

# Analytical Methods

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ARTICLE

## Development a cloud point extraction method for spectrophotometric nano determination of silver in real samples

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A cloud-point extraction process using micellar medium had been investigated for the spectrophotometric determination of Ag(I) in some real samples. The proposed method was based on the selective reaction between silver ion and azo dye reagent, 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (CPAHPD), in the presence of cetyltrimethyl-ammonium bromide (CTAB) and potassium iodide salt at pH 5.5. The optimal reaction conditions were studied and the analytical characteristics of the method were obtained. Linearity for Ag(I) concentration was obeyed in the range of 0.3–5.0 ng mL<sup>-1</sup>. The molar absorptivity was calculated to be 1.55 × 10<sup>7</sup> L mol<sup>-1</sup> cm<sup>-1</sup> at 666 nm, whereas Sandell's sensitivity was found as 0.007 ng cm<sup>-2</sup>. The detection and quantification limits were 0.095 and 0.297 ng mL<sup>-1</sup>, respectively. The interference effect of different anions and cations was also examined. The proposed method was successfully used to determine Ag(I) in sulphargin, radiological films, panchromatic plates, human hair, tea and water samples.

### Introduction

Silver is a substantial element in our modernistic life. Silver, in addition to its compounds are widely used in the production of photographic film or paper, jewellery, mirrors, dental fillings and other electrical and electronic applications.<sup>1–3</sup> Because of its bacteriostatic properties, it also plays an important role in the made up of drugs, foods, beverages, polymeric materials and in filters and other equipments to purify water.<sup>4</sup> In many countries, silver fattened filters are used for drinking water preparation.<sup>5</sup> On the other hand, these widespread applications have led to increased silver content of environmental water, and the monitoring of this element in a great variety of environmental and biological samples is critical due to its potential toxicity even at low concentrations.<sup>6,7</sup> For epidermal health, silver is considered of being a contaminant, while it usually interacts competitively with essential nutrients, especially with selenium, copper, vitamin E and vitamin B12 at low concentration levels.<sup>5</sup> Silver accumulation in the body may leads to a grayish-blue skin discoloration (known as Argyria). Therefore, the development of simple and highly sensitive methods to evaluate of Ag is required for the sake of its utility as well as toxicity.

The analysis of Ag ions at low concentration in the presence of other cations at high concentration requires very sensitive techniques. The most common methods for the determination of silver ions are electrothermal atomic absorption spectrometry (ETAAS)<sup>8</sup>, inductively coupled plasma atomic emission spectrometry (ICP OES)<sup>9</sup>, inductively coupled

plasma mass spectroscopy (ICP-MS)<sup>10</sup>, energy-dispersive X-ray fluorescence technique (EDXRF)<sup>11</sup>, fluorescence<sup>12</sup>, flame atomic absorption spectrometry (FAAS)<sup>13</sup>, spectrophotometry<sup>14</sup>, and stripping voltammetry<sup>15</sup> methods. Unfortunately, their sensitivity is usually insufficient for the low concentrations in environmental samples. Consequently, a preconcentration and matrix elimination step is required. The most widely used techniques for separation and preconcentration of trace amounts of silver are liquid–liquid extraction<sup>16</sup>, coprecipitation with tellurium<sup>17</sup>, absorption of silver on powdered rhodamine<sup>18</sup>, ion exchange resin<sup>19</sup>, fire assay with platinum metal in the presence of cuprous sulfide as collector<sup>20</sup>, solid phase extraction (SPE)<sup>21–24</sup> and cloud point extraction.<sup>25–29</sup>

Among these techniques, a cloud point extraction (CPE) has several important features such as low-priced, safety, small time, easier manipulation, no necessity for large amounts of organic solvents, higher preconcentration factor and easier linkage to any analytical instruments such as spectrophotometer, flame atomic absorption spectrometry and especially ET-AAS that do not require the extract to be diluted.<sup>30</sup>

CPE, based on the clouding phenomena of surface active agents, has become more and more charming<sup>31</sup> in case of positive and negative micelles aggregates, the phenomenon rarely occurs, because electrostatic repulsion that prevents phase separation in most cases. In the presence of any salt, long-tailed cationic surfactants can self-assemble in aqueous solution into long flexible wormlike micelle aggregates, thus rendering the viscosity of solution.<sup>32,33</sup> Recently, the cloud-point extraction is used for preconcentration of trace quantities of some cations prior to their spectrophotometric determination.<sup>34,35</sup>

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In the present work, we reported the results of cloud point extraction for preconcentration of silver after the formation of a hydrophobic complex with 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (CPAHPD) which form a complex easily with silver ion because of the great affinity between the soft heavy metal ion, Ag, and soft coordination centers, nitrogen and oxygen atoms.<sup>22-24</sup> The proposed method is applied to the determination of Ag(I) in many real samples.

## Experimental

### Apparatus

All the absorption spectra measurements were carried out using a SHIMADZU UV-VIS-NIR spectrophotometer (model UV-3600) with scanning speed 400 nm/min, slit width 2.0 nm and equipped with 1.0 cm matched quartz cells. A Perkin Elmer model 5300 DV; ICP-AES (Waltham, MA, USA) was used for all ICP-AES measurements. An Orion research model 601A/digital ionalyzer fitted with a combined glass-calomel electrode was used for pH adjustment and checking the pH value of buffer solutions. A centrifuge with 25-mL graduated tubes (Superior, Germany) was used to accelerate the phase separation process.

### Reagents

All chemicals were of analytical grade purchased from Merck Company (Darmstadt, Germany). A stock solution of silver ions was prepared by dissolving appropriate amounts of AgNO<sub>3</sub> in doubly distilled water and kept in a dark bottle. Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water. The pipettes and vessels used for trace analysis were kept in 10 % nitric acid solution for 24 h and were subsequently washed four times with doubly distilled water. 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (CPAHPD) used in the present investigation was prepared according to the procedure described previously.<sup>36</sup> Appropriate weight of CPAHPD was dissolved in 100 mL of absolute ethanol to prepare 4 × 10<sup>-3</sup> mol L<sup>-1</sup> solution.

The surfactant, cetyltrimethylammonium bromide (CTAB) (obtained from Sigma Company) was used without further purification. A 3 × 10<sup>-3</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB) solution in water was prepared. A 0.3 mol L<sup>-1</sup> KI solution was prepared using doubly distilled water. Thiel buffer solutions of different pH's from 2.0–12.0 were prepared by mixing 100 mL in different proportions of A and B mixtures where mixture A consists of 0.2 M boric acid + 0.05 M succinic acid + 0.05 M sodium sulphate and mixture B is 0.05 M sodium tetraborate.<sup>37</sup>

### General procedure

An aliquot of the solution containing 7.5–125 ng of Ag(I) ion was transferred into a 25 mL graduated tube containing 1.5 mL of 4 × 10<sup>-3</sup> mol L<sup>-1</sup> CPAHPD solution, 4.0 mL of pH 5.5 thiel buffer solution and 2.0 mL of 3 × 10<sup>-3</sup> mol L<sup>-1</sup> CTAB solution.

After that the solution was diluted to 20 mL with doubly distilled water and allowed to stand for 5.0 min at room temperature. Then 3.0 mL of 0.3 mol L<sup>-1</sup> KI solution was added and made up to the mark with doubly distilled water. Separation of two phases was accelerated by centrifugation for 5.0 min at 4000 rpm. Then, the aqueous phase could be isolated by overturn the tube. After that the surfactant-rich phase was dissolved and diluted to 1.0 mL using dimethylformamide (DMF) and transferred into a 1.0-cm quartz cell. The absorbance of the solution was measured at 666 nm against a blank solution prepared in the same way except that silver ion.

### Determination of silver by ICP OES

The samples and the standard solutions should contain 5.0 % (v/v) HNO<sub>3</sub> to keep Ag(I) in solution and also to eliminate the interferences from bromide, chromate, iodate, iodide, permanganate, and chloride which may precipitate silver. Then standard atomic emission conditions for silver measurement were applied.

### Determination of silver(I) in sulphargin (silver sulphadiazine burning cream) and developed radiological films

A 5.0 g of silver sulphadiazine cream was weighed and dissolved in nitric acid/perchloric acid/H<sub>2</sub>O<sub>2</sub> as described by Abbaspour *et al.*<sup>38</sup> The radiological film sample was dissolved in a hot 1 : 1 nitric acid–water and the pH of the resulting solution was adapted to about 5.5 using a diluted solution of sodium hydroxide. The silver contents of the solutions were determined using the proposed method applying the standard additions method. This method is usually presented as the separate addition of several different equally-spaced standard amounts of silver ion to separate aliquots of test solution. Measurement is followed by extrapolation of the calibration line to zero response. The use of several spiking concentrations is justified in the standard paradigm by the idea that it helps to check that the calibration is truly linear.

### Determination of silver in panchromatic plates

A known amount (about 2.0318 g) of plate was treated with 25 mL of sodium hydroxide until the gelatinous film separated from the rigid support, which was discarded after washing. Then 25 mL of concentrated HNO<sub>3</sub> was added and heated until the silver dissolved completely. This solution was filtered and diluted to 100 mL with water. A suitable aliquot was analyzed by the above general procedure.

### Determination of silver in human hair

Human hair sample was immersed in acetone for 30 min, washed with water and then dried. About 3.0 g of sample was weighed accurately, 32 mL of a mixture of HClO<sub>4</sub> and HNO<sub>3</sub> (1:8, v/v) was added to it, and then it was digested at lower temperature and dried at elevated temperature. To the residue several drops of H<sub>2</sub>SO<sub>4</sub> (1:1, v/v) were added, the residue leached out with water and the solution transferred

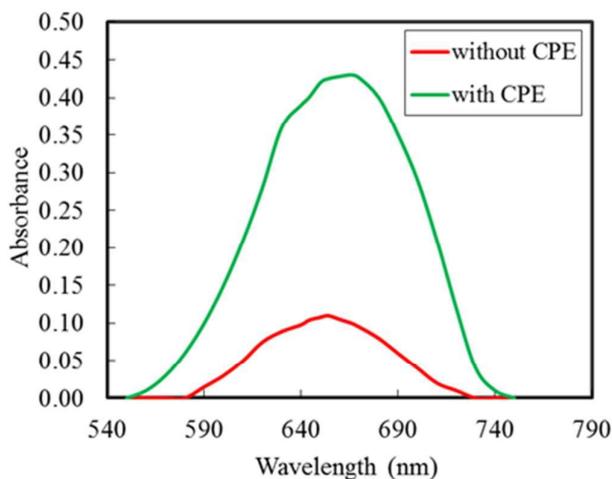
into a 100 mL measuring flask. The pH value was adjusted to 5.5 and the solution was diluted to 100 mL. 25 mL of the diluted solution was measured at a time.

#### Determination of silver in tea samples

To determine Ag(I) in tea, a precisely known weight of tea sample was digested in the same steps as hair sample then 5.0 mL of diluted solution was measured at a time. The amount of Ag ion in the tea sample was determined according to the above procedure. A method of standard addition was done.

### Results and discussion

CPAHPD shows maximum absorbance at 551 nm using pH 5.5. Ag(I) in acidic buffer medium reacts with CPAHPD in the presence of CTAB and the absorbance of solution shift to bathochromic at 654 nm. The solution became turbid after addition of the iodide ion. Therefore the ternary complex of Ag(I)–CPAHPD–CTAB can be extracted by CPE method. After isolation of surfactant-rich phase and dissolving it in DMF, immediately the absorbance of this solution was measured at 666 nm [Fig. 1] against a blank solution prepared in the same manner except that silver ion.



**Fig. 1** Absorption spectra for  $3.0 \text{ ng mL}^{-1}$  Ag(I) complexed with  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CPAHPD using  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CTAB at pH 5.5 with CPE and for  $5000 \text{ ng mL}^{-1}$  Ag(I) without CPE.

#### Optimization of the system

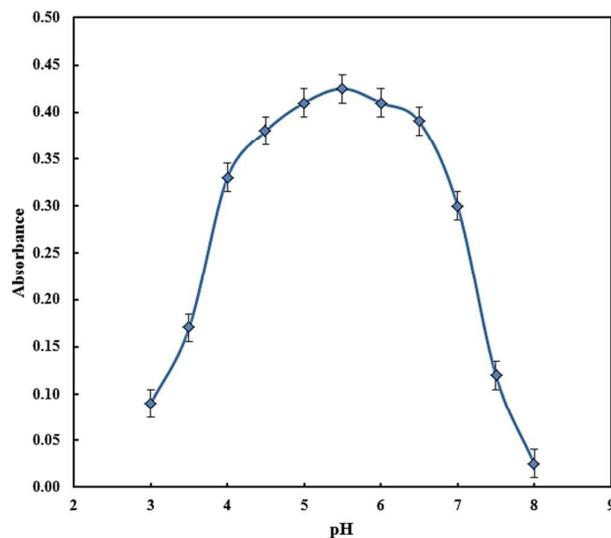
The reagent concentration and other reaction conditions must be optimized to increase the sensitivity of the developed method. These conditions were optimized by fixing all parameters to be constant and optimizing one each time.

The effect of pH on the absorbance at a constant concentration of complex in surfactant-rich phase was investigated in the range of 1.93–12.7. Different types of buffers {acetate (3.6–5.6), borate (8.0–10.0), phosphate (5.8–8.0), thiel (2.0–12.0) and universal (1.93–12.7)} were examined.

The optimum one was thiel buffer, and the best values of pH were between pH 4.5 – 6.5 [Fig. 2]. So the pH 5.5 was selected for all further studies, since the results was higher concordant at this value. The complexation reaction at pH values lower than 3.0 is incomplete due to protonation of CPAHPD and complexation reaction is incomplete. The decrease in absorbance at pH values higher than 8.5 could be due to the hydrolysis of Ag(I).

Effect of CPAHPD concentration on the extraction and determination of Ag(I) was investigated in the range of  $(0.4\text{--}4.0) \times 10^{-4} \text{ mol L}^{-1}$ . The sensitivity of the method increased by increasing CPAHPD concentration up to  $2.0 \times 10^{-4} \text{ mol L}^{-1}$  and remained constant at higher concentrations. Therefore,  $2.2 \times 10^{-4} \text{ mol L}^{-1}$  of CPAHPD was used in further works. The results are shown in Fig. 3. The slight decrease in absorbance after  $2 \times 10^{-4} \text{ mol L}^{-1}$  CPAHPD which is about 2.5 % is due to the concentration of uncomplexed CPAHPD in surfactant-rich phase increases significantly, therefore much probably cause decrease of absorbance change at concentrations higher  $2 \times 10^{-4} \text{ mol L}^{-1}$  is due to the fact that free CPAHPD competes with the complexes in extraction to surfactant-rich phase.

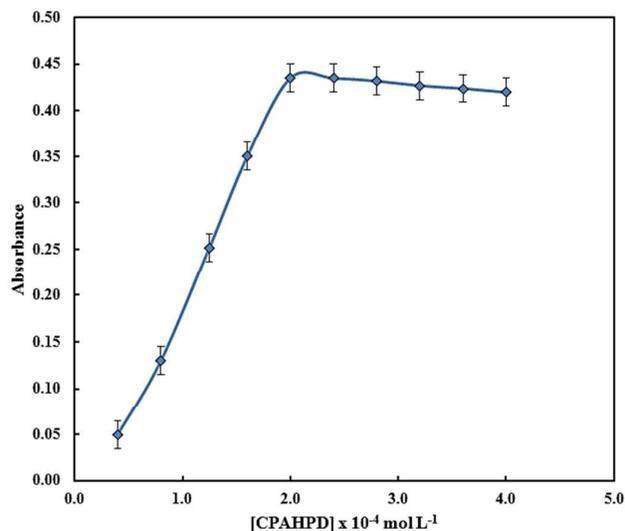
The effects of different surfactants on the Ag(I)–CPAHPD system were investigated. The results indicated that, in the presence of non-ionic or anionic surfactants, the Ag(I)–CPAHPD chromogenic system gives a low absorption, whereas in the presence of cationic surfactants, the absorption of the chromogenic system increases markedly. Various cationic surfactants enhance the absorbance in the following sequence: CTAB > CPB > CPC. Accordingly, CTAB was the best additive. Moreover, the effect of CTAB concentration on the



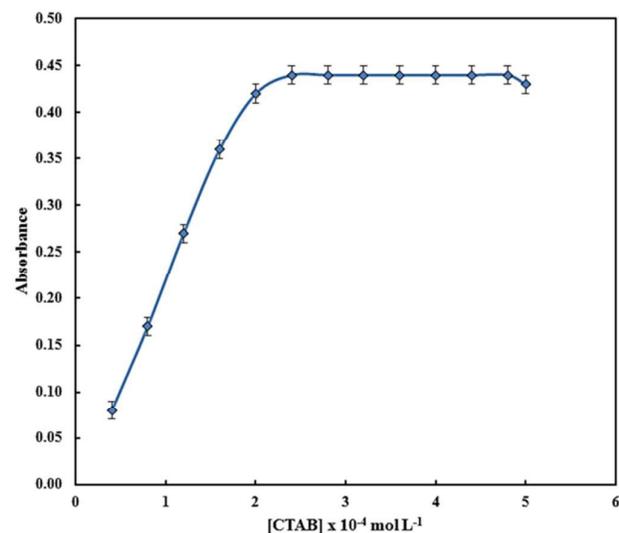
**Fig. 2** Effect of pH on complexation of  $3.0 \text{ ng mL}^{-1}$  Ag(I) with  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CPAHPD using  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CTAB.

extraction and determination of Ag(I) was investigated in the range  $(0.4\text{--}4.0) \times 10^{-4} \text{ mol L}^{-1}$ . The results are shown in Fig. 4. The absorbance increased by increasing in CTAB concentration up to  $2.0 \times 10^{-4} \text{ mol L}^{-1}$  and remained constant at higher concentrations. Therefore,  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CTAB was chosen as the optimum.

As described in introduction section, addition of salts can cause cationic surfactant solutions to separate into two phases, immiscible surfactant rich and surfactant-poor phases. Therefore, different concentrations of potassium iodide were added to prompt micellar growth and extraction of the formed complex. The effect of iodide concentrations was studied in



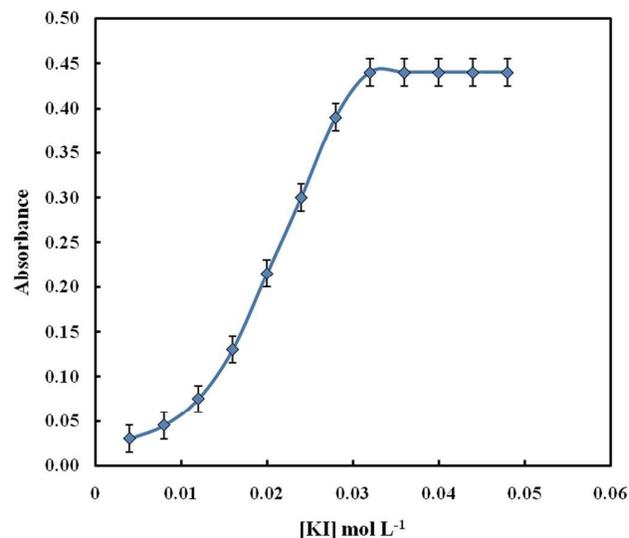
**Fig. 3** Effect of reagent concentration on the complexation of  $3.0 \text{ ng mL}^{-1}$  Ag(I) using  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CTAB at pH 5.5.



**Fig. 4** Effect of CTAB concentration on complexation of  $3.0 \text{ ng mL}^{-1}$  with  $2 \times 10^{-4} \text{ mol L}^{-1}$  CPAHPD at pH 5.5.

the range of  $(4.0\text{--}5.0) \times 10^{-2} \text{ mol L}^{-1}$ . The results showed that addition of  $3.2 \times 10^{-2} \text{ mol L}^{-1}$  iodide sufficed for maximum extraction of the complex and the absorbance remained constant at higher concentrations. A concentration of  $3.6 \times 10^{-2} \text{ mol L}^{-1}$  iodide was selected for further works as exhibited in Fig. 5.

Effect of time on the reaction and also on the CPE procedure was investigated. The results showed that the complex formation of Ag(I)–CPAHPD was completed in 5.0 min and 5.0 min centrifugation at 4000 rpm was found to be enough for complete CPE.

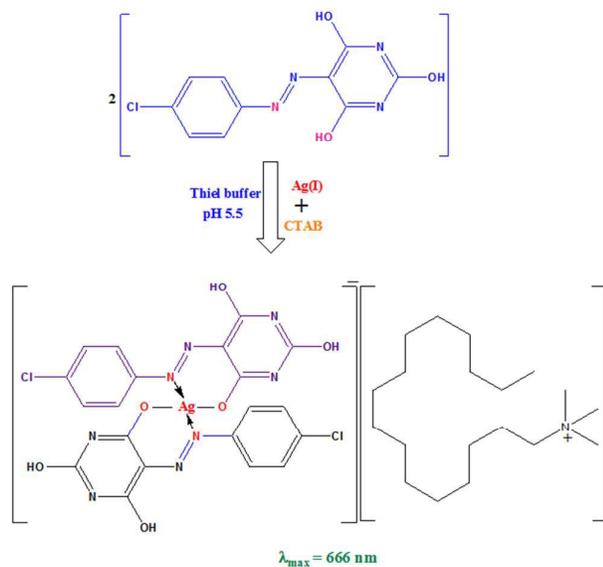


**Fig. 5** Effect of KI concentration on complexation of  $3.0 \text{ ng mL}^{-1}$  Ag(I) with  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CPAHPD using  $2.4 \times 10^{-4} \text{ mol L}^{-1}$  CTAB at pH 5.5.

Because the surfactant-rich phase was precipitate, different solvents were tried to select the best one producing optimal results regarding sensitivity. Among acetone, acetonitrile, methanol, ethanol and DMF, DMF gave the best results due to the high color development and low overlapping of spectra of components. Therefore, 1.0 mL DMF was selected in order to dissolve the appropriate amount of the precipitated complex for and measurement of the absorbance of that dissolved complex and also a suitable preconcentration factor was obtained. Therefore, a preconcentration factor of 25 was obtained using the proposed method where the initial volume was 25 mL.

#### Stoichiometric ratio

The nature of the formed complex was established at the optimum conditions described above using the two spectrophotometric methods, molar ratio and continuous variation methods. The plot of the absorbance values versus the molar ratio of CPAHPD to Ag(I), which obtained by varying the CPAHPD concentration, showed an inflection at molar ratio 2.0, indicating presence of two CPAHPD molecules in the formed complex. Moreover, the Job's method showed an inflection at mole fraction of 0.3 of Ag(I) which give an evidence that the ratio of CPAHPD to Ag(I) equal 2.0. For ternary complex with CTAB, the obtained results referred that 1:1 complex is formed between Ag- CPAHPD complex and CTAB. Consequently, the results indicated that the stoichiometric ratio was (2:1:1) [CPAHPD: Ag(I) : CTAB],



**Scheme 1** The proposed reaction between CPAHPD and Ag(I) in presence of CTAB.

[Scheme 1]. The conditional formation constant ( $\log K$ ), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 5.67, whereas the true constant was 5.45.

#### Analytical characteristics

Table 1 summarizes the analytical characteristics of the optimized method including regression equation, linear range, the limit of detection (LOD) and limit of quantitation (LOQ) which were determined<sup>39</sup> using the formula:

$$\text{LOD or LOQ} = \kappa \text{SD}_a / b,$$

where  $\kappa = 3$  for LOD and 10 for LOQ,  $\text{SD}_a$  the standard deviation of the blank and  $b$  is the slope of calibration curve. The values of LOD and LOQ were 0.095 to 0.297  $\text{ng mL}^{-1}$ , respectively. Because the amount of Ag(I) in 25 mL of sample solution is measured and after preconcentration by CPE final volume is 1.0 mL, the maximum preconcentration factor of the solution is 25. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the calibration graph in aqueous media (before CPE method), for Ag(I) was 325. The relative standard deviation (RSD) for six replicate measurements of 3.0  $\text{ng mL}^{-1}$  of Ag(I) was 1.25%.

#### Selectivity

To evaluate the selectivity of this method, the effects of foreign ions on the determination of Ag(I) were investigated. The effect of different cations and anions on the determination of 3.0  $\text{ng mL}^{-1}$  by the proposed method was studied. An ion was considered to be an interfering when it caused a variation greater or less than  $\pm 5.0\%$  in the absorbance of the sample. For the determination of 3.0  $\text{ng mL}^{-1}$  Ag(I) by this method, the foreign ions can be tolerated at the levels given in Table 2. Thiocyanate, and cyanide seriously interfere, resulting in negative errors. These interferences can

be eliminated by sample digestion with nitric acid. This method then has a high selectivity.

**Table 1** Analytical features of the present method

Parameters	After CPE	Before CPE
Amount of DMF	1.0	---
pH	5.5	5.5
Optimum [CPAHPD] ( $\text{mol L}^{-1}$ )	$2.4 \times 10^{-4}$	$2.4 \times 10^{-4}$
Reaction time (min)	5.0	5.0
Stirring time (min)	5.0	---
Beer's range ( $\text{ng mL}^{-1}$ )	0.3 – 5.0	200 – 5000
Ringbom range ( $\text{ng mL}^{-1}$ )	0.5 – 18.8	300 – 4920
Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$1.55 \times 10^7$	$3.39 \times 10^3$
Sandell sensitivity ( $\text{ng cm}^{-2}$ )	0.007	0.32
<i>Regression equation</i>		
Slope	143	0.44
Intercept	-0.004	0.007
Correlation coefficient ( $r$ )	0.9997	0.9988
RSD <sup>a</sup> (%)	1.25	2.32
Detection limits ( $\text{ng mL}^{-1}$ )	0.095	58.03
Quantification limits ( $\text{ng mL}^{-1}$ )	0.297	191.5
Preconcentration factor	25	---
Improvement factor	325	---

<sup>a</sup> Relative standard deviation for six replicates

#### Analytical Applications

##### Determination of silver in silver sulphadiazine and in developed radiological film

The proposed method was successfully applied to the determination of Ag(I) ion in sulphadiazine cream and the radiological film samples. Ag(I) in both samples was determined using the CPE with spectrophotometric applying the standard addition method and the results are summarized in Table 3. The results obtained were compared with those obtained from ICP OES analysis and were found in a good agreement.

**Table 2** Tolerance limits for the determination of 3.0  $\text{ng mL}^{-1}$  of Ag(I) using CPAHPD (relative error  $\pm 5.0\%$ )

Ion added	Tolerate, mg
$\text{Na}^+$ , borate, tartaric acid	120
$\text{Li}^+$ , $\text{Al}^{3+}$ , $\text{Cl}^-$ , oxalate, $\text{C}_2\text{O}_4^{2-}$	100
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Br}^-$ , $\text{B}^{3+}$ , $\text{ClO}_3^-$	75
$\text{Mn}^{2+}$ , $\text{Ce}^{4+}$ , $\text{W}^{6+}$ , $\text{U}^{4+}$	50
$\text{F}^-$ , $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Cr}^{4+}$ , $\text{Mo}^{6+}$	30
$\text{Ti}^{4+}$ , $\text{Bi}^{3+}$ , $\text{V(V)}$ , $\text{Cr}^{6+}$ , $\text{Zr}^{4+}$	20
$\text{Tl}^{3+}$ , $\text{Cd}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Sn}^{4+}$ , $\text{Zn}^{2+}$ , $\text{Cu}^{2+}$	12
$\text{Ru}^{3+}$ , $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Os}^{8+}$	8.0
$\text{Cr}^{3+}$ , $\text{La}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$	5.0
$\text{Se}^{4+}$ , $\text{Te}^{4+}$ , $\text{Au}^{3+}$ , $\text{S}_2$ , $\text{Zr}^{4+}$	2.0
$\text{Ir}^{3+}$ , $\text{Rh}^{3+}$ , $\text{Th}^{4+}$	1.0
$\text{Pt}^{4+}$	0.5
$\text{CN}^-$ , $\text{SCN}^-$	0.1

##### Determination of silver ion developed panchromatic plates

As a practical application, the method was successfully applied to determine silver in developed panchromatic plates

used in offset printing. Suitable aliquots of sample solutions were analyzed by the proposed method, and also by ICP OES (Table 3).

#### Determination of silver ion in human hair and tea samples

The proposed method was applied for the determination of Ag(I) in human hair and tea samples. The results are checked with parallel determinations by direct ICP OES. The data obtained in the analysis are given in Table 4. The precision shown for the samples studied is also satisfactory.

#### Determination of silver ion in some water samples

Aiming to demonstrate the usefulness of the proposed procedure, a set of water samples was analyzed. The proposed method was performed on these water samples at the optimum conditions which summarized in Table 1. Accuracy

and precision were evaluated by comparing the obtained results with these obtained using ICP OES [Table 5]. Applying the paired *t*-test and *F*-value, no significant difference at 95 % confidence level was observed. As could be seen, the recoveries for the spiked samples were in the acceptable range.

Performance of the proposed method was evaluated using the *t*-value (for accuracy) and *F*-test (for precision) compared with the ICP OES method at 95 % confidence levels for five degrees of freedom.<sup>39</sup> The results showed that the calculated values of *t*-test and *F*-value did not exceed the theoretical values indicating that there are no significant difference between the present method and the reference method.

**Table 3** Analytical data of silver determined in sulphadiazine and radiological film (*n* = 6).

Sample	Ag(I) added (ng mL <sup>-1</sup> )	Found <sup>a</sup> (ng g <sup>-1</sup> ) × 5		Recovery %	<i>t</i> -test <sup>b</sup>	<i>F</i> -value <sup>b</sup>
		Proposed	ICP OES			
Silver	0.0	0.8 ± 0.4	0.8 ± 0.6	---	0.96	2.22
sulphadiazine	1.5	2.3 ± 0.3	2.2 ± 0.8	100.9	1.07	2.47
	3.0	3.7 ± 0.4	3.7 ± 0.8	99.7	1.21	2.83
	4.0	4.8 ± 0.5	4.8 ± 0.1	100.2	0.87	2.04
Radiological film	0.0	1.3 ± 0.6	1.3 ± 0.9	---	1.23	2.97
	1.0	2.2 ± 0.4	2.3 ± 0.8	99.6	0.97	2.27
	2.0	3.3 ± 0.2	3.3 ± 0.7	100.3	1.14	2.66
	3.0	4.2 ± 0.3	4.3 ± 0.9	99.8	1.05	2.43
Photographic plate	0.0	4.6 ± 0.6	4.5 ± 0.3	---	1.11	2.53
	0.2	4.7 ± 0.5	4.8 ± 0.4	99.8	0.92	2.22
	0.4	5.0 ± 0.3	5.0 ± 0.8	100.2	1.08	2.47
	0.5	5.0 ± 0.4	5.1 ± 0.9	99.2	1.48	3.35

<sup>a</sup>: Results average of six consecutive measurements.

<sup>b</sup>: Theoretical values for *t* and *F* at 95% confidence limit are 2.57 and 5.05, respectively.

**Table 4** The analytical results of silver in hair and tea samples

Sample	Ag(I) added (μg g <sup>-1</sup> )	Found <sup>a</sup> (μg g <sup>-1</sup> )		Recovery (%)
		Proposed	ICP OES	
Human hair	---	0.04	0.04	---
	0.01	0.05 ± 0.02	0.05 ± 0.06	102.0
	0.02	0.06 ± 0.02	0.06 ± 0.04	98.3
	0.03	0.07 ± 0.03	0.07 ± 0.07	98.6
Red tea sample	---	0.16	0.16	---
	0.20	0.18 ± 0.3	0.18 ± 0.7	98.9
	0.40	0.20 ± 0.6	0.20 ± 0.4	100.5
	0.60	0.22 ± 0.2	0.22 ± 0.5	99.1
green tea sample	---	0.14	0.14	---
	0.10	0.15 ± 0.3	0.15 ± 0.6	100.0
	0.20	0.16 ± 0.4	0.16 ± 0.7	100.0
	0.30	0.17 ± 0.3	0.17 ± 0.7	98.8

<sup>a</sup>: Mean ± SD (*n* = 6).

**Table 5** Determination of Ag(I) in wastewater and recoveries for different water samples.

Sample	Ag(I) added (ng mL <sup>-1</sup> )	Found <sup>a</sup> (ng mL <sup>-1</sup> )		Recovery (%)	t- test	F-value
		Proposed	ICP OES			
Waste water <sup>b</sup>	–	62.4 ± 1.8	62.5 ± 1.6	–	1.21	2.71
	10	72.3 ± 1.6	72.6 ± 1.7	99.9	0.97	2.43
	20	82.1 ± 1.4	82.0 ± 1.8	99.7	1.06	2.55
Mineral water <sup>c</sup>	–	ND <sup>d</sup>	–	–	–	–
	10	9.8 ± 0.2	9.8 ± 0.9	98.3	1.42	3.13
	20	19.8 ± 0.5	19.8 ± 0.8	99.1	1.17	2.66
Rain water <sup>e</sup>	–	ND	–	–	–	–
	10	9.8 ± 0.2	9.8 ± 0.7	98.2	1.37	2.98
	20	19.7 ± 0.5	19.8 ± 1	98.7	1.25	2.81
Tap water <sup>f</sup>	–	ND	–	–	–	–
	10	10.0 ± 0.2	9.9 ± 0.9	100.0	0.87	2.26
	20	19.6 ± 0.4	19.7 ± 1	98.1	1.40	3.06
River water <sup>g</sup>	–	ND	–	–	–	–
	10	10.2 ± 0.2	10.1 ± 0.8	101.8	1.22	2.75
	20	20.2 ± 0.5	19.9 ± 0.9	101.0	1.03	2.49
Sea water <sup>h</sup>	–	ND	–	–	–	–
	10	9.9 ± 0.3	9.8 ± 1.1	99.2	0.96	2.38
	20	19.8 ± 0.5	20.2 ± 1.3	99.2	1.01	2.44

<sup>a</sup> Mean of six extraction.

<sup>b</sup> From a rinse water of photography.

<sup>c</sup> From Sewa mineral water

<sup>d</sup> Not detected.

<sup>e</sup> Collected at Shobra city, Egypt (Feb. 2015).

<sup>f</sup> From drinking water system of Benha, Egypt.

<sup>g</sup> From Benha river water (Nile river).

<sup>h</sup> Mediterranean sea water.

## Conclusions

The present procedure donates a simple, very sensitive and low cost spectrophotometric method for CPE of Ag(I). After a successful determination of trace quantities of silver, the method had been applied to some real samples. A comparison between the proposed method with the previously reported spectrophotometric methods<sup>41–51</sup> for determination of Ag(I) (Table 6) indicates that the present method has a higher sensitive and lower wider linear range. The method is safe, simple, rapid and inexpensive for the determination of trace quantities of silver to real samples.

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Table 6 Comparison of reagents for spectrophotometric determination of silver

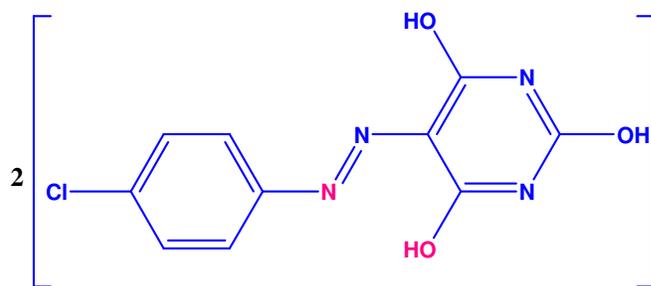
Reagent	pH/Surfactant	$\lambda_{\max}$ (nm)	$\epsilon \times 10^4$ L mol <sup>-1</sup> cm <sup>-1</sup>	Linear range ( $\mu\text{g mL}^{-1}$ )	Ref.
2-(5-Chloro-2-pyridylazo) -5-diethylaminoaniline	(pH 10), SDS	530	6.7	0.05–1.2	[41]
Thio-Michler's ketone	(pH 5), SDS	535	9.4	0.0–0.4	[42]
2-(5-Bromo-2-pyridylazo) -5-dimethylaminophenol	(pH 6.8-8), SDS	542	6.5	0.1–1.6	[43]
2-(3,5-Dibromo-2-pyridylazo) -5-diethylaminophenol	(pH 5), SDS	565	6.4	0.02–0.48	[44]
Sulfochlorophenolazo Thiorhodanine	(pH 2.8), Triton X-100	540	39.4	0.0–/0.8	[45]
Tetra-(4-chlorophenyl) -porphyrin	(pH 10), TritonX-100	426	3.88	0.0–0.32	[46]
Dithizone	(weak acid)	500		0.05–1	[47]
o-Carboxyl-benzenediazo aminoazobenzene	(pH 11), OP	540	8.2	0.0–0.48	[48]
2-(2-quinolyazo)-5- diethylaminoaniline	(pH 6.5), SDS	580	13.9	0.01–0.6	[49]
2-(2-Quinolyazo)-5- diethylaminophenol	pH 3.5 - 8.0, SPE	590	13.0	0.01–0.6	[50]
2-(2-Quinolyazo)-5- diethylaminoaniline	pH 6.5, SDS	590	13.6	0.01–0.6	[51]
5-(4'-Chlorophenylazo)-6-hydroxypyrimidine- 2,4-dione	pH 5.5, CTAB, CPE	666	1550	0.3–5.0 (ngmL <sup>-1</sup> )	This work

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