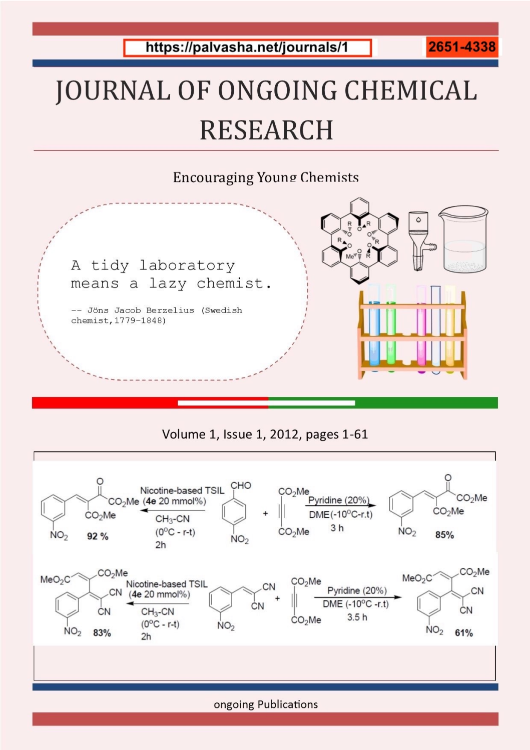
SINGLE DROP MICROEXTRACTION TO ANALYZE TRACE OF SILVER COMPLEXED WITH 8-HYDROXYQUINOLINE IN FRESH AND WASTE WATER SAMPLES USING A MULTIVARIATE APPROACH



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A tidy laboratory means a lazy chemist.

-- Jöns Jacob Berzelius (Swedish chemist,1779-1848)

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Research Article

Single Drop Microextraction To Analyze Trace Of Silver Complexed With 8-hydroxyquinoline In Fresh And Waste Water Samples Using A Multivariate Approach

Naeemullah*, Abdul Haseeb, Faheem Shah, Tasneem Gul Kazi,
For affiliations and correspondence, see the last page.

Abstract

Single drop microextraction (SDME) combined with electrothermal atomic absorption spectrometry was proposed to extract Silver (Ag) from aqueous samples into a drop of ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6]), after complexation with 8-hydroxyquinoline (8HQ). The multivariate strategy was applied to estimate the optimum values of experimental factors for the recovery of Ag. The limit of detection and enhancement factor were 1.12 ng L^{-1} and 80, respectively. The validity and accuracy of proposed method was checked by analysis of real water sample through standard addition method. The proposed method was successfully applied to determine Ag in different fresh canal water samples.

Keywords: 8-hydroxyquinoline, electrothermal atomic absorption spectrometry, single drop microextraction, silver, ionic liquid,

INTRODUCTION

Silver metal has grabbed much attention in current literature due to their environmental and the subject of much attention due to their environmental risk . The exposure of Ag to the environment are mainly due widespread application in commercial and industrial scales. The Ag compounds has an important part of modern industry, medicine, thus it provides a gateway to enters the environment through industrial wastes [Hu et al, 2002]. The contamination of the environment with toxic heavy metals is perceived as major and widely distributed pollutants in the environment [Tuzen et al, 2006; Turkmen et al, 2008; Uluozlu et al, 2007].

The Ag is considered to a serious threat to the aquatic environment due to their toxicity to many aquatic organisms in very low concentrations. It also interacts with essential nutrients in biological system, that might lead to potential toxicity [Bowen, 1966; Purcell et al, 1999]. A great deal of work and information are required to point out the toxic mechanism of Ag ions in biological system [8]. The development of analytical tools to monitor the low level of target analyte has a key role for the regular monitoring in different environmental samples. The direct analysis of the trace level of the target analyte in complex matrix sample might be difficult due to their very low concentration and the matrix interferences effect, a preconcentration step is necessary to overcome the sensitivity and matrix effect. There are a large number of methods have been designed for the extraction and preconcentration of Ag ions in real samples [Mendes et al, 1994; Camagong et al, 2002; Ding et al, 2006]. Liquid liquid extraction (LLE) is considered to be one of the most applicable preconcentration or matrix isolation approached in the determination of metal ions. The LLE has some drawbacks which limited their applications such as time-consuming, unsatisfactory enrichment factors, large organic solvents and secondary wastes.

Recently a great efforts have been put forward on miniaturizing the LLE approaches by reducing the amount of the extracting solvent into a single drop [Liang et al, 2008]. Single drop microextraction SDME is based on the distribution effect of the analytes between a microdrop of extraction solvent at the tip of a microsyringe needle and aqueous sample solution. In the first step a drop of the required solvent is exposed to the sample solution due to their extraction capability the target analyte is then transferred from the bulk sample into the solvent drop. After extracting for a prescribed period of time, the microdrop is retracted back into the microsyringe and transferred to the instrumentation for further analysis [Lambropoulou et al, 2004]. The SDME approach could be easily combined with with atomic spectrometry techniques that required at microliter samples for analysis such as ETAAS [Fan, 2007].

Room temperature ionic liquids (RTILs) have attract much attention in modern era of science due to their unique properties such as negligible vapor pressure, non-flammability and their extraction capability for different organic compounds and metal ions [Liu et al, 2005;Pandey et al, 2006]. It is well documented in literature that RTIL are as green alternative solvent for extraction of metal ions [GuorTzo et al, 2003; Naoki et al, 2005; Zaijun et al, 2007]. There rae limited work has been done to used RTIL in SDME couple with ETAAS for trace Ag ion determination.

The aim of this work is to combine SDME with ETAAS to monitor the trace level of Ag ion in real water samples. The effect of various variable has a key role in the proposed SDME method was fully optimized. Multivariate strategy is a simple and reliable statistical approach has to be used, to find find the adequate experimental conditions to produce the best response of the desired method

RESULTS AND DISCUSSION

Optimization of experimental variables

The variables such as pH, concentration of complexing agent (8HQ), volume of ionic liquid, volume of samples, stirring rate and extraction time were studied to examine the efficiency of the desired method. The factors and their levels are given in (Table 1).

Table 1: Variable and levels used for the Plackett–Burman designs in the factorial design

Variables	Symbol	Low (−)	High (+)
Drop Volume (µL)	DV	2	6
Complexing Agent (8HQ mol L^{-1})	C	1.0 × 10^{-3}	10 × 10^{-3}
pH	P	3	10
Extraction Time (min)	ET	2	12
Volume of Sample (mL)	VS	2	5
Stirring Rate (rpm)	SR	200	600

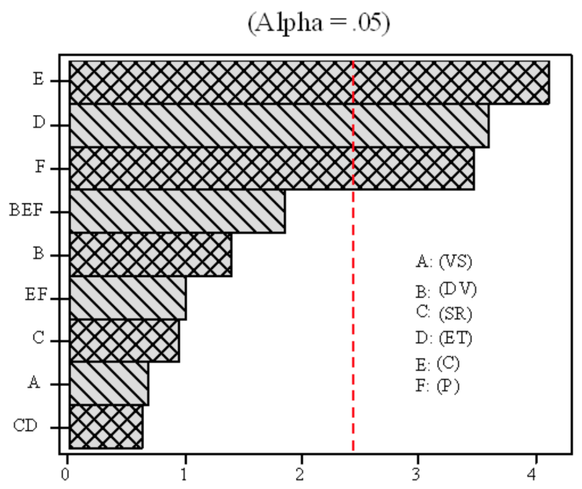

Figure 1: Pareto chart for the significance of response of the variables: drop volume of RTIL (DV), volume of sample (VS), concentration of complexing agent (C), pH (P), extraction time (ET) and stirraning rate (SR)

The sample/standards volume of 2 mL was kept constant throughout the procedure. The impact of the target variables on the proposed method at two levels (low and high) were examined on percentage (%) recovery as shown in (Table 2) and screening out by using a Pareto chart of the standardized effect (Fig. 1). From inference tests, the results produced a minimum t-value at the 95.0% confidence interval of 2.4, and we consider that a factor is significant when the t-value is higher than 2.4.

Estimated effects of variables

Considering for the proposed SDME procedure for Ag determination in single drop using 8-HQ as complexing agent. six variables (drop volume of RTIL (DV), volume of sample (VS), concentration of complexing agent (C), pH (P), extraction time (ET) and stirring rate (SR) were selected to optimize the (%)recovery of Ag by multivariate technique. The Plackett–Burman design is shown in (Table 2).

Table 2: Plackett–Burman design for the significant variable determination (n=6)

Exp.	VS	DV	SR	ET	C	P	% Rec.
1	+	-	-	-	+	-	38
2	+	+	-	-	-	+	45
3	+	+	+	-	-	-	40
4	+	+	+	+	-	-	54
5	-	+	+	+	+	-	70
6	+	-	+	+	+	+	92
7	-	+	-	+	+	+	85
8	+	-	+	-	+	+	60
9	+	+	-	+	-	+	61
10	-	+	+	-	+	-	50
11	-	-	+	+	-	+	58
12	+	-	-	+	+	-	66
13	-	+	-	-	+	+	60
14	-	-	+	-	-	+	35
15	-	-	-	+	-	-	30
16	-	-	-	-	-	-	25

The resulting values (1–16) are being the % recoveries of Ag (average values of six replicates). From the results of the PBD, the most significant effects were observed for concentration of complexing agent (C), pH and extraction time (ET) on %recovery of Ag. In experiments 6 and 7, the 92% and 85% Ag recoveries were observed at maximum (+) level of C, while the other two factors, i.e., ET and pH were also at their maximum (+) level. It can be seen in experiments 5 and 12, that C and ET are at higher level while pH is at lower level, the recoveries of Ag were 70% and 66%, respectively indicated that pH has a significant effect on the formation and extraction of Ag-8HQ complex. In experiments 9 and 11, the ET was at its lower level, yielding 61% and 58% recovery of Ag respectively, which clearly indicated the significant effect of time on extraction recovery of Ag. The combined effects of pH and ET was significant as shown in experiments 1 and 3, where 38 and 40% recovery was obtained at their lower levels. The same trend was observed at low levels of C and ET (experiments 3 and 14). Experiments 15 and 16 indicated the combined effect of all three variables (ET, C and P), at (-) levels. The selected levels of VS, SR and DV for the proposed procedure showed no significant effect (p=0.315). The significant effects of understudy variable on the (% recovery) of Ag were found in decreasing order of

C>ET > P> DV >SR>VS as shown in (Fig. 1).

Optimization by central composite designs

After screening the variables three factors (C, ET and P) were optimized to provide the maximum recovery of Ag and removed factor(DV, SR and VS) that were not statistically significant from the model A central 2^3+ star orthogonal composite design with six degree of freedom and involving 16 new experiments was carried out to optimize the variables (Table 3).

Table 3: Central 23 +star orthogonal composite design (n = 16) for the set of (C), (ET) and (P)

Experiments	A (P)	B (ET)	C (C)	% Recovery
1	${}_aP^o$	${}_bE^o$	${}_cC^o$	99
2	-	-	-	20
3	+	-	-	18
4	-	+	-	22
5	+	+	-	20
6	-	-	+	26
7	+	-	+	30
8	-	+	+	40
9	+	+	+	60
10	$+P^1$	${}_bE^o$	${}_cC^o$	20
11	$+P^2$	${}_bE^o$	${}_cC^o$	55
12	${}_aP^o$	$-E^1$	${}_cC^o$	20
13	${}_aP^o$	$+E^2$	${}_cC^o$	80
14	${}_aP^o$	${}_bE^o$	$+C^1$	30
15	${}_aP^o$	${}_bE^o$	$+C^2$	82
16	${}_aP^o$	${}_bE^o$	${}_cC^o$	98

$P^1 = 0.6$, $P^2 = 12.38$, $P^o = 6.5$, $E^1 = 1.4$ min, $E^2 = 15.4$ min, $E^o = 7$ min, $C^1 = 2.1$ mol L^{-1} $C^2 = 13.1$ mol L^{-1}, $C^o = 5.5$ mol L^{-1}

The study of estimated response surfaces data for variables, [C]/[ET] and [C]/[P] on the % recovery of Ag is shown in Fig. 2 (A and B). The volume of C has significant effect on % recovery of Ag, its minimum volume give only 58% Ag recovery (experiment 11). It was observed in experiments 1 and 16 that at optimized levels of all three variables (${}_aP^0$, ${}_bE^0$ and ${}_cC^0$), recovery of Ag was 98–99% respectively. On the other hand in experiment 11, higher concentration of complexing reagent (5×10^{-3} mol L^{-1}), showed a little effect on Ag recovery. Decreased Ag extraction efficiency was observed in experiment 15, where extraction time was much higher than optimized value, same trend was observed at minimum extraction time (experiment 14). The pH of the sample solution was the next significant factor evaluated for its effect on the Ag recovery. Maximum and minimum values for pH added only 56 and 66% recovery, as shown in experiments 12 and 13 respectively.

After plotting three dimensional (3D) response surfaces, calculation was made by using quadratic equation. The results indicated that the recoveries were quantitative at (5×10^{-3} mol L^{-1}) of C and of ET (8.0 min) as shown in (Fig. 2). It is desirable to employ the shortest equilibrium time, which compromise completion of the reaction and efficient separation of phases.

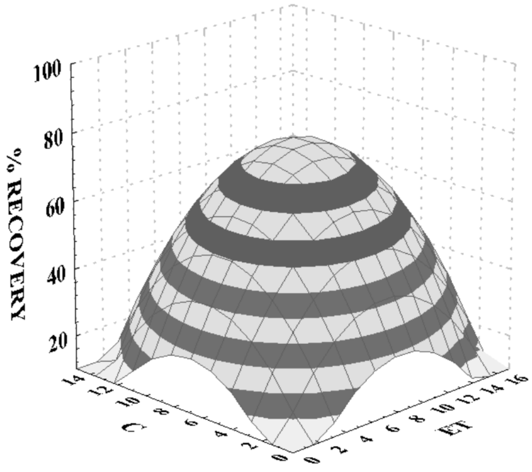

Figure 2: Three dimension (3D) surface response for % recovery of silvr(I) by SDME: Interaction b/w [C] (mol/L) and [ET] (min)

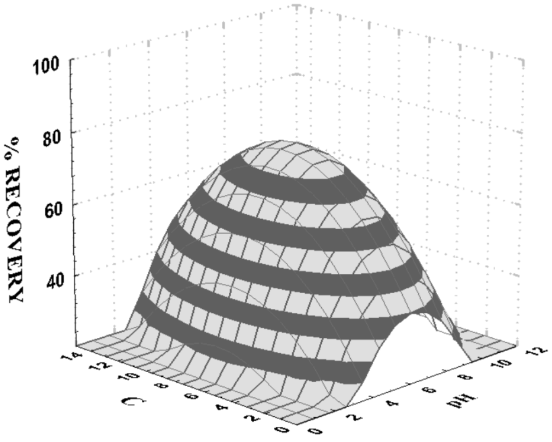

Figure 3: Three dimension (3D) surface response for % recovery of silvr(I) by SDME: interaction b/w [C] (mol/L) and pH [P]

While on other side longer time may result in drop dissolution and has a high incidence of drop loss, and thus poor accuracy and precision. The pH of the sample solution was the next significant factor which plays a unique role in metal-chelate complex formation and subsequent extraction (Fig. 3). 8HQ is bidentate ligand which has lone pair of electrons that are responsible for metal complex formation. When we provide an acidic medium the active sites (atoms having lone pair of electron) become protonated which might be still not further available for complex formation and lead to low extraction efficiency due to limited Ag–8HQ complex formation. While on other hand in highly basic medium mostly metals get precipitated.

Interferences

The selectivity of the present method was investigated by interference study. The different interferences ions present in the real sample might react with with 8HQ and decreased the extraction capability of the proposed method. The experiment was designed to carry out the following study in an Ag solution (10 ng L^{-1}) of at different interfering to analytes ratio as shown in (Table 4).

Table 4: selectivity and Effect of foreign ions on the preconcentration and determination of silver(I)

Coexisting Ions	**Interference/ analyte amount**
Ba^{2+} , Mg^{2+}, Ca^{2+}, $Na^{+,}$ $K^{+,}$ Li^{+},PO_4^{3-}, SO_4^{2-}	>10000
F^{-}, CO_3^{2-}	5000
Cr^{3+}, Fe^{3+}, Zn^{2+}	2000
Cd^{2+}, Pb^{+2}, Al^{3+}	1000
Fe^{3+} , Al^{3+} , Fe^{2+}, Co^{2+}, Ni^{2+}	500

The effect of the alkali and alkaline earth elements have generally very because it is not formed stable complexes with 8HQ. Excess of high concentration of 8HQ reagent was used for the complete chelation of the selected ions even in the presence of interferent ions.

Table 5: Analytical performance and figure of merit of the proposed method

Without SDME	Calibration equation (C in ng L^{-1})	A = 0.0935C+0.0129
With SDME		A = 5.0292C–0.7552
Without SDME	Concentration range (ng L^{-1})	500–15,000
With SDME		5–200
Without SDME	LOD^{a} (ng L^{-1})	66.5
With SDME		1.12
Without SDME	R^2 (correlation coefficient)	0.9970
With SDME		0.9954
Without SDME	Repeatability (RSD%)^{b} (n=10)	3.5 (500 ng L^{-1})
With SDME		4.5 (20 ng L^{-1})
Enrichment factor^{c}		80

[a] Silver(I) concentration was 20 ng L^{-1} for which the R.S.D. was obtained. [b] Limit of detection. Calculated as three times the S.D. (3σ) of the blank signal. [c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Analytical figures of merit

The analytical capability of the desire method was found to be linear with a correlation coefficient (R^2) of 0.9954 at the concentration range of (5–200 ng L^{-1}) and subjecting to SDME methods at optimum values of all understudy variables. The repeatability of the proposed method was checked by RSD using on a standard solution containing 10 ng L^{-1} Ag. The limit of detection (LOD) and enhancement factor of the proposed methods are given in (Table 5).

We also used spiking addition method for Validity of the proposed method Ag at three concentration levels (2.0–10.0 µg L^{-1}) in a real water sample as shown in (Tables 6) by using the equation as follows:

$$R(\%) = [(C_m - C_o) / m] \times 100$$

Where C_m is a value of metal in a spiked sample, C_o the value of metal in a sample, and *m* is the amount of metal spiked. These results demonstrate the applicability of developed procedure for Ag determination in fresh canal water samples. As can be seen recoveries between 96 and 100% were obtained, which again confirm the accuracy of the method.

Table 6: Determination of silver in certified reference material and real water samples by Standard addition method

Certified reference material	Certified values (µg L^{-1})	Measured values (µg L^{-1})	Recovery %
SRM 1643e	1.07 ± 0.075	1.04 ±0.012	97.2 %
Samples	Added (µg L^{-1})	Measured (µg L^{-1})	Recovery (%)
Canal water	0	3.23±0.964*	---
	2	5.21±0.822	99.0
	5	8.16±0.432	98.6
	10	13.04±0.642	98.1
Waste water	0	6.68±1.02	---
	2	8.64±1.12	98.0
	5	11.57±1.22	97.8
	10	16.4±1.34	97.2

Key: *Mean ± S.D. (n = 3). Certified reference material (SRM)

Application

The proposed method has successfully applied to real water samples to checked out the applicability of the desire method as shown in (Table 6). The concentrations of the target analyte was quantified to be in the range of 0.124–0.542µg L^{-1}. The acceptable level of the Ag is 0.1 mg L^{-1} in drinking water disinfection acoording to WHO, but the United States Environmental Protection Agency (USEPA) recommends 0.05 mg L^{-1} as maximum [EPA, 2017].

EXPERIMENTAL

Chemical Reagents and glassware

Ultrapure water obtained from ELGA labwater system (Bucks, UK), was used throughout the work. Stock standard solution of Ag at a concentration of 1000 µg L^{-1} was obtained from the Fluka Kamica (Bush, Switzerland).Working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. 1-Butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$ was purchased from Sigma-Aldrich (Germany) and used as obtained. Concentrated nitric acid, hydrochloric acid were analytical reagent grade from Merck (Darmstadt, Germany) and were checked for possible trace Ag contamination by preparing blanks for each procedure. The 8-hydroxyquinoline (8HQ) was obtained from (Merck), prepared by dissolving appropriate amount of reagent in 10 mL ethanol (Merck) and diluting to 100 mL with 0.01 mol L^{-1} acetic acid, the prepared reagent was kept in refrigerator at 4°C for one week. The 0.1 mol L^{-1} acetate and phosphate buffer were used to control the pH of the solutions. The pH of the samples was adjusted to the desired pH by the addition of (0.1 mol L^{-1} HCl/ NaOH) solution in the buffers. The glass and plastic wares were soaked in 10% nitric acid overnight and rinsed many times with deionized water to avoid contamination.

Instrumentation

A pH meter (Ecoscan Ion 6, Malaysia) was employed for pH adjustments. Global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations. A Perkin Elmer Model A Analyst 700 (Norwalk, CT) atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer and deuterium lamp background correction was employed. The operating conditions of the hollow cathode lamp were those recommended by the manufacturer. Pyrolytically coated graphite tubes were used throughout. A Ag hollow-cathode lamp was used as radiation source at 328.1 nm. The graphite furnace heating program was set for different steps: drying temperature °C (120/15/20)/ramp/hold (s), ashing temperature (°C)/ramp/hold (s) (500/5/15), atomization temperature (°C)/ramp/hold (s) (1900/0/3) and cleaning temperature (°C)/ramp/hold (s) (2100/1/2). A 10 µL microsyringe (Hamilton) was employed to introduce extracting phase to the solution and to inject it into the graphite furnace.

Sample collection and pretreatment procedure

The fresh surface water (canals) and waste water were collected on alternate month in 2015 from twenty (20) different sampling sites of Jamshoro, Sindh (southern part of Pakistan) with the help of Global positioning system (GPS). The sampling network was designed to cover a wide range of determinates of whole district. The industrial waste water samples of understudy areas were also collected. The samples were collected in Van Dorn plastic bottles (1.5 L capacity) and were kept in well stoppered polyethylene plastic bottles previously soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. All water samples were filtered through a 0.45 micropore size membrane filter, to remove suspended particulate matter and were stored at 4°C to avoid risk of contamination.

Procedure for SDME

2 mL of each standard and real sample were taken into vials (5-mL capacity) with PTFE septum and magnetic bar. Then 100 µL acetate/borate buffers to adjust a pH range of (3–10) and 100 µL (1.0×10^{-3}–10.0×10^{-3} mol L^{-1}) 8HQ solution were added to obtain the desire working values. The vial was placed on a magnetic stirrer with a stirring rate of (200–600 rpm). Then (1–5 µL) volume of $[C_4MIM][PF_6]$ was drawn into the microsyringe and the syringe was fixed above the vial with a clamp. After introducing the needle through the septum, the needle tip was immersed into the sample solution and the microdrop was exposed. The microdrop was left for 10 min under constant stirring and it was aspirated back into the microsyringe and inserted manually into the graphite furnace as shown graphically in (Fig. 1).

Calibration was performed using aqueous standard solutions submitted to the same SDME procedure as described above. Before each extraction, microsyringe was rinsed with ethanol to avoid formation of air bubbles and the carryover of compounds between extractions. The experimental data were evaluated with the help of Minitab 13.2 (Minitab Inc., State College, PA, USA) and STATISTICA computer program 2007.

Experimental design

Plackett–Burman design

The Plackett–Burman design (PBD) is used for screening the multifactor to derive valid and robust statistical significant factors that influence the SDME. The application of this experimental design reduced the development time of the methods and provided less ambiguous extraction conditions, hence facilitating data interpretation. To estimate the optimum levels of factors for the proposed procedure at two levels Plackett–Burman design with only 16 experiments were described instead of the 2^5=32 required for full factorial designs. The low (-) and high (+) levels of all factors were specified in (Table 1), while optimization by Plackett–Burman matrix is shown in (Table 2). These results can be visualized by standardized (P=95.0%) Pareto chart of main effects shown in (Fig. 2).

Central 2^3+ star orthogonal composite design

After screening out the variables with insignificant effect on the recovery of analyte, remaining three factors were optimized to provide the maximum metal recovery. A central 2^3+ star, orthogonal composite design with six degree of freedom and involving 16 new experiments was performed to optimize the variables, concentration of complexing agent (C), extraction time (ET) and pH (P) for recovery of Ag as shown in (Table 3).

CONCLUSION

In the proposed method a simple and efficient extraction approached have launched for Ag using 4 µL of ionic liquid [C4MIM] [PF6] to solution prior to ETAAS. The ionic liquid used in this experiment also contributed to the sensitivity improvement. The main objective of this method is to achieved reliable and prestigious result by using miniaturizing solvent volume (4 µL) and low sample consumption for monitoring of Ag in real water samples. Trace and ultra-trace levels of Ag in water samples could be detected in very low concentration. The proposed method is better for having lower detection limits when compared to other methods. These results indicated that the proposed method is efficient to trace out the trace level of the target analyte and considered to be an alternative of the traditional methods.

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Corresponding: Naeemullah
Email: naeemullah433@yahoo.com
Phone:
Fax:

Naeemullah: CNational Centre of Excellence In analytical Chemistry University of Sindh, Jamshoro 76080, Pakistan

Abdul Haseeb: Pakistan arab Refinery Company, Muzaffargarh, Pakistan

Faheem Shah: Department of Chemistry, Comsats Institute of Information Technology, abbottabad-22060, Pakistan

Tasneem Gul Kazi: National Centre of Excellence In analytical Chemistry, University of Sindh, Jamshoro-76080, Pakistan