining in the aqueous phase were then determined by the flame atomic absorption spectroscopy. The amount of the analytes adsorbed onto the sorbent was determined through the difference and the capacity of the sorbent was found to be 29.0, 34.9 and 37.3 mg g^{-1} for Co(II), Ni(II) and Cu(II), respectively.

3.10. *Analytical performance*

The standard solutions of Co(II), Ni(II) and Cu(II) (25 mL) were processed according to the proposed method and the calibration curves exhibited linearity over the range of 10–150, 10–120 and 10–250 ng L^{-1} with the correlation coefficient of (R^2) 0.9997, 0.9989 and 0.9995, respectively. The equation of the calibration graphs for Co(II), Ni(II) and Cu(II) were $A=7.53\times10^{-3}C+0.043$, $A=6.56\times10^{-3}C+0.038$ and $A=2.89\times10^{-3}C+0.026$ (where A is the absorbance and C is the concentration of the ions in ng L^{-1}). The enhancement factors defined as the ratio of the slope of the calibration curves with and without preconcentration were found to be 198, 205 and 206, for Co(II), Ni(II) and Cu(II), respectively. The relative standard deviations (RSD) for seven replicate measurements at 100 ng L^{-1} and 20 ng L^{-1} level were 5.47% and 6.51% for Co(II), 4.98% and 5.62% for Ni(II) and 3.12% and 4.92 % for Cu(II), respectively. The limits of detection defined as $3S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration curve) were found to be 2.5, 2.8 and 2.6 ng L^{-1} for Co(II), Ni(II) and Cu(II), respectively.

Table 2
Effect of foreign ions on the recovery of analytes.

Ion	Add as	Mole ratio (interfering ion/Cu^{2+})	Recovery[a] (%)		
			Co(II)	Ni(II)	Cu(II)
Bi^{3+}	$Bi(NO_3)\cdot5H_2O$	1000	98.3 ± 3.7	102.5 ± 1.9	96.0 ± 2.7
Ca^{2+}	$CaCl_2\cdot2H_2O$	1000	99.7 ± 4.5	96.0 ± 4.5	99.1 ± 2.6
Mg^{2+}	$MgCl_2\cdot6H_2O$	1000	98.9 ± 3.5	99.2 ± 4.1	103.4 ± 3.3
K^{+}	KBr	1000	96.5 ± 3.5	103.2 ± 2.8	97.3 ± 1.9
Ba^{2+}	$BaCl_2\cdot2H_2O$	1000	99.6 ± 4.1	96.4 ± 3.5	98.9 ± 1.5
Sb^{3+}	$SbCl_3$	1000	97.8 ± 2.7	99.1 ± 3.7	101.5 ± 3.4
Fe^{3+}	$Fe(NO_3)\cdot9H_2O$	750	97.1 ± 3.6	95.5 ± 3.5	101.5 ± 3.5
Zn^{2+}	$Zn(NO_3)_2\cdot6H_2O$	750	96.1 ± 2.6	100.9 ± 3.7	97.3 ± 1.5
Ag^{+}	$AgNO_3$	500	95.9 ± 1.5	98.0 ± 2.6	96.7 ± 3.5
Hg^{2+}	$HgCl_2$	500	98.4 ± 2.9	104.5 ± 3.1	95.5 ± 4.1
Cr^{3+}	$CrCl_3\cdot6H_2O$	250	103.7 ± 4.1	98.5 ± 2.5	96.1 ± 2.1
Cd^{2+}	$Cd(NO_3)_2\cdot2H_2O$	250	97.6 ± 3.1	103.5 ± 3.8	98.5 ± 3.4
Pb^{2+}	$Pb(NO_3)_2$	100	100.5 ± 3.9	98.7 ± 3.6	99.5 ± 3.7

[a] Each number is the average and standard deviation of three independent measurements.

3.11. *Applications*

The procedure was applied for the determination of Co(II), Ni(II) and Cu(II) in tap water, well water, mineral water, river water (Zayandehrood river, Esfahan/Iran) as well as the Caspian sea water samples. The reliability was checked through the recovery experiments. The results of this investigation (Table 3) reveal that the recoveries of the spiked sample were good. The accuracy of the proposed method was further verified by the determination of the Co, Ni and Cu in 10 mL of certified sea water (NASS-2) diluted to 25 mL. The concentrations of copper and nickel in the sample were found to be 107 ± 8 and 256 ± 28 ng L^{-1}, respectively, and are in good agreement with the certified values 109.0 ± 11 ng L^{-1} for Cu and 257.0 ± 27 ng L^{-1} for Ni at 95% confidence level. However, Co(II) was not detected as its amount (4 ± 1 ng L^{-1}) was less than the limit of quantification of the proposed method (8.0 ng L^{-1}). Thus, the method is reliable for the determination of the Co, Cu and Ni in natural water samples

4. Conclusion

A new microextraction technique based on the suspension of nanoparticles in the surfactant media for the metal determination with ETAAS was introduced. The proposed method was based on the metal extraction from the aqueous phase into the alumina nanoparticles suspended in the surfactant solution media. The nanoparticles settled down in the surfactant rich phase upon the

Table 3
Determination of analytes in water samples.

Sample	Co(II) (ng L^{-1})			Ni(II) (ng L^{-1})			Cu(II) (ng L^{-1})		
	Added	Found [a]	Recovery (%)	Added	Found [a]	Recovery (%)	Added	Found [a]	Recovery (%)
Tap water	0	18.4 ± 0.5	–	0	14.7 ± 0.3	–	0	80.5 ± 2.2	–
	5	23.2 ± 0.9	96.0	5	19.6 ± 0.3	98.0	5	85.3 ± 1.5	96.0
	10	28.3 ± 0.4	99.0	10	24.4 ± 0.7	97.0	10	90.6 ± 3.7	101.0
Well water	0	17.6 ± 0.5	–	0	12.3 ± 0.4	–	0	79.4 ± 1.9	–
	5	22.7 ± 0.6	102.0	5	17.1 ± 0.5	96.0	5	84.6 ± 2.3	104.0
	10	27.4 ± 0.6	98.0	10	22.1 ± 0.8	98.0	10	89.1 ± 3.0	97.0
River water	0	57.1 ± 1.2	–	0	73.8 ± 1.5	–	0	148.3 ± 4.1	–
	20	77.0 ± 1.7	99.5	20	93.2 ± 1.2	97.0	20	168.9 ± 4.8	103.0
	30	87.5 ± 1.5	101.3	30	103.4 ± 2.5	98.6	30	178.6 ± 4.5	101.0
Caspian sea water	0	23.7 ± 0.7	–	0	96.9 ± 2.4	–	0	191.4 ± 4.9	–
	20	43.5 ± 1.1	99.0	20	117.2 ± 3.1	101.5	20	211.2 ± 4.0	99.0
	30	53.2 ± 1.3	98.3	30	126.3 ± 3.9	98.0	30	221.0 ± 4.5	98.6
Mineral water*	0	16.9 ± 0.5	–	0	14.5 ± 0.3	–	0	34.6 ± 1.1	–
	5	21.8 ± 0.7	98.0	5	19.7 ± 0.5	104.0	5	39.8 ± 1.3	104.0
	10	26.5 ± 0.4	96.0	10	24.0 ± 0.4	95.0	10	44.3 ± 1.8	97.0
Mineral water*	0	18.7 ± 0.7	–	0	13.1 ± 0.6	–	0	35.9 ± 1.5	–
	5	23.9 ± 0.9	104.0	5	17.9 ± 0.5	96.0	5	40.8 ± 1.7	98.0
	10	28.4 ± 0.9	97.0	10	23.2 ± 0.4	101.0	10	45.4 ± 1.9	95.0

* Mineral bottled water from different branches.
[a] Each number is the average and standard deviation of three independent measurements.

phase separation based on the cloud point of the mixture. In comparison to the solid phase microextraction [33–37], the sorbent is not frangible; the interfacial area between the extracting media and the aqueous phase is comparable to that in the dispersive liquid phase microextraction [16,38–42] and the method is totally organic solvent free which makes it compatible with green chemistry. The other benefits of the method are its simplicity, ease of operation, good accuracy and precision, short extraction time, low cost, and a high enrichment factor. Future work will be directed toward extending the method with other nanoparticles and modified nanoparticles (with organic ligands) for the separation and preconcentration of different inorganic and organic species.

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