

Cloud Point Extraction for Pre-Concentration and Spectrophotometric Determination of Trace Amounts of Silver Ions

Azhar A. Ghali*

Department of Pharmaceutical Chemistry, College of Pharmacy, University of Al-Qadisiyah, Al Diwaniyah, Iraq

Received: 15th June, 2020; Revised: 18th July, 2020; Accepted: 20th August, 2020; Available Online: 25th September, 2020

ABSTRACT

During the last years, the cloud point extraction was applied for determination, separation, and enrichment of the elements. The current study used cloud point extraction (CPE) for the extraction of Ag(I) ions pre-concentration from watery solutions by a non-ionic surfactant (Triton X-114) and chelating agent a 6-(4-bromo-phenylazo)m-anisidine[6-(4-BrPAA)], then estimation by using the spectrophotometry at 514 nm. Several condition effects on the efficiency of the cloud-point extraction included Triton X-114 concentration, [6-(4-BrPAA)] concentration, pH, time, and incubation temperature. The silver reacts with [6-(4-BrPAA)] to produce complex at a ratio of one to one. 0.009 to 1.5 $\mu\text{g mL}^{-1}$ is the range of linearity. The detection limit and quantification of Ag(I) ion were 0.0054 and 0.0182 $\mu\text{g mL}^{-1}$, respectively. The interference of the cations was examined. The cloud-point extraction was used for the evaluation of silver concentration in the water specimen.

Keywords: Azo compound, Cloud-point extraction, Environment analysis, Silver determination, Spectrophotometry.

International Journal of Drug Delivery Technology (2020); DOI: 10.25258/ijddt.10.3.27

How to cite this article: Ghali AA. Cloud point extraction for pre-concentration and spectrophotometric determination of trace amounts of silver ions. International Journal of Drug Delivery Technology. 2020;10(3):459-464.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

The silver has no benefit in the human body, but it has great importance in electrical devices, dental and pharmaceutical compounds, photographic film, and fungicides manufacturing.^{1,2} The corrosion-resistance alloys and high-strength alloys were composed of silver. The applications composed of silver are widely used, which leads to released silver in the environment after the damage of apparatuses associated with releasing copper, zinc, arsenic, and antimony.³ In another meaning, the silver has toxic effects on biological tissues.⁴

Accumulation of silver in body tissue results in changing the color of the skin to blue-grey color (argyria). The threshold amount of permitted silver values was determined in different types of samples and different geographic areas.⁵ The silver is present in the environment and water in very little amount, therefore, the water sample is very important for the examination of silver concentration.

High-performance liquid chromatography is the method used for determination of silver,⁶ atomic absorption spectrometry (AAS),⁷⁻¹⁰ inductively coupled plasma atomic emission spectrometry (ICP-AES),¹¹ also, inductively coupled plasma mass spectrometry (ICP-MS),^{12,13} kinetic,¹⁴⁻¹⁷ capillary zone electrophoresis (CZE),¹⁸ flow injection analysis (FIA),¹⁹ fluorimetric,²⁰ and spectrophotometric.²¹⁻³³

The spectrophotometric is an assay used commonly because the methods are simple, high accuracy, available instrument, and high speed.³⁴ There are several methods used as pre-concentration methods and for different separation of the silver at low levels, like solid-phase extraction,³⁵ precipitation.³⁶ liquid-liquid extractions,^{37,38} sorbent extraction on many adsorbents, like activated carbon,³⁹ ion exchange,⁴⁰ or flotation⁴¹ are necessary. It requires high confidence levels and estimation of the trace elements. Some of the methods cause contamination of the samples, are time-consuming, and tedious.⁴²

Cloud point extraction (CPE) is environmentally friendly, modern, and liquid-liquid extraction methods. It was given great focusing and attention in analytic sciences. Furthermore, it is convenient, safe, efficient, economic, required short extraction time, low cost, not flammable, nonvolatile, and surfactants are nontoxic.^{43,44}

Cloud point extraction (CPE) is a method dependent on the clouding principle and determination of the changes that occur in the parameters, such as, solution pH, concentration, temperature, and time. Method of cloud point extraction is used to isolate between the hydrophilic and the hydrophobic substances, and it has most common in biology and the environmental.^{45,46}

Cloud point extraction (CPE) is a potential analytical method for preconcentration and extraction of element cations

*Author for Correspondence: azharghali35@yahoo.com

after the production of the sparingly water-soluble complexes. 6-(4-bromophenylazo) m-anisidine[6-(4BrPAA)] is used in cloud point preconcentration for copper.⁴⁷ The 6-(4BrPAA) advanced is involved in the stability in solutions, sufficient hydrophobicity, and silver extraction. The current study showed that cloud point extraction is very sensitive, high selectivity, and very simple in many types of samples by using [6-(4BrPAA)] and Triton X-114.

MATERIALS AND METHODS

Apparatus

The absorption range is done by Shimadzu UV-vis spectrophotometer (model UV-1800) and equipped with 1 cm matched quartz cells. The pH was measured by Wellhem 7110 (Germany) pH meter with a combined glass-calomel electrode, while a Hettich® Zentrifugen EBA 20 centrifuge (Germany) was used for facilitating the separation process. The water bath (Optima WB710, Japan) with good temperature control was used for cloud point temperature experiments. To characterize the created reagent and complex, FT-IR spectrometric (Shimadzu 8400S, Japan) was used, KBr discs (Japan), in the frequency 4,000 to 400 cm^{-1} .

Reagents

Preparation of the stock standard solutions of silver was done by adding amounts of AgNO_3 in doubly distilled water and put it in dark. Working standard solutions were prepared by several graduated of standard stock solution. The chelating reagent solution at $1 \times 10^{-3} \text{ mol L}^{-1}$ was prepared by dissolving the appropriate weight of [6-(4BrPAA)] in absolute ethanol. The Triton X-114 was provided from Acros Organics (20% v/v) of Triton X-114 that formed from adding a concentrated solution (20 mL) in doubly distilled water (DDW) 100 mL. Buffer solutions were prepared from acetic acid or ammonium hydroxide and ammonium acetate.

Procedure for CPE

Adding water to the solution inside the tube that composed of silver at 0.009 to $1.5 \mu\text{g mL}^{-1}$, with 6-(4BrPAA) at 0.5 mL of 0.001 mol L^{-1} , the buffer at 1 mL at pH is 5.5, and Triton X-114 0.25 mL (20%), then diluted from DDW 10 mL, the mixture solution incubates at 60°C for 10 minutes. The phase separation was done by using a centrifuge at 5,000 rpm for 5 minutes. Then, it is cooled by the ice bath for the viscosity to become high. The ethanol 1.5 mL was mixed with the surfactant-rich phase at 100 μL to decrease the viscosity and transferred to quartz cell (5 mm) to evaluate the absorbance at 514 nm against a blank solution prepared in the same procedure without that silver ion.

RESULTS AND DISCUSSION

Absorption Spectra

6-(4BrPAA)-silver complex showed absorption spectra in acetate buffer (pH = 5.5), Figure 1. 6-(4BrPAA) revealed top absorbance at 426 nm. The silver-6-(4BrPAA) is a pink mixture, shown as 514 nm. The optimization was done at

several measurements for the establishment of the many conditions by using all parameters. The concentration of reagent concentration optimized for increasing the developed methods.

Effect of pH

The pH of the absorbance at a constant of the complex was 3 to 8 with acetate buffer (pH = 4.5–6.5), Figure 2. The selected pH for the studies is 5.5. The complexation reaction at pH values lower than 4 is incomplete due to the protonation of 6-(4BrPAA) and the complexation reaction is incomplete. The pH of more than 6.5 is causing a decrease in the absorbance for silver hydrolysis.

Effect of 6-(4BrPAA) Concentration

The concentration of 6-(4BrPAA) has a significant effect on the extraction and determination of the produced complex with silver was determined at 0.1 to 0.9 mL from $1 \times 10^{-3} \text{ M}$ of the 6-(4BrPAA). It can be seen from Figure 3 that the sensitivity becomes higher with increasing of 6-(4BrPAA) levels more than $5 \times 10^{-5} \text{ mol L}^{-1}$, above which it starts to decline. Therefore, $5 \times 10^{-5} \text{ mol L}^{-1}$ of 6-(4BrPAA) was selected for further work. The slight decrease in absorbance after $5 \times 10^{-5} \text{ mol L}^{-1}$ 6-(4BrPAA)

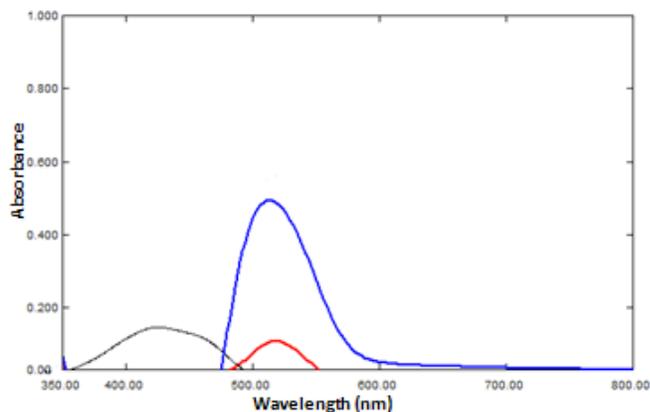


Figure 1: Absorption spectra (1 —) Reagent 6-(4BrPAA) = $6 \times 10^{-5} \text{ M}$ (2 —) Ag(I) -6-(4BrPAA) complex without CPE; Ag(I) = $15 \mu\text{g mL}^{-1}$, 0.5 mL of 6-(4BrPAA) = $1 \times 10^{-3} \text{ M}$; buffer pH = 5.5 (1 mL) (3 —); Ag(I)- 6-(4BrPAA) complex with CPE; Ag(I) = $0.8 \mu\text{g mL}^{-1}$, 0.5 mL of 6-(4BrPAA) = $1 \times 10^{-3} \text{ M}$; Buffer pH = 5.5 (1 mL), 0.25 mL of 20% (v/v) Triton X-114

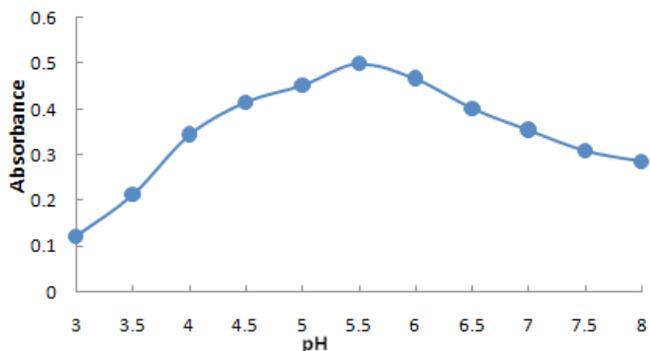


Figure 2: Effect of pH on the absorbance of the Ag(I)- 6-(4BrPAA) complex; Conditions: Ag(I) = $0.8 \mu\text{g mL}^{-1}$, 0.5 mL of 6-(4BrPAA) = $1 \times 10^{-3} \text{ M}$, 0.25 mL of 20% (v/v) Triton X-114, temperature: 60°C

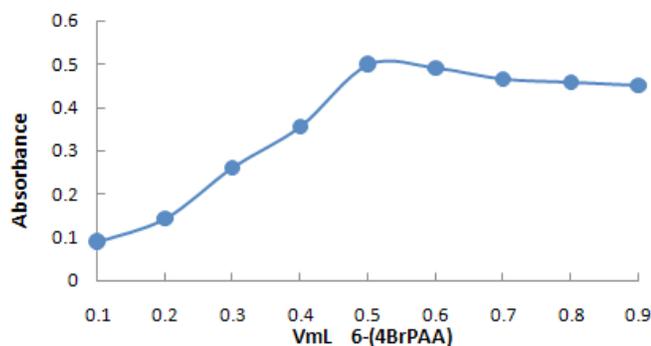


Figure 3: Effect of 6-(4-BrPAA) concentration = 1×10^{-3} M on the absorbance of Ag(I)-6-(4BrPAA) complex; Conditions: Ag(I) = $0.8 \mu\text{g mL}^{-1}$, buffer pH = 5.5 (1 mL), 0.25 mL of 20% (v/v) Triton X-114, temperature: 60°C

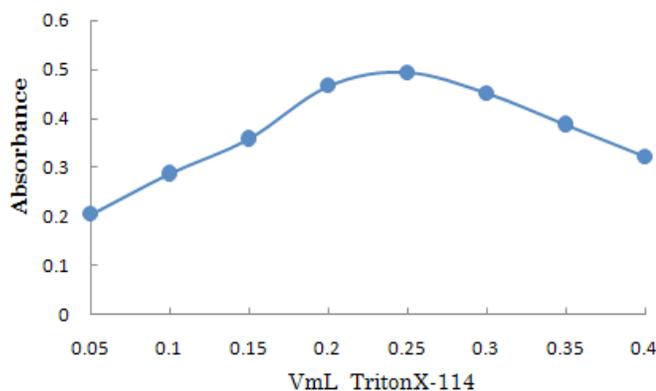


Figure 4: Effect of TritonX114 concentration on the absorbance of Ag(I)-6-(4BrPAA) complex; Conditions: Ag (I) = $0.8 \mu\text{g mL}^{-1}$, 0.5 mL of 6-(4BrPAA) = 1×10^{-3} M, buffer pH = 5.5 (1 mL), temperature: 60°C

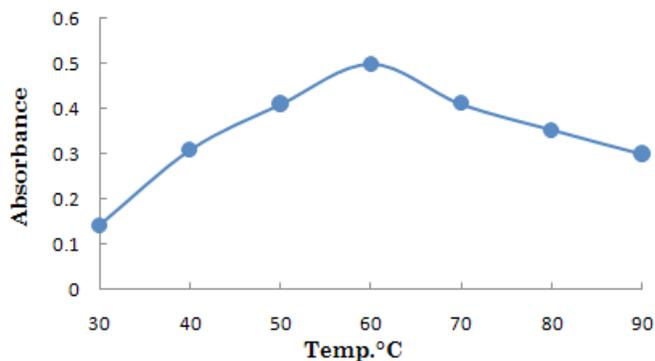
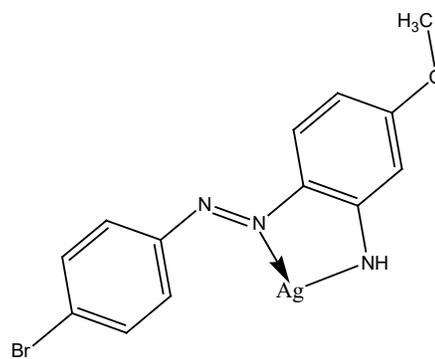


Figure 5: Effect of temperature on the absorbance of Ag (I)-6-(4-BrPAA) complex; Conditions: Ag(I) = $0.8 \mu\text{g mL}^{-1}$, 0.5 mL of 6-(4-BrPAA) = 1×10^{-3} M, buffer pH = 5.5 (1 mL), 0.25 mL of 20% (v/v) Triton X-114

is due to 6-(4BrPAA) level with surfactant-rich phase, so it results in a decrease of absorbance change at concentrations higher $5 \times 10^{-5} \text{ mol L}^{-1}$ is due to 6-(4BrPAA) reaction with the complexes in extraction to surfactant-rich phase.

Effect of Triton X-114 Concentration

The concentration of the non-ionic surfactant is the main parameters which affect on the phase volume ratio. In our report, the Triton X-114 was used due to low cost, common



Scheme 1: Proposed structural formula between 6-(4BrPAA) and Ag(I)

availability and low toxic. Furthermore, the high density of Triton X-114 helps to separation phase by the centrifuge. Triton X-114 at cloud point 23 to 26°C is used in the preconcentration of the chelates and the molecules. The absorption is varying as shown in Figure 4. The solution (10 mL) containing cations and all the reagents in the presence of 0.05 to 0.4 mL from 20% (v/v) Triton X-114 was prepared. The absorption becomes low at lower concentrations because of not enough to entrap the complex. If the Triton X-114 volume becomes higher than 0.2 mL, the complex absorption becomes more. If the Triton X-114 becomes more than 0.3 mL, the absorption becomes low due to the volume of the micellar phase increase. Hence, 0.25 mL of 20% (v/v) was chosen for further studies.

The effect of temperature and time on the reaction is shown in Figure 5. The complex production of silver-6-(4BrPAA) was at a temperature of 40 to 70°C . Decomposition of 6-(4BrPAA) in high temperatures and leads to absorbance decreasing. The extraction depended on the time of the incubation (5 to 20 minutes). Time of the incubation (10 minutes) is the best time for quantitative extraction.

Stoichiometric Ratio

The nature of the complex was formed at the optimum status as found above by the two spectrophotometric techniques, continuous variation methods, and molar ratio. The plot of the absorbance values vs. the molar ratio of 6-(4BrPAA) to silver, which was gotten by the different 6-(4BrPAA) levels, reveals the inflection at molar ratio 1, meaning the formation of 6-(4BrPAA) in the complex. Furthermore, the continuous variation assay demonstrated the inflection at a mole fraction of 0.5 of silver that provides the ratio of 6-(4BrPAA) to silver equal 1. The final data found that the stoichiometric ratio of silver:6-(4BrPAA) is 1:1 (Scheme 1). The stability constant is found to be $0.4 \times 10^5 \text{ L.mol}^{-1}$.

Characteristics of the Method

The graph was drawn depending on the pre-concentration of the sample (10 mL) with Triton X-114. Table 1 demonstrated analytical properties. At the experimental status, the calibration graph of Ag was linear (0.009 – $1.5 \mu\text{g mL}^{-1}$). The enhancement factor of about 43 obtained by preconcentrating sample (10 mL) could consider it is satisfactory as compared with other cloud point extraction techniques as shown in Table 2.

Table 1: Analytical features of the present method

Parameter	After CPE	Before CPE
λ_{\max} (nm)	514	516
*Regression equation	$y = 0.604x + 0.018$	$y = 0.004x + 0.008$
Correlation coefficient (r)	0.9997	0.9993
C.L. for the slope ($b \pm tsb$) at 95%	0.604 ± 0	0.004 ± 0
C.L. for the intercept ($a \pm tsb$) at 95%	0.018 ± 0	0.008 ± 0
Concentration range ($\mu\text{g mL}^{-1}$)	0.009–1.5	0.05–5
Limit of detection ($\mu\text{g mL}^{-1}$)	0.0054	0
Limit of quantitation ($\mu\text{g mL}^{-1}$)	0.0182	0
Sandell's sensitivity ($\mu\text{g.cm}^{-2}$)	0.0104	0.1298
Molar absorptivity ($\text{L.mol}^{-1}.\text{cm}^{-1}$)	10,263	827.1
Composition of complex (M:L)**	1:1	1:1
RSD% (n = 6) at $0.8 \mu\text{g mL}^{-1}$	1.9	2.9
***PF	83.33	-
****EF	12.4	-

*A = a + bC; C mean Cu concentration in $\mu\text{g mL}^{-1}$; **Job's and mole ratio methods used; ***PF is the monitoring of ratio of aqueous phase volume to surface-rich phase; ****EF is determination ratio of the slope of curves that have gotten with or without CPE

Table 2: Comparison of the proposed method with reported methods for pre-concentration and CPE of Ag(I)

RSD%	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Enrichment factors	Ref.
4.9	0.004	0.01–0.5	20	48
4.2	0.0012	0.005–0.1	60	49
3.6	0.3	1–500	33	50
2.6	2.2	10–200	20	51
2.6	1	5–450	24	52
2.14	0.56	3–200	43	53
2	0.7	4–220	-	54
1.9	5.4	9–1,500	12.4	This work

Table 3: Tolerance limits for the determination of $0.7 \mu\text{g mL}^{-1}$ of Ag(I) using 6-(4BrPAA) (relative error $\pm 5\%$)

Ion added	Tolerance ratio
K^+, Na^+	350
Mo(V), Sb(III)	300
$\text{Cd}^{2+}, \text{Pb}^{2+}, \text{Hg}^{2+}$	280
$\text{Li}^+, \text{Mn}^{2+}$	250
$\text{Ba}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}$	200
$\text{Fe}^{3+}, \text{Co}^{2+}, \text{Zn}^{2+}$	150
$\text{Ni}^{2+}, \text{Cu}^{2+}$	100

Selectivity of the Method for Silver

The strange ions' effect on the determination of silver ($0.7 \mu\text{g mL}^{-1}$) by the suggested technique was tested. The ion tolerable amount was taken as the silver. The interference ratio results in error not more than 5% in the absorbance value, as shown in Table 3. The data reveals the (+) ions do not have marked a significant effect on the determination and separation of the silver under the testing conditions.

Application

The suggested technique was used for the detection of the

Table 4: Ag(I) in different water samples (n = 3)

Sample	Ag ($\mu\text{g.mL}^{-1}$)		
	Added	Found	Recovery (%)
Tap water ^b	0	ND ^a	-
	0.5	0.5	100
	1	1.01	101
River water ^c	0	ND	-
	0.5	0.499	99.8
	1	1.003	100.3
Rainwater ^d	0	ND	-
	0.5	0.507	101.4
	1	0.998	99.8
Waste water ^e	0	0.046	-
	0.5	0.544	98.6
	1	1.047	100.1

^aNot detected; ^bFrom drinking water system of Al-Diwaniya city, Iraq; ^cShatt Al-diwaneya water; ^dCollected at Al-Diwaniya city, Iraq (November 2019); ^eFrom rinse water of photography

silver in a water sample. The samples (10 mL) were treated by 6-(4BrPAA) and Triton X-114. The final data is shown in Table 4.

CONCLUSION

The reagent 6-(4-bromo phenylazo) m-anisidine[6-(4BrBAA)] has proved that silver is a selective reagent as compared to other spectrophotometric techniques. It is easily applicable for the evaluation of silver level in water samples, which provided us with strong and supported results. The method is done based on the cloud point extraction of the complex of silver with 6-(4BrPAA), which is used for the evaluation of silver. The suggested methods need cheap instrumentation and good selectivity, which offers safety, precision, and high accuracy could apply in the calculation of copper concentration in the samples. The surfactant used with copper, as well as, extraction of toxic solvent was avoided. It is characterized as rapid, simple and cheap.

REFERENCES

- Grayson M. Kirk-Othmer Encyclopedia of Chemical Technology, 21, John Wiley and Sons, New York, NY, USA, 3rd edition, 1980.
- Smith IC, Carson B. L. Trace Metals in the Environment, Ann Arbor Science Publishers, Ann Arbor, Mich, USA, 1977;2.
- Soager R. Metallic Raw Materials Dictionary. Bank Tobel. Zurich, Switzerland, 1984.
- Manzoori JL, Abdolmohammad-Zadeh H, Amjadi M. Ultra-trace determination of silver in water samples by electrothermal atomic absorption spectrometry after preconcentration with a ligand-less cloud point extraction methodology. *Journal of Hazardous Materials*.2007;144: 458–463.
- Resano M, Aramend'ya M, Garc'ya-Ruiz E, Crespo C, Belarra MA. Solid sampling-graphite furnace atomic absorption spectrometry for the direct determination of silver at trace and ultratrace levels, *Analytica Chimica Acta*. 2006;571: 142– 149.
- Wang L, Hu Q, Yang G, Yin J, Yuan Z. Online solid phase extraction reverse phase liquid chromatographic determination of lead, cadmium, silver and mercury in water. *Fenxi Huaxue*. 2004; 32:421–427.
- Chakrapani G, Mahanta PL, Murty DSR, Gomathy B. Preconcentration of traces of gold, silver and palladium on activated carbon and its determination in geological samples by flame AAS after wet ashing, *Talanta*. 2001;53:1139–1147.
- Pandey J, Sudhakar P, Koshy VJ. Determination of silver at submicrogram levels by absorption spectrophotometry, *Ind. J. Chem. Tech*. 2003;10:295–297.
- S'ramkova' J, Kotrly' S, Jakoubkova' P. Precision attainable in the determination of silver by flame atomic absorption spectrometry: analysis of thermoelectric silver-doped tellurides. *Anal. Chim. Acta*. 2000;408: 183–190.
- Baron MG, Herrin RT, Armstrong DE. The measurement of silver in road salt by electrothermal atomic absorption spectrometry. *Analyst* . 2000;125: 123–126.
- Argekar AA, Kulkarni MJ, Mathur JN, Page A, Iyer GRH. ICP-AES determination of silver after chemical separation from uranium matrix. *Talanta* .1995;42: 1937–1942.
- Hu J, Liu Z, Wang H. Determination of trace silver in super alloys and steels by inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta*. 2002; 451: 329–335.
- Chang CC, Liu HT, Jiang SJ. Bandpass reaction cell inductively coupled plasma mass spectrometry for the determination of silver and cadmium in samples in the presence of excess Zr,Nb and Mo. *Anal. Chim. Acta* . 2003;493: 213–218.
- Mastoi GM, Khaskheli AA, Ansari IA, Khuhawar MY. Kinetic spectrophotometric determination of silver(I) by the catalytic effect on the oxidation of chromotropic acid by bromate, *Paks. J. Chem. Soc*. 1997;19: 273–278.
- Grosse YuI, Miller AD. Highly sensitive kinetic method for determination of silver in rocks, *Metody Anal. Redkometal. miner. Rud. Gorn. Porod*. 1971; 2: 52–64.
- Reddy VK, Chennaiah A, Reddy PR, Reddy TS. Kinetic-photometric determination of silver(I) based on its catalytic effect on reaction between potassium ferrocyanide and 2-hydroxy-4- methoxybenzophenone thioemcarbazon, *Chem Anal*. 2003; 48:733–740.
- Grosse YuI, Miller AD. Kinetic determination of silver in natural material, *Zavodskaya Lab*. 1974;40:262–263.
- Aguilar M, Farran A, Martinez M. Determination of gold (I) and silver (I) cyanide in ores by capillary zone electrophoresis. *J. Chromatogr*. 1993;635: 127–131.
- Fujimura K, Odake T, Takiguchi H, Watanabe N, Sawada T. Flow injection spectrophotometric determination of sub mg/ dm³ silver in a strongly acidic solution containing concentrated copper(II) using a pyridylazo reagent. *Anal. Sci*. 2011; 27: 1197–1201.
- Kabasakalis V. Fluorimetric determination of silver by brilliant green in aqueous systems and its application in photographic fixing solutions,. *Anal. Lett*. 1994;27:2789–2798.
- Nagaraja P, Kumar MSH, Yathirajan HS. Silver enhanced reduction of 2,3,5-triphenyl-2H-tetrazolium by semicarbazide hydrochloride (SHC) for the spectrophotometric determination of traces silver(I), *Anal. Sci*. 2002;18:815–820.
- Ivanova C, Popova S. Spectrophotometric determination of silver with brompyrogallol red (BPR) and 1,10-phenantroline in the presence of gelatin. *J. Univ. Chem.Tech. Met* .2002; 37: 33–38.
- Gao HW, Wang L, Tao M. Primary-secondary wavelength spectrophotometric determination of trace amounts of silver in waste water with 2,4-dibromo-6-carboxy-benzendiazoaminoazobenzene (DBCBAAB). *Paks. J. Chem. Soc*. 2000;22:275–280.
- Kawatkar SG, Manol PS, A simple and sensitive spectrophotometric method for determination of silver(I) with resacetophenone guanylhydrazone (RAG). *Acta Cie. Ind*. 1998; 24:167–169.
- Tsiouris S, Aravanopoulos F, Papadoyannis I, Sofoniou MN, Polyzopoulos M, Christodoulou, Samanidou V., Zachariadis G., Constantinidou H. Soil silver content of agricultural areas subjected to cloud seeding with AgI. *Frez. Env. Bull*. 2002;11: 697–702.
- Gao HW. Reanalysis of silver chelate solution and determination of trace amounts of silver in waste water. *Asian J. Chem*. 1999;11:740–745.
- Salinas F, Espinosa-Mansilla A, Lopez de Alba AP. Extraction-spectrophotometric determination of silver in ores, electronic flow- solders and white metals with 2-carboxybenzaldehyde thiosemicarbazone (2CBTSC). *Analyst*. 1995;120: 2857–2860.
- Singh BG, Gupta RD, Bhatia PG. Determination of silver, platinum or gold and copper in ternary mixtures with potassium thiocarbonate. *Analyst*. 1982; 29: 85.
- Fulong Z, Hang Z. Different approaches to the determination of silver ion at low levels by flow injection analysis. *Anal. Chem. Acta*. 1988;15:206-213.
- Ischenko NN, Ganago LI, Ivanova IF. Flotation-spectrophotometric determination of silver. *J. Anal. Chem*. 1997; 52: 768–769

31. Guo X.J., Deng Q.L., Peng B., Gao J.Z., Kang J.W. Catalytic spectrophotometric determination of ultratrace amounts of silver with solubilizing effect on nonionic surfactant. *Chin. J. Chem.* 2002;20:39–44.
32. Shul C. H., Chang L. Spectrophotometric determination of silver with 2-(3,5-dibromo-2-pyridylazo)-5-diethyl-aminophenol in the presence of anionic surfactant. *Talanta.* 1982;29:85-88.
33. Kassem M. A. Development of a cloud-point extraction method for spectrophotometric nano determination of silver in real samples. *Anal. Meth.* 2015;7:6747-6754.
34. Pairet M, Van-Ryn J, Schierok H, Mauz A, TrummLitz G, Engelhardt G. Differential inhibition of cyclooxygenases-1 and -2 by meloxicam and its 42 -isomer, *Inflammatory Res.* 1998;47:270.
35. Lemos V. A., Baliza P. X. Amberlite XAD-2 Functionalized with 2-Aminothiophenol as a New Sorbent for On-line Preconcentration of Cadmium and Copper. *Talanta.* 2005;67: 564–570.
36. Soylak M., Saracoglu S., Divrikli U., Elci L. Coprecipitation of Heavy Metals with Erbium Hydroxide for Their Flame Atomic Absorption Spectrometric Determinations in Environmental Samples. *Talanta.* 2005;66:1098–1102.
37. Sanaz J, Araz B, Payam H, Mohammad RMH, Yaghoob A. Dispersive Liquid-liquid Microextraction of Silver Prior to Determination by Microsample Introduction-flame Atomic Absorption Spectrometry. *Anal. Lett.* 2009;42:2214-2231.
38. Mohammadi SZ, Afzali D, Taher MA, Baghelani YM. Ligandless Dispersive Liquid-liquid Microextraction for the Separation of Trace Amounts of Silver Ions in Water Samples and Flame Atomic Absorption Spectrometry Determination. *Talanta.* 2009;80:875-879.
39. Soylak M, Elci L, Dogan M. A Sorbent Extraction Procedure for Preconcentration of Gold, Silver and Palladium on an Activated Carbon Column. *Anal. Lett.* 2000;33:513-525.
40. Scaccia S, Zappa G, Basisli N. Ion Chromatographic Preconcentration of Cu and Cd from Ultra High Purity Water and Determination by Electrothermal Atomic Absorption Spectrometry. *J. Chromatogr. A.* 2001;915:167-175.
41. Cundeva K, Stafilov T, Pavlovska G. Flotation Separation of Cobalt and Copper from Fresh Waters and Their Determination by Electrothermal Atomic Absorption Spectrometry. *Microchem. J.* 2000;65:165-175.
42. Rahman MA, Kaneco S, Amin MN, Suzuki T, Ohta K. Determination of silver in environmental samples by tungsten wire preconcentration method—electrothermal atomic absorption spectrometry. *Talanta.* 2004;62:1047-1050.
43. Ingrid H. Cloud point extraction utilizable for separation and preconcentration of (ultra)trace elements in biological fluids before their determination by spectrometric methods: a brief review. *Chem.* 2016; 71: 869–879.
44. Pallabi S., Kamalika S. Cloud point extraction: A sustainable method of elemental preconcentration and speciation. *Journal of Industrial and Engineering Chemistry.* 2014;20: 1209-1219.
45. Pytlakowska K, Kozik V, Dabioch M. Complex-forming organic ligands in cloud-point extraction of metal ions: A review. *Talanta.* 2013;11:202–228.
46. Liu W, Zhu LY, Jin BB, Helali M. Dynamic modeling of parallel mechanism based on particle system. *J. Mech. Eng. Res. Dev.* 2016;39:483–491.
47. Azhar AG, Ashwoq SH. Cloud Point Extraction for the Separation, Preconcentration and Spectrophotometric Determination of Trace Copper (II) In Herbal Plants Samples Using New Synthesized Reagent. *Journal of Global Pharma Technology.* 2019;11:817-826.
48. Silva MAMD, Curtius AJ. Determination of trace elements in water samples by ultrasonic nebulization inductively coupled plasma mass spectrometry after cloud point extraction. *Spectrochim. Acta B.* 2000;55:803-813.
49. Manzoori JL, Abdolmohammad-Zadeh H., Amjadi M. Ultra-trace determination of silver in water samples by electrothermal atomic absorption spectrometry after preconcentration with a ligand-less cloud point extraction methodology. *J. Hazard. Mater.* 2007;144:458–463.
50. Xiupei Y, Zhihui J, Xiaocui Y, Gu Li, Xiangjun L. Cloud point extraction-flame atomic absorption spectrometry for preconcentration and determination of trace amounts of silver ions in water samples. *Saudi Journal of Biological Sciences.* 2017; 24:589–594.
51. Shariati S, Yamini Y. Cloud point extraction and simultaneous determination of zirconium and hafnium using ICP-OES. *J. Colloid Interface Sci.* 2006;298:419–425.
52. Gao Y., Wu P., Li W., Xuan Y., Hou X. Simultaneous and selective preconcentration of trace Cu and Ag by one-step displacement cloud point extraction for FAAS determination. *Talanta.* 2010;81: 586–590
53. Manzoori JL, Karim-Nezhad G. Selective cloud point extraction and preconcentration of trace amounts of silver as a dithizone complex prior to flame atomic absorption spectrometric determination. *Anal. Chim. Acta.* 2003;484:155–161.
54. Javadi N, Dalali N. Cloud-point extraction for on-line trace determination of copper(II) by flame atomic absorption spectrometry. *J. Iran. Chem. Soc.* 2011;8:231–239.