

غربالگری و بهینه‌سازی شرایط آزمایش برای اندازه‌گیری نقره بر اساس میکرواستخراج فاز مایع با حلال قابل تغییر

فرشته حیدری*، مجید رمضانی، نسیم بیات، مریم قلعه نوئی

بخش شیمی، دانشکده علوم، دانشگاه آزاد اسلامی واحد اراک، اراک، ایران

تاریخ دریافت: ۲۷ مرداد ۱۳۹۶ تاریخ پذیرش: ۲۸ شهریور ۱۳۹۶

Screening and Optimization of Experimental Condition for the Determination of Silver Based on Switchable Solvent Liquid Phase Microextraction

Fereshteh Heydari*, Majid Ramezani, Nasim Bayat, Maryam Ghalenoie

Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University,

P.O.Box: 38135-567, Arak, Iran

Received: 18 August 2017

Accepted: 14 September 2017

چکیده

میکرواستخراج فاز مایع جدید با استفاده از حلال آبدوست قابل تغییر کوبل شده با اسپکترومتری جذب اتمی شعله برای پیش تغلیظ و استخراج نقره بکار برده شد. در این تحقیق، تری اتیل آمین به‌عنوان حلال سبز قابل تغییر استفاده گردید. کمپلکس نقره با ۱- (۲- پیریدیل آزو)-۲- نفتول به درون فاز آلی با تبدیل تری اتیل آمین کربنات پروتونه شده به تری اتیل آمین، استخراج می‌شود. شرایط آزمایش با طراحی پلاکت-برمن و باکس-بنکن بررسی و بهینه شد. پارامترهای تجزیه‌ای مثل حد تشخیص، انحراف استاندارد نسبی و فاکتور تغلیظ روش به ترتیب ۰/۳۵ میکروگرم بر لیتر، ۱/۴٪ و ۶۸ بدست آمد. منحنی کالیبراسیون دارای گستره خطی ۲-۵۰۰ میکروگرم بر لیتر با ضریب همبستگی ۰/۹۹۷ بود. روش پیشنهادی به طور موفقیت‌آمیزی برای اندازه‌گیری و استخراج مقادیر ناچیز یون نقره در چندین نمونه آب بکار برده شد.

واژه‌های کلیدی

حلال آبدوست قابل تغییر؛ نقره؛ طراحی پلاکت برمن و باکس-بنکن؛ نمونه‌های آب.

Abstract

A novel switchable-hydrophilicity solvent based liquid phase microextraction (SHS-LPME) coupled with flame atomic absorption spectrometry has been applied for preconcentration and extraction of Ag(I). In this study, Triethylamine (TEA) was selected as switchable solvent. The Ag (I)-1-(2-pyridylazo)-2-naphthol complex was extracted into organic phase by converting the protonated carbonate (P-TEA-C) to TEA. The experimental conditions were optimized using Plackett-Burman and Box-Behnken design methods. Under the optimum conditions, the detection limit, relative standard deviation and the enrichment factor were $0.35 \mu\text{g L}^{-1}$, 1.4% and 68, respectively. The calibration graph was linear over the range 2 to $500 \mu\text{g L}^{-1}$ with correlation coefficient of 0.997. The proposed method was successfully applied to determine of trace silver in water samples.

Keywords

Switchable-Hydrophilicity Solvent; Silver; Plackett-Burman and Box-Behnken Design; Water Samples.

1. INTRODUCTION

Silver, as a precious metal is used in many branches of industry and medicine. Compounds and products containing silver are present in batteries, alloys, photographic materials, mirrors, coins, cosmetics and ornament [1]. Also, silver impregnated filters are used for drinking water preparation and as well as in the processing of foods, drugs and beverages [2-4]. Ag is present as impurity in copper, zinc, arsenic, antimony ores

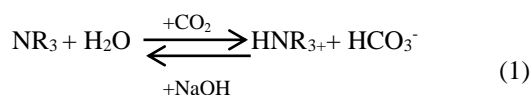
and another source that during operate of these sources of silver, environmental pollutions are come into being. Therefore, due to industrial wastes, pollution of water sources exposure to the solute silver compounds for a long time were reported. High concentrations or long time exposure to silver can cause significant health problems in living organisms [5-6].

The World Health Organization (WHO) reports that humans are able to tolerate concentrations up

*Corresponding Author: fereshte.heydari60@gmail.com

to 0.1 mg L⁻¹ of Ag(I) in water without any health risk. So, due to the positive and negative effects of silver, determination of trace amounts of silver is important in many fields [1]. Direct determination of trace amount of metals in environmental samples is difficult due to low concentration and matrix effects [7]. Therefore to solve these problems, a preliminary separation and pre-concentration prior to analysis is required. Up to now, several methods have been reported for the separation and preconcentration of Ag(I) from various matrices, including liquid-liquid extraction (LLE) [8], solid phase extraction (SPE) [9], cloud point extraction (CPE) [10] and dispersive liquid-liquid microextraction (DLLME) [11]. However, some of these methods have some drawbacks for example long extraction time, consumption of large volumes of harmful organic solvents which are often hazardous and produce secondary waste [12]. Using toxic and environmentally damaging solvents is one of the most important disadvantages of recent analytical techniques. Choosing appropriate solvents for a process is very important. Recently, a new generation solvent called "switchable hydrophilicity solvents (SHS)" has been developed by Jessop et al. [13]. A switchable solvent may be defined as a liquid that can be reversibly converted from one form that is miscible with water (hydrophilic form) to another (hydrophobic form). Switchable solvents contain an amine dissolved in water which can be switched between the two forms by the addition of CO₂ and afterward returns to its non-ionic form by nitrogen, inert gas and/or addition of sodium hydroxide [14]. A chemical reaction of the CO₂ and water changes miscibility of amine and generates a water-soluble carbonate salt of the protonated amine [15]. CO₂ is used as the trigger for the switching process in extraction techniques due to it being inexpensive, non-toxic and easily removable. One of the main advantages of using SHSs is their ability to extract the analytes in a homogeneous phase without dispersive solvent. Recently, these solvents have been used widely in applications such as extraction, separation and reaction [16-17].

In the present study, we have used SHS as a relatively new solvent for the extraction of Ag (I) from water samples. Dry ice was applied as a reagent. A new variant of DLLME combined with homemade extraction vessel was used to accelerate the dispersion of the extraction solvent in the sample solution. The final separation was obtained using sodium hydroxide (Eq. (1)).



NR₃=Triethylamine (TEA)

In this work, after complete phase separation, organic solvent was aggregated and readily transferred to a narrow neck tube by injecting a few milliliters of distillation water of part (2) extraction vessel. Finally, the collected extraction phase in the narrow neck section was injected to FAAS system using a microinjection system. The influence of different experimental parameters which may affect the extraction performance was studied using a Plackett–Burman design (PBD) for screening and a Box–Behnken design (BBD) for optimizing the significant parameters.

2. EXPERIMENTAL

2.1. Reagents

All reagents used were of analytical grade. The glassware was kept in a 5% (v/v) nitric acid solution overnight and subsequently washed with double-distilled water. Analytical grade Ag(I) nitrate and nitrate salts of other cations (all from Merck, Darmstadt, Germany) were available with high purity and used without further purification. Working solutions of Ag(I) were prepared daily by diluting a 1000 mg L⁻¹ stock solution. The pH of sample solutions was adjusted with the aid of hydrochloric acid and ammonia. 1-(2-Pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) as chelating agent was prepared by dissolving an appropriate amount of reagent in methanol. Triethylamine, NaOH and 65% HNO₃ were purchased from Merck Company (Darmstadt, Germany).

2.2. Instrumentation

A Shimadzu flame atomic absorption spectrophotometer (AA-680) equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of Ag(I). An Ag(I) hollow cathode lamp from Hamamatsu, Photonic Co. Ltd, L233-series was employed as the radiation source at a wavelength of 328.1 nm and acetylene flow rate of 1.8 Lmin⁻¹. A pH meter (Metrohm Lab-827, Switzerland) was used for adjustment of pH solution. A vortex mixer (IKA Vortex Genius 3, Germany) was used for complete mixing of sample solution. A Behdad Universal Centrifuge (Tehran, Iran) was used to achieve complete phase separation. The homemade extraction vessel, was used for extraction process.

2.3. Synthesis of switchable solvent

In this study, the switchable solvent was synthesized in an equal volume mixture of triethylamine and water. 200.0 mL of ultrapure water and 200.0 mL of triethylamine were added in 1.0 L glass beaker on magnetic stirrer. A two-

phase system was formed after stirring the mixture. Afterwards, dry ice (~20 g) was added gradually to the beaker under vigorous stirring until the solution became cloudy. The addition of dry ice was repeated 20 times to obtain a single protonated triethylamine carbonate. Next, the mixture was stirred for 2 h at room temperature to ensure the complete protonation of trimethylamine. 400.0 mL of the protonated triethylamine switchable solvent can be easily prepared.

2.4. Switchable solvent based microextraction procedure

10.0 mL of aqueous sample containing Ag(I) (100 µg/L), 4×10^{-4} mol L⁻¹ of PAN was adjusted at pH=9.5 and transferred into a 25.0 mL extraction vessel. First 750 µL of protonated triethylamine carbonate as extraction solvent was quickly added into the extraction vessel using 1.0 mL Hamilton syringe. Afterwards, 1.6 mL of NaOH solution (10 mol L⁻¹) was injected and a cloudy solution was formed. At this stage, the protonated triethylamine carbonate was converted to TEA and afterwards the Ag (I)–PAN complex in the aqueous phase was extracted into the fine droplets of TEA. The cloudy solution was fiercely vortexed for 0.5 minute and then was centrifuged at 3000 rpm for 5 minutes. A thin layer of organic phase including the extracted analytes was accumulated on the top surface of the aqueous phase. To direct the collected triethylamine phase into the capillary tube, attached to the top of the vial (part 1), an appropriate volume of distilled water was introduced into the vial through the glass tube fixed on its side (part (2)). Finally, the organic phase (approximately 150 ± 5 µL) was manually withdrawn by 250.0 µL Hamilton gas-tight syringe, diluted to 300.0 µL with methanol

and introduced to the microinjection system coupled to a FAAS nebulizer for analysis. Schematic representation of the developed SHS-LPME steps is presented in Fig. 1.

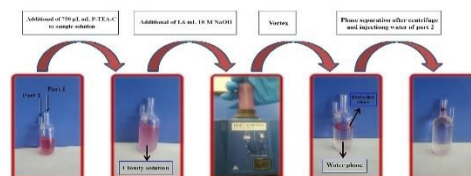


Fig. 1. Schematic representation of the developed SHS-LPME steps.

2.5. Sample preparation

The water samples were collected from different part of Arak, Iran. The water samples were filtered using 0.45 µm micropore membranes, adjusted to the pH of 9.5 and stored in glass containers at 4°C.

2.6. Experimental design strategy

In this study, the experimental design was applied to reduce numbers of experiments and to get effective factors. The Plackett–Burman design [18] was used as a screening approach to clarify the effective factors in extraction of Ag (I) by switchable-hydrophilicity solvent based liquid phase microextraction (SHS-LPME) method from aqueous solution. Based on preliminary experiments, a P–B design was applied to evaluate the main effects of the seven factors (sample pH, concentration of chelating agent, volume of extraction solvent, amount of NaOH, salt effect, vortex time and centrifugation time). The factors, their levels, and the runs of P–B design are shown in Table 1.

Table 1. Factors, levels, Runs and their results in the PBD.

Absorbance	X ₇	X ₆	X ₅	X ₄	X ₃	X ₂	X ₁	Run
0.301	5	0.5	1.5	0.75	0.5	0.0003	9	1
0.119	2	0.0	2.0	0.50	1.0	0.0005	7	2
0.145	2	1.0	1.0	1.00	1.0	0.0001	11	3
0.102	8	0.0	1.0	0.50	1.0	0.0001	11	4
0.302	5	0.5	1.5	0.75	0.5	0.0003	9	5
0.187	8	1.0	2.0	0.50	0.0	0.0001	11	6
0.079	8	0.0	2.0	1.00	1.0	0.0001	7	7
0.120	8	1.0	1.0	1.00	1.0	0.0005	7	8
0.201	8	0.0	2.0	1.00	0.0	0.0005	11	9
0.300	5	0.5	1.5	0.75	0.5	0.0003	9	10
0.175	2	0.0	1.0	1.00	0.0	0.0005	11	11
0.023	2	0.0	1.0	0.50	0.0	0.0001	7	12
0.289	2	1.0	2.0	0.50	1.0	0.0005	11	13
0.065	2	1.0	2.0	1.00	0.0	0.0001	7	14
0.034	8	1.0	1.0	0.50	0.0	0.0005	7	15

Factor	Levels		
	Low	Central	High
(X ₁) pH	7	9	11
(X ₂) PAN Concentration (mol L ⁻¹)	0.0001	0.0003	0.0005
(X ₃) Salt (mL of NaCl (10%v/v))	0	0.5	1
(X ₄) SHS volume (mL)	0.5	0.75	1
(X ₅) NaOH volume (mL)	1	1.5	2
(X ₆) Vortex time (min)	0	0.5	1
(X ₇) Centrifugation time (min)	2	5	8

Table 2. Design matrix by BBD

Run	X1	X2	X3	Absorbance
1	11	0.0003	1.0	0.178
2	7	0.0001	1.5	0.109
3	9	0.0005	2.0	0.198
4	9	0.0003	1.5	0.291
5	9	0.0001	1.0	0.102
6	11	0.0003	2.0	0.167
7	7	0.0003	2.0	0.148
8	9	0.0003	1.5	0.297
9	9	0.0003	1.5	0.295
10	11	0.0001	1.5	0.098
11	9	0.0001	2.0	0.160
12	11	0.0005	1.5	0.240
13	9	0.0005	1.0	0.221
14	7	0.0003	1.0	0.104
15	7	0.0005	1.5	0.117

Factor	Levels		
	Low	Central	High
(X ₁) pH	7	9	11
(X ₂) PAN concentration (mol L ⁻¹)	0.0001	0.0003	0.0005
(X ₃) Volume NaOH (mL)	1	1.5	2

In the next step, after choosing the effective factors, a Box–Behnken design (BBD) was performed in order to determine the optimum conditions and the investigation of the variables interaction. In the BBD, the number of experimental runs (N) is obtained by the Eq. (2):

$$N = 2K(k-1) + C_0 \quad (2)$$

where K is the number of variables, and C₀ is number of the center points [19]. In this study, after P–B design, three factors were chosen and in following analyzed by BBD on two levels and at a triplicate center point. By considering equation (2), 15 experiments were required in this design including three center points and they were performed randomly (Table 2). According to Table 2, these factors include: pH of solution (X₁), PAN concentration (X₂, mol L⁻¹) and volume of NaOH 10 mol L⁻¹ (X₃, mL). All the statistics were carried out by Minitab (Version 17.0) software.

3. RESULT AND DISCUSSION

3.1. Plackett–Burman design

A Plackett–Burman design was used for seven factors to select the main effects in extraction of Ag(I) by SHS-LPME method (Table 1). For this purpose, 15 experiments were performed randomly and the analysis of variance (ANOVA)

results were evaluated for determination of the main effects. The effect of the studied factors in the Plackett–Burman design was shown in Fig. 2 in the form of a Pareto chart in 95% confidence level. According to Fig. 2, pH of sample solution was the most significant factor on the extraction efficiency. Also, sodium hydroxide volume and concentration of chelating agent were the next most significant factors. Based on Pareto chart, volume of extraction solvent, salt effect, vortex time and centrifugation time had no significant effect on the response and must be eliminated to optimize with BBD and were fixed at a middle level.

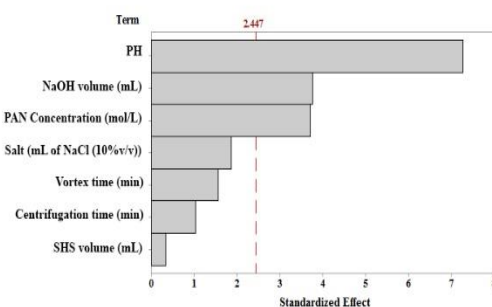


Fig. 2. Standardized main effects Pareto chart for the Plackett–Burman design. The vertical line in the chart defines the 95% confidence interval.

3.2. Box–Behnken design

In this step, 15 tests were performed and (ANOVA) was used in order to evaluate the statistical significance of the purposed method and the results are shown in Table 3. P-value and lack of fit (LOF) are important parameters in ANOVA table. If p-value is less than 0.05, then the model is statistically significant. The LOF parameter indicates the variation of signals around the fitted model. According to the obtained results, the p-value for lack-of-fit is 0.37 which confirms a good fitting of model to responses. Also the coefficients of R^2 (99.90%) and adjusted R^2 (99.73%) indicate a good relationship between responses and the fitted model. The relationship of the significant factors was obtained from the Eq. (3).

$$A = 0.29433 + 0.02563X_1 + 0.03838X_2 + 0.00850X_3 - 0.08717X_1^2 - 0.06617X_2^2 - 0.05792X_3^2 + 0.03350X_1 X_2 - 0.01375X_1 X_3 - 0.02025X_2 X_3 \quad (3)$$

Fig. 3a to 3c shows the three-dimensional response surface plots using Eq. (3), when one of the variables is fixed at the central point and two factors are allowed to vary. Fig. 3a shows the response surface obtained by plotting the pH versus the PAN concentration at the fix volume of NaOH (1.5 mL); Fig. 3b shows the response surface obtained as a function of pH and volume of NaOH while concentration of chelating agent was kept at the $3 \times 10^{-4} \text{ mol L}^{-1}$ and Fig. 3c shows the response surface obtained for volume of NaOH and concentration of chelating agent while pH was constant at 9. Based on the surface plots in Fig. 3a–c, extraction efficiency of Ag(I) by SHS-LPME methods was maximized around the

center point. According to the overall result of the BBD, the optimum experimental conditions were chosen: the concentration of chelating agent: $4 \times 10^{-4} \text{ mol L}^{-1}$; pH, 9.5 and volume of NaOH: 1.6 mL.

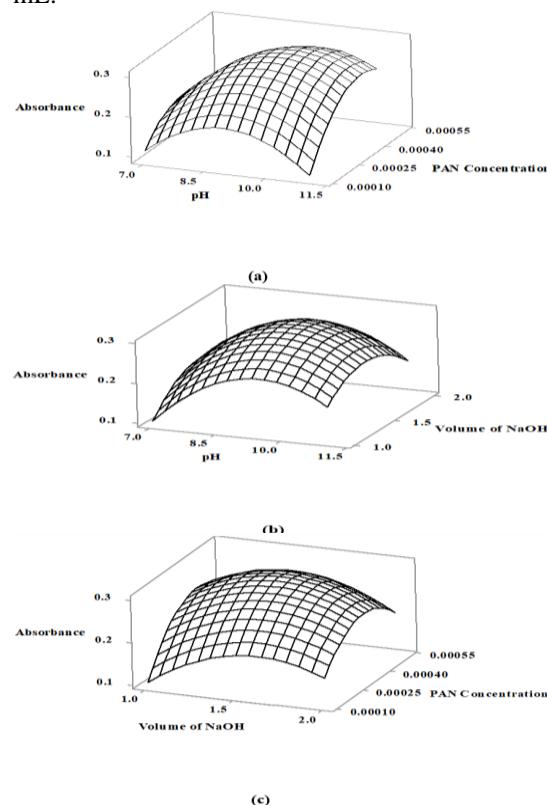


Fig. 3. Response surface plots: (a) pH vs. PAN concentration (mol L^{-1}), (b) pH vs. NaOH volume (mL), (c) NaOH volume (mL) vs. PAN concentration (mol L^{-1}).

Table 3. ANOVA for BBD.

Source	DF ^a	Adj SS	Adj MS	F-Value ^b	P-Value
X ₁	1	0.005253	0.005253	373.00	0.000
X ₂	1	0.011781	0.011781	836.53	0.000
X ₃	1	0.000578	0.000578	41.04	0.001
X ₁ ²	1	0.028054	0.028054	1992.02	0.000
X ₂ ²	1	0.016165	0.016165	1147.81	0.000
X ₃ ²	1	0.012385	0.012385	879.43	0.000
X ₁ X ₂	1	0.004489	0.004489	318.75	0.000
X ₁ X ₃	1	0.000756	0.000756	53.70	0.000
X ₂ X ₃	1	0.001640	0.001640	116.47	0.000
Lack-of-Fit	3	0.000052	0.000017	1.85	0.370
Pure Error	2	0.000019	0.000009		
Total	14	0.073989			

^aDF: degrees of freedom.

^bTest for comparing variance of model with variance of residual (error).

3.3. Effect of coexisting ions

The effects of common coexisting ions on the extraction recovery of Ag(I) were studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than 5%. For this purpose,

appropriate amounts of the other ions were added to 10 mL sample solutions containing $100 \mu\text{g L}^{-1}$ of Ag(I) and the SHS-LPME procedure was performed and the results are given in Table 4. It demonstrates that the common coexisting ions at these levels of concentrations did not have

significant effect on the extraction of Ag(I) using developed method.

Table 4. Effect of foreign ions in the determination of 100 $\mu\text{g L}^{-1}$ Ag(I) using the SHS-LPME.

Ions	Ion/Ag(I)
Hg ²⁺ , Mn ²⁺ , Cr ³⁺	25
Cd ²⁺ , Ni ²⁺ , Fe ³⁺ , Pb ²⁺ , Cu ²⁺	50
Zn ²⁺ , Co ²⁺	100
Al ³⁺	1000
Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Mg ²⁺	2000

3.4. Analytical performance

The performance of proposed method was obtained by several analytical characteristics such as limit of detection (LOD), enrichment factor (EF) and linearity along with the relative standard deviation (RSD) under the optimized conditions. The equation of the calibration curve obtained after applying the preconcentration procedure was $A = 0.8782 \times C_{\text{Ag}} + 0.0136$, where A is absorbance and C_{Ag} is concentration of Ag⁺ ions. The calibration curve was exhibited linearity over the range of 2-500 $\mu\text{g L}^{-1}$ with a correlation coefficient (r^2) of 0.997. The limit of detection, (LOD) based on 3Sb/m (Sb and m are standard

deviation of the blank and slope of the calibration equation, respectively) was 0.35 $\mu\text{g L}^{-1}$. The relative standard deviation (RSD) for 10 replicate measurements of 100 $\mu\text{g L}^{-1}$ Ag(I) was 1.4 %. Enrichment factor was obtained 68 which was calculated from the slope ratio of calibration curve with (0.8782) and without (0.0129) preconcentration by the SHS-LPME procedure. Table 5 compares the characteristic data of the present method with those reported in literatures. As can be seen from Table 5, the proposed method has a low detection limit, wide linear dynamic range, good enrichment factor and relative standard deviation and these characteristics are comparable or even better than most of the other methods.

3.5. Analysis real sample

For accessing the capability of the method, several water samples were applied for the determination Ag (I) content and the results were given in Table 6. The accuracy of the method was checked by spiking samples at different values of Ag (I) and calculation of the recovery was carried out. As a result in Table 6, the recoveries of Ag (I) ions were satisfied in the range between 96.31% and 102.32%.

Table 5. Comparison of analytical characteristic of the proposed method with some published method for determination of Ag(I).

Method	Instrument	LOD ($\mu\text{g L}^{-1}$) ^a	EF/PF ^b	RSD (%)	Ref.
CPE	FAAS	1.4	45	2.1	[10]
CPE	FAAS	10	35	1.85	[20]
DLLME	FAAS	0.41	35	3.1	[21]
UAE-DLLME ^c	UV-Vis	0.45	35	3.2	[22]
USAEME ^d	ETAAS	6.8	9.8	5.5	[23]
SHS-LPME	FAAS	0.35	68	1.4	This work

^aLOD: Limit of detection; ^bEF: enhancement factor; PF: preconcentration factor; ^cUAE-DLLME: Ultrasound-assisted emulsification dispersive liquid-liquid microextraction; ^dUSAEME: Ultrasound-assisted emulsification microextraction.

Table 6. Determination of Ag (I) in water samples.

Sample	Ag spiked ($\mu\text{g L}^{-1}$)	Ag found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water (Arak, Iran)	0	ND	-
	50	48.40 \pm 0.12	96.8
	100	99.77 \pm 0.54	99.77
Well water (Arak, Iran)	0	ND	-
	50	49.39 \pm 0.34	98.78
	100	96.31 \pm 0.28	96.31
Mineral water (Sarband mountain, Arak, Iran)	0	ND	-
	50	50.14 \pm 0.91	100.28
	100	99.07 \pm 0.78	99.07
Marzan Abad river (Arak, Iran)	0	ND	-
	50	49.98 \pm 0.92	99.9
	100	100.90 \pm 0.35	100.90
Hossein Abad river (Arak, Iran)	0	ND	-
	50	51.07 \pm 0.21	102.14
	100	102.32 \pm 0.43	102.32

4. CONCLUSIONS

A green approach towards the preconcentration and determination of Ag(I) in water samples was achieved using switchable-hydrophilicity solvent based liquid phase microextraction (SHS-LPME) method. The method is highly environmentally friendly as low amounts of organic waste are produced due to the use of switchable solvent. For switching SHS between the two forms, CO₂ and NaOH were applied. The synthesis of switchable solvent was easy with high stability. The main advantage of this solvent is that it allows the extraction of the analytes in a homogeneous phase without dispersive solvent and is easily operated without additional experimental steps. In this study, the homemade extraction vessel was used in order to ease withdrawal of the extraction solvent in the sample solution. Affecting parameters on the extraction efficiency were investigated and optimized by using an experimental design first as a Plackett–Burman design for screening and second as a Box–Behnken design for obtaining optimal condition for significant factors.

REFERENCES

- [1] L. Kocurova, I.S. Balogh, L. Nagy, F. Billes, A. Simon and V. Andruch, Application of a bisindocarbocyanine reagent for dispersive liquid–liquid microextraction of silver with subsequent spectrophotometric determination, *Microchem. J.* 99 (2011) 514–522.
- [2] I.M. Dittert, D.L.G. Borges, B. Welz, A.J. Curtius and H. Becker-Ross, Determination of silver in geological samples using high-resolution continuum source electrothermal atomic absorption spectrometry and direct solid sampling, *Microchim. Acta* 167 (2009) 21–26.
- [3] G. Absalan, M. Akhond, A.Z. Ghanizadeh, Z.A. Abedi and B. Tamami, Benzil derivative of polyacryloylhydrazide as a new sorbent for separation, preconcentration and measurement of silver(I) ion, *Sep. Purif. Technol.* 56 (2007) 231–236.
- [4] T. Daşbaşı, Ş. Saçmacı, S. Şahan, Ş. Kartal and A. Ülgen, Synthesis, characterization and application of a new chelating resin for on-line separation, preconcentration and determination of Ag(I) by flame atomic absorption spectrometry, *Talanta* 103 (2013) 1–7.
- [5] Agency for Toxic Substances and Disease Registry, Toxicological Profile for Silver TP_90-24), Department of Health and Human Services, Public Health Service, Atlanta, GA, USA, 1990.
- [6] D. Afzali, A.R. Mohadesi, B.B. Jahromi and M. Falahnejad, Separation of trace amount of silver using dispersive liquid–liquid based on solidification of floating organic drop microextraction, *Anal. Chim. Acta* 684 (2011) 54–58.
- [7] J. Chena, S. Xiao, X. Wu, K. Fang and W. Liu, Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction, *Talanta*, 67 (2005) 992–996.
- [8] O. Ortet and A.P. Paiva, Liquid–Liquid Extraction of Silver from Chloride Media by N, N' -Tetrasubstituted Dithiomalonamide Derivatives, *Sep. Sci. Technol.* 45 (2010) 1130–1138.
- [9] M.K. Rofouei, M. Payehghadr, M. Shamsipur and A. Ahmadalinezhad, Solid phase extraction of ultra-traces silver(I) using octadecyl silica membrane disks modified by 1,3-bis(2-cyanobenzene) triazene (CBT) ligand prior to determination by flame atomic absorption, *J. Hazard. Mater.* 168 (2009) 1184–1187.
- [10] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi and M. Soylak, Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples, *J. Hazard. Mater.* 168 (2009) 1022–1027.
- [11] P. Liang and L. Peng, Determination of silver (I) ion in water samples by graphite furnace atomic absorption spectrometry after preconcentration with dispersive liquid-liquid microextraction, *Microchim. Acta* 168 (2010) 45–50.
- [12] Z.A. Allothman, M.A. Habila, E. Yilmaz, N.M. Al-Harbi and M. Soylak, Supramolecular microextraction of cobalt from water samples before its microsampling flame atomic absorption spectrometric detection, *Int. J. Environ. Anal. Chem.* 95 (2015) 1311–1320.
- [13] P.G. Jessop, D. J. Heldebrant, X. Li, C.A. Eckert and C.L. Liotta, Green chemistry: Reversible nonpolar-to-polar solvent, *Nature* 436 (2005) 1102.
- [14] E. Yilmaz and M. Soylak, Switchable solvent-based liquid phase microextraction of copper (II): optimization and application to environmental samples, *J. Anal. At. Spectrom.* 30 (2015) 1629–1635.
- [15] J. Durelle, J.R. Vanderveen, Y. Quan, C.B. Chalifoux, J.E. Kostin and P.G. Jessop, Extending the range of switchable-hydrophilicity solvents, *Phys. Chem. Chem. Phys.* 17 (2015) 5308–5313.

- [16] J.R. Vanderveen, J. Durelle and P.G. Jessop, Design and evaluation of switchable-hydrophilicity solvents, *Green Chem.* 16 (2014) 1187-1197.
- [17] M. Ezoddin, K. Abdi and N. Lamei, Development of air assisted liquid phase microextraction based on switchable hydrophilicity solvent for the determination of palladium in environmental samples, *Talanta* 153 (2016) 247-252.
- [18] A. Asfaram, M. Ghaedi and A. Goudarzi, Optimization of ultrasound-assisted dispersive solid-phase microextraction based on nanoparticles followed by spectrophotometry for the simultaneous determination of dyes using experimental design, *Ultrason. Sonochem.* 32 (2016) 407-417.
- [19] Y. Zhou, J.Z. Song, F.F.K. Choi, H.F. Wu, C.F. Qiao, L.S. Ding, S.L. Gesang and H.X. Xu, An experimental design approach using response surface techniques to obtain optimal liquid chromatography and mass spectrometry conditions to determine the alkaloids in *Meconopsis* species, *J. Chromatogr. A* 1216 (2009)7013-7023.
- [20] H. Tavallali, S. Yazdandoust and M. Yazdandoust, Cloud point extraction for the preconcentration of silver and palladium in real samples and determination by atomic absorption spectrometry, *CLEAN – Soil, Air, Water* 38 (2010) 242-247.
- [21] S. Rastegarzadeh, N. Pourreza and A. Larki, Determination of trace silver in water, wastewater and ore samples Using dispersive liquid–liquid microextraction coupled with flame atomic absorption spectrometry, *Ind. Eng. Chem. Res.* 2240 (2014) 1–5.
- [22] X. Wen, L. Kong, M. Chen, Q. Deng, X. Zhao and J. Guo, A new coupling of spectrophotometric determination with ultrasound-assisted emulsification dispersive liquid–liquid microextraction of trace silver, *Spectrochim. Acta A* 97 (2012) 782-787.
- [23] G. Khayatian and B. Pourbahram, Ultrasound-assisted emulsification microextraction and preconcentration of trace amounts of silver ions as a cyclam complex, *J. Anal. Sci. Technol.* 7 (2016) 1-8.