



## Original Research Article

# Eco-friendly trace analysis of silver in beer/wine samples using a new co-polymeric nanocomposite based-ultrasound assisted-cloud point extraction combined with spectrophotometry

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## ABSTRACT

In this study, a new magnetic nanocomposite based on the tris(2-hydroxymethyl)aminomethane-modified poly(styrene-co-*N*-maleimide) copolymer and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared as a new micellar interface for pre-concentration of trace levels of silver from aqueous solutions by ultrasound assisted-cloud point extraction (UA-CPE). The structure of the nanocomposite was characterized by using some instrumental tools in detail. The method is selectively based on charge transfer among silver and reagents at pH 5.0, and detection by micro-volume UV–vis spectrophotometry at 346 nm. The main variables affecting extraction efficiency were evaluated and optimized in detail. Under the optimized conditions, the method shows good linear relationships in ranges of 2.5–125 µg L<sup>-1</sup> and 4–160 µg L<sup>-1</sup> by two calibration curves (established in solvent and beer/wine matrices) with a better determination coefficient (*r*<sup>2</sup>) than 0.992. The limits of detection, repeatability/intermediate precision (as RSDs%, 5, 25 and 100 µg L<sup>-1</sup>, *n*: 5) and recovery percentages were 0.85/1.21 µg L<sup>-1</sup>, 3.5–7.1% and 91.5–98.5%, respectively. From pre-concentration of 25-mL sample solution, a pre-concentration factor was found to be 62.5 with sensitivity enhancement of 23.2-fold in calibration. A matrix effect was not observed for the triplicate measurements of 100 µg L<sup>-1</sup> Ag<sup>+</sup> in the presence of various interfering species. The method accuracy was validated with the outcome of validation that was carried out. The method after two sample preparation procedures was successfully applied to reliable determination of total Ag in beer and wine samples. The total Ag levels were in range of 2.5–4.2 and 2.7–5.5 µg L<sup>-1</sup> in beer and wine samples, respectively.

## 1. Introduction

Silver (Ag) is an important element that is widely used in human life. Because of its bacteriostatic properties, silver compounds are often used in filters and other equipment's to purify swimming pool and drinking waters, and used in the processing of foods, drugs, and beverages. In many countries, Ag impregnated filters are used for drinking water preparation. In mammals, Ag usually interacts competitively with essential nutrients, especially with selenium, copper, Vitamin E and Vitamin B<sub>12</sub> (Katarina et al., 2006). In fact, the concentration of Ag in environmental samples is at trace and ultra-trace levels. According to World Health Organization (WHO), average Ag concentrations in natural waters are 0.2–0.3 µg L<sup>-1</sup>, in drinking water in the USA that had not been treated with Ag for disinfection purposes varied between “non-detectable” and 5 µg L<sup>-1</sup> (WHO, 2003). Ag is both vital and toxic for many biological systems and its content in drink and tap water samples

is increased with the increasing use of Ag compounds and Ag containing products in both industry and in medicine. Therefore, it is of great importance to develop a new analytical method for the separation, pre-concentration, sensitive and selective determination of trace levels of silver from the sample matrix.

Many efforts have been made by researchers around the world to determine low Ag levels. Several atomic/molecular spectroscopic techniques have been used to determine trace Ag<sup>+</sup> ions in real samples such as flame atomic absorption spectrometry (FAAS) (Ghaedi et al., 2009; Mohammadi et al., 2009; Araújo et al., 2010; Gao et al., 2010; Gürkan et al., 2016; Omididi et al., 2015; Yang et al., 2017; Karimi et al., 2011), electrothermal atomic absorption spectrometry (ETAAS) (Manzoori et al., 2007) and/or graphite furnace atomic absorption spectrometry (GFAAS) (Afzali et al., 2011), including spectrophotometry (Fouladvandi and Elhami, 2017; Zengin, 2019).

Among these detection techniques, the use of UV–vis spectroscopic

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techniques can be considered as direct, fast, simple, easy to use and less expensive alternatives. Also, the sensitivity and selectivity of spectrophotometry can greatly be improved when it is used with a suitable chromogenic or fluorogenic reagent for detection of the analyte in the UV-vis region. Two important limitations in its determination of different sample matrices occur when level of analyte is lower than the LOQs of spectrophotometry and where there is a matrix effect on the analytical signal. To overcome these problems, a separation/pre-concentration procedure is usually necessary prior to determination of analyte by spectrophotometry. The authors have reported many techniques in literature for the separation and extraction of  $\text{Ag}^+$  ions from different matrices and its pre-concentration in the same or another phase such as cloud point extraction (CPE) (Ghaedi et al., 2009; Gao et al., 2010; Gürkan et al., 2016; Yang et al., 2017; Manzoori et al., 2007; Zengin, 2019), solid phase extraction (SPE) (Araújo et al., 2010), dispersive liquid-liquid microextraction (DLLM) (Gao et al., 2010; Fouladvandi and Elhami, 2017), DLLM based on solidification of floating organic drop (DLLM-SFOD) (Afzali et al., 2011), homogenous liquid-liquid extraction (HLE) (Ghiasvand et al., 2005), solvent extraction in room temperature ionic liquids (SE-RTILs) (Shimojo and Goto, 2004), adsorption (Kholmogorova et al., 2020), ion-exchange resin (Chamsaz and Riazi, 2012), and on line pre-concentration using carbon nanotubes (CNTs) prior to detection by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Yu et al., 2013) in combination with atomic and molecular spectrometric detection tools, including directly determination of multi-elements containing trace/ultra-trace  $\text{Ag}^+$  ions in wine samples by inductively coupled plasma-mass spectrometry (ICP-MS) without pre-concentration (Plotka-Wasyłka et al., 2018).

However, most of the pre-concentration procedures such as solvent extraction, HLE, adsorption, ion-exchange, SPE and its further modes used to improve selectivity and detection power of the method in trace analysis are tedious, time-consuming, needs expert user in his/her area and may cause sample contamination. The CPE procedure is a new and eco-friendly LLE technology and has gained large attention in separation science. CPE is based on the clouding phenomena of surfactants (Bezerra et al., 2005). The changes in the experimental parameters (like solution pH, temperature, alone surfactant or mixed surfactant concentration, salting-out effect, and time) lead to phase separation. It can be used to separate the hydrophobic and hydrophilic material, and it is economic, safe, environmental benign, efficient and convenient. It has drawn wide application in both life science and environmental science, including food processing. Recently, in order to shorten procedure time and reduce steps needed or to improve selectivity, and thus greatly improve extraction efficiency; different ways such as vortex-inducing, ultrasound and microwave energies which help sample preparation have been used in conventional CPE. The UA-CPE procedure, which is one of further modes of CPE, using an ultrasonic bath system, allows the preparation of several samples directly in the sample container, preventing sample losses and minimizing contamination. Moreover, diluted reagents in UA-CPE are normally used, decreasing blank values (thus, improving detection limit) and reducing both reagent and time consumption unlike traditional CPE (Hagarová and Urfk, 2006).

Recently, magnetic NPs with and without modification have wide application in separation of heavy metals. The magnetic nanocomposite based on  $\text{Fe}_3\text{O}_4$ @styrene-maleic anhydride copolymer (Abdolmohammad-Zadeh and Salmasi, 2018) has successfully been used in extraction and pre-concentration of  $\text{Ag}^+$  ions and  $\text{Ag}$  NPs. Also, the chitosan, which is a natural bio-polymer with a  $\text{pK}_a$  of 6.5, at pH 5.0 (Katarina et al., 2006), and a cross-linked chitosan modified with histidine moiety at pH 6.0 (Hosoba et al., 2009a,b) containing hydroxyl, amine, N-acetyl amide/imidazole and carboxylic functional groups for chelation of  $\text{Ag}^+$  ions were selectively used in analysis step in real time samples by means of detection tools, which are sensitive, but expensive, complex and requiring expert-user in his/her area such as ET-AAS, ICP-MS and ICP-OES. To provide an improvement in selectivity and

sensitivity of the extraction process by UA-CPE, fast, easy to use, efficient and versatile separation capability of magnetic cyclic nanocomposite was combined with hydrophilic poly(styrene-co-N-maleimide) modified with tris(2-hydroxymethyl) aminomethane (Tris) as a chelator, poly(SMIm) for extraction and pre-concentration of trace  $\text{Ag}^+$  ions from sample matrix at micellar interface.

In the current study, for the first time, the UA-CPE combined with micro-volume spectrophotometry for total  $\text{Ag}$  determination is reported. The pH-dependent coordination ligand, poly(SMIm) modified and magnetized with Tris and  $\text{Fe}_3\text{O}_4$  NPs, in presence of histidine, formaldehyde and ionic surfactant, sodium dodecyl sulfate (SDS) as synergistic agents was employed for the selective extraction of silver. The cyclic imidic copolymer matrix and histidine serve as primary and secondary chelators via their functional groups. However, SDS acts as an ion-pairing or counter-ion in the pre-concentration step while formaldehyde acts as a charge/proton transfer agent by Cannizzaro disproportionation in pH-dependent coordination step. This study covers and discusses (i) the optimization of UA-CPE parameters for extractable complex formation, (ii) the detailed charge transfer (CT) mechanism among the selected reagents and silver, (iii) silver detection, (iv) analytical applications and validation studies by the one- and two-sided Student's t-tests, (v) the possible effect of interfering ions, and (vi) future trends.

## 2. Experimental

### 2.1. Reagents, standard solutions and samples

Ultra-pure water (resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) obtained by a Lab-conco water purification system (Kansas City, USA) was used throughout this study. All glass wares, pipettes and plastic tubes were cleaned by soaking in 5.0% (v/v)  $\text{HNO}_3$  solution during one day, later were rinsed five times with ultra-pure water before starting of experiment. The standard working solutions of  $\text{Ag}^+$  ions at  $\mu\text{g L}^{-1}$  levels used for calibration were prepared daily by diluting a  $1000 \text{ mg L}^{-1}$  metal stock solutions purchased from Merck (Darmstadt, Germany) with  $0.2 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution immediately before use. The calibration solutions were obtained daily by stepwise dilution of stock solution with dilute  $\text{HNO}_3$  and water. Histidine solution,  $0.02 \text{ mol L}^{-1}$  as promoter in formation of CT complex was prepared by dissolving suitable amounts of reagent in dilute NaOH solution ( $10 \text{ mL}$  of  $0.2 \text{ mmol L}^{-1}$ ), and diluting with water. Formaldehyde solution, 0.1% (v/v)  $\text{CH}_2\text{O}$  as reductant was prepared by dilution of solution of 37% (w/w) supplied from Sigma-Aldrich (St. Louis, MO, USA) in  $10 \text{ mL}$  of methanol as stabilizer to prevent polymerization, and stored in dark at  $4^\circ\text{C}$ . The modified- and magnetized-imide copolymer matrix with Tris and magnetite ( $\text{Fe}_3\text{O}_4$ ), respectively (as  $0.1 \text{ g}/100 \text{ mL}$ ) was prepared by dissolution of its suitable amounts in tetrahydrofuran (THF). The ionic and non-ionic surfactants, SDS (4.0% (w/v)), and polyethylene glycol tert-octylphenyl ethers (Triton X-114 plus Triton X-100) (5.0% (v/v) in 4:1 ratio, v/v) as mixed extractants, obtained from Sigma, were prepared by dissolving appropriate amounts of surfactant in  $100\text{-mL}$  volumetric flasks, and vortex-mixing a homogeneous clear solution when necessary. The pH of the sample solutions was adjusted with universal Britton-Robinson buffer (BR buffer, containing equal-molar concentration of phosphoric, boric acid and citric acids) (each,  $0.04 \text{ mol L}^{-1}$ , pH 5.0) buffer solution.

Beverage samples (with alcohol degree of 2.5–4.0% for beer, 4–12% for wine) were supplied from local markets (Sivas, Turkey) to evaluate the applicability of the method. Due to the lack of a certified sample compatible with the sample matrix, for accuracy of the method two standard reference materials (SRMs) supplied from National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA) were analyzed: SRM 1643a Trace elements in natural water and SRM 1643d Trace elements in water.

## 2.2. Instrumentation

All the absorbance measurements were performed with a double beam spectrophotometer with micro-cell sample holder (Shimadzu UV-1800 model, Kyoto, Japan). The maximum absorbance of the ion-pair complex based on CT in a cell of 400  $\mu\text{L}$  was measured at 346 nm against sample blank (in THF as diluent) without analyte for background correction. FT-IR spectra were taken using a Bruker (Alpha 12,283,105 model, Billerica, MA, Germany) spectrometer (with direct sampling at ATR mode without KBr pellet) in the range of 4000–400  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  resolutions.  $^1\text{H-NMR}$  spectra (in DMSO, D<sub>6</sub>, 400 MHz, single pulse) were recorded on a JEOL JNM-ECZ400S/L1 spectrometer (JEOL Ltd., Akishima, Tokyo, Japan) operating at 298 K with tetramethylsilane (TMS) as an internal standard. Chemical shifts ( $\delta$ ) are quoted in ppm and coupling constants ( $J$ ) are measured in Hertz (Hz). The XRD pattern was recorded by Rigaku Miniflex 600 x-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. A scanning electron microscope with energy dispersion of X ray (SEM and/or SEM/EDX) (TESCAN MIRA3 model, Czech Republic) was additionally used to study the morphological characteristics of the magnetic nanocomposite. The pH measurements were performed using a digital pH meter (Selecta-2001 plus, Barcelano, Spain) supplied with a glass-calomel electrode. A centrifuge (Hettich universal 320 model, Darmstadt, Germany) was used to speed up the phase separation. A programmable ultrasonic bath (UCP-10 model, Seoul, Korea) was used for incubation with temperature ranging from 0 to 80 °C and ultrasound frequency of 40 kHz at power of 300 W. An ultrasound agitator was used for acceleration of the mass transfer in the extraction process.

## 2.3. Preparation of the magnetic nanocomposite, poly(SMIm)-Tris-Fe<sub>3</sub>O<sub>4</sub> NPs

Synthesis of the poly(SMA) by radical polymerization, surface modification with Tris (as poly(SMIm)-Tris) by thermal process at 150 °C for selective chelation of Ag<sup>+</sup> ions, and then its magnetization with Fe<sub>3</sub>O<sub>4</sub> NPs (as poly(SMIm)-Tris-Fe<sub>3</sub>O<sub>4</sub> NPs), including pure Fe<sub>3</sub>O<sub>4</sub> NPs, was sequentially performed, and the details related to this synthesis were given and discussed in our first two studies (Zengin, 2019; Zengin et al., 2020).

## 2.4. Collection, and preparation of samples to analysis

The detection of total Ag by spectrophotometry were evaluated by analysis of the selected beverage samples such as beer and wine. All the beverage samples were supplied from a local supermarket in Sivas, Turkey.

At initial, a 0.1% (v/v) 2-octanol solution was added to the beverage samples (10–15 mL, for each one) to prevent foaming; they were then degassed for 5 min using an ultrasonic bath (40 kHz, 300 W). Potassium metabisulfite (5 mg L<sup>-1</sup>, 1.0 mL) was also added to the samples to destroy any protein. Aliquots (5.0 mL) of the pre-treated and homogenized samples were transferred to a 25-mL flasks. Before analysis by standard addition method, to control the possible transformations of the analyte forms during pre-treatment steps and keep in form of free Ag<sup>+</sup> ions where silver chloride is used for the treatment of wines to remove fermentation and storage-related abnormal odors (odors caused by reduction reactions in polyphenols/anthocyanin's-rich medium, characterized by the presence of hydrogen sulfide and thiols) (International Oenological Codex, 2014), all sample solutions were subjected to two wet digestion processes as follows:

(i) In extraction step with acidic thiourea, 3.0 mL of 0.02% (w/v) thiourea in 5.0 mL of 2.0% (v/v) HNO<sub>3</sub> was added to the sample solution, and sonicated for 12 min at 50 °C in ultrasonic bath until a clear solution is obtained. After cooling to room temperature, the resulting mixtures were filtered using a membrane filter of 0.45- $\mu\text{m}$ . The pH of the sample solutions was adjusted to 5.0 using dilute NaOH (2.0 or 0.2 mol L<sup>-1</sup>) and completed to 25 mL with water.

(ii) In extraction step with dilute oxidant acid mixture, 5.0 mL of mixture of 3.0 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.3 mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (3:2, v/v) was added to the sample solution, and then 5.0 mL 1.0 mol L<sup>-1</sup> CH<sub>3</sub>COOH and 2.5 mL of 1.0 mg L<sup>-1</sup> Bi(III) completely to oxidize and release organic/inorganic matrix-bound silver (like protein bound Ag, Ag colloids, Ag<sub>2</sub>S at sub-ppb levels) to free Ag<sup>+</sup> ions equivalents to total Ag were sequentially added to this mixture, and thoroughly sonicated for 7 min at 40 °C in ultrasonic bath until a clear solution is obtained. After cooling to room temperature, the resulting mixtures were filtered using a membrane filter of 0.45- $\mu\text{m}$ . The pH of the sample solutions was adjusted to 5.0 using dilute NaOH (2.0 or 0.2 mol L<sup>-1</sup>) and completed to 25 mL with water.

In a similar way, sample blanks, including suitable amounts of two SRMs, were prepared without analyte, and submitted to the same extraction procedures in order to evaluate analyte contamination by reagents used. All the measurements and processing were performed at least in five times, and their mean values plus standard deviations were considered.

Finally, 5.0 mL of the extracted samples were in parallel submitted to UA-CPE procedure after pre-treatment with two sample preparation procedures. The total Ag contents of the samples were determined via spectrophotometry using the multiple standard addition method around the LOQs against sample blanks to control the possible matrix effect.

## 2.5. UA-CPE procedure

A typical UA-CPE requires the following steps: an aliquot (5.0 mL) of the pre-treated sample solutions in two separate calibration ranges of 2.5–125 and 4–160  $\mu\text{g L}^{-1}$  of Ag<sup>+</sup> ions (in solvent and beer/wine matrices) in optimization step, and 25-mL of a sample solution containing no more than 0.25  $\mu\text{g}$  of Ag(I) in pre-concentration step for 250  $\mu\text{L}$  of Tris-modified poly(SMIm) copolymer in THF (up to 0.1 g/100 mL), 100  $\mu\text{L}$  of 0.02 mol L<sup>-1</sup> Histidine, 250  $\mu\text{L}$  of 0.1% (v/v) CH<sub>2</sub>O, 1.3 mL of 5.0% (v/v) of Triton X-114 plus Triton X-100 (4:1, v/v), 60  $\mu\text{L}$  of 4.0% (w/v) SDS and 4.0 mmol L<sup>-1</sup> KCl, were sequentially mixed in a centrifuge tube of 50-mL, adjusted to pH 5.0 with 100  $\mu\text{L}$  of 0.04 mol L<sup>-1</sup> B-R buffer solution, and then completed to 50 mL by the water. The mixture was sonicated for 12 min at 45 °C. After reaching to equilibria for efficient and complete complex formation, separation of the phases was achieved by centrifugation at 3000 rpm for 5 min. Due to become viscous of the surfactant-rich phase, the bulk aqueous phase was easily separated and decanted. To reduce the viscosity of the surfactant-rich phase for spectrophotometric measurements and facilitate the sample proceeding, it was diluted to a volume of 0.4 mL with THF as diluent of both micellar phase and Tris-modified imide copolymer matrix. Finally, after extraction with two sample preparation procedures, the total Ag contents of the selected beverages were in parallel determined by spectrophotometry at 346 nm against sample blank using the multiple standard addition method around the method LOQs in order to control the possible matrix effect. Also, it has been observed that in analysis of sample matrices with degrees of alcohol ranging from 2.5–12%, there is not a significant matrix effect with signal enhancements of 6.31% and 12.7% in slope and intercept of the matrix-matched calibration curve, respectively to represent the sample matrix.

## 2.6. Statistical analysis

The average and standard deviation of the analyte concentrations were calculated for analysis of each sample matrix. The obtained results for two SRMs and samples were statistically evaluated by employing the Student's *t* test, and the calculated *t*-values were compared with the tabulated *t*-value for four and eight degrees of freedom at the 95% confidence level.

### 3. Results and discussion

#### 3.1. Structural and morphological characterization of nanocomposite by FT-IR, <sup>1</sup>H-NMR, XRD and SEM/EDX

Surface functional groups on the copolymer structures before and after modification were comparatively evaluated and characterized by using ATR-FTIR and <sup>1</sup>H-NMR spectra of solids converted to film form. From spectral data of reaction products that progress with ring opening and closing, imidation process was verified by means of imide ring peaks appearing at 1780, 1721 and 1708 cm<sup>-1</sup>. After modification, the intensity of absorption band at 620 cm<sup>-1</sup> gradually increased as a result of incorporation of Fe<sub>3</sub>O<sub>4</sub> NPs into the copolymer matrix while the only two absorption bands at 800 and 896 cm<sup>-1</sup> from the absorption bands of 580, 620, 800 and 896 cm<sup>-1</sup> appeared in IR spectrum of pure Fe<sub>3</sub>O<sub>4</sub> NPs were disappeared. This suggests the successful binding and thoroughly dispersion of Fe<sub>3</sub>O<sub>4</sub> NPs to polymer matrix. Other remaining FT-IR, <sup>1</sup>H-NMR and XRD spectral/diffraction peak details related to surface functional groups and crystal (or amorphous) structure of magnetic copolymer where the Fe<sub>3</sub>O<sub>4</sub> NPs exhibits partly a homogenous dispersion in copolymer matrix before and after modification were represented and discussed in detail in our preliminary two studies (Zengin, 2019; Zengin et al., 2020).

Additionally, scanning electron microscopy (SEM) was employed to explore the surface morphology and elemental analysis of the synthesized composite material. Figs S1(a–c) show the SEM images of poly(SMA), poly(SMIm)-Tris and poly(SMAm)-TrisA-Fe<sub>3</sub>O<sub>4</sub> polymeric nanocomposite, respectively. The morphology of poly(SMIm)-Tris reveals that the imidic copolymer has more homogenous and plate-like structure than that of original poly(SMA) in spongy structure in Figs S1(a), and the average diameter of the observed particles in SEM image can be estimated to be lower than 100 nm in nanoscale with reasonable monotony and grainy shape in Figs S1(b). The SEM image of poly(SMIm)-Tris-Fe<sub>3</sub>O<sub>4</sub> demonstrates an aggregate structure that consists of magnetic nanoscale crystallites that are collected as small pseudo-spherical particles with approximate sizes in the range of 10–50 nm and are stacked with each other, which makes plate-like morphology in Figs S1(c). The successful synthesis of the magnetic nanocomposite was qualitatively further confirmed by the chemical composition analyzed by energy dispersive X-ray (EDX). Figs S1(d) shows the distribution of C, O, Fe and N elements. The low abundance of the N peak on the background in the EDX spectrum is relatively due to the fact that the Tris-modified copolymer matrix containing a single N-atom has a relatively large molar mass as a result of modification with Tris. In fact, this peak is more evident in the imidic copolymer matrix (based on ring closure by condensation) obtained by thermal treatment of amidic copolymer, poly(SMAm) at 150 °C. Na and Cl residual peaks are due to the separation and purification processes by filtration after the precipitation of the copolymer matrix with dilute aqueous ethanolic solution of NaCl.

#### 3.2. The mechanism for extraction of trace Ag<sup>+</sup> ions

Prior information on the extraction mechanism, explanations and their literature supports were moved to ESI, and details are easily accessible from there (Supplementary material).

It is believed that extraction mechanism proceeds by proton coupled CT among reagents participating into the extraction process at pH 5.0 for pre-concentration/determination of trace Ag<sup>+</sup> ions by the present method as follows:

(1) 2CH<sub>2</sub>C=O + H<sub>2</sub>O → HCOOH and CH<sub>3</sub>OH, base catalyzed Cannizzaro disproportionation in presence of histidine at pH 5.0

(2) HCOOH + His → HisH<sup>+</sup> + HCOO<sup>-</sup>, proton transfer

(3) AgL<sup>+</sup> + HisH<sup>+</sup> → AgL(His)<sup>+</sup> + H<sup>+</sup>, proton transfer and pH dependent complex formation where L is Tris-modified cyclic poly(SMIm) with carbonyl, tertiary N-atom groups

(4a) 2AgL<sup>+</sup> + H<sub>2</sub>O → Ag(OH)L<sup>+</sup> + H<sup>+</sup> + Ag,

(4b) 2AgL(His)<sup>+</sup> + H<sub>2</sub>O → Ag(OH)L(His)<sup>+</sup> + H<sup>+</sup> + Ag,

ligand or ligands induced disproportionation as a function of pH at 195 and 343 nm with isobestic point at 312 or 310 nm

(4c) 2Ag(OH)L(His)<sup>+</sup> + H<sub>2</sub>O → Ag(OH)<sub>3</sub>His + AgL<sup>+</sup> + His + H<sup>+</sup>, further disproportionation due to be instable or metastable of Ag<sup>2+</sup> ions with pK<sub>a1,2</sub> values of 5.35 and 8.35 where CT process is about four times faster at pH = 5.5 (Asmus et al., 1978; Kestner and Allred, 1972; Ali et al., 2004).

Finally, ion-pair formation based on CT selectively proceeds by extracting into the core and/or surface of the mixed nonionic surfactant micelles in presence of SDS as both stabilizer and counter-ion acting like a concentration-dependent auxiliary ligand at pH 5.0 as follows:

(5) AgL<sup>+</sup> + ionic surfactant, SDS → [AgL(SDS)] Ion-pair formation, before detection at 346 nm by micro-volume UV–vis spectrophotometer

#### 3.3. Optimization of the main variables affecting extraction process

During use of poly(SMIm)-Tris-Fe<sub>3</sub>O<sub>4</sub> NPs functional nanocomposite in UA-CPE process for accurate/reliable analysis of trace Ag<sup>+</sup> ions, it is needed to standardize it. There is need to the CRMs being compatible with the sample matrix for standardization of nanostructure especially when having selective surface functional groups for Ag<sup>+</sup> ions. At this condition, in case of using the newly synthesized-functional co-polymeric structure at hydrophilic character as selective and sensitive probe for the analytical determination purposes, it is recommended to (i) optimize the effective parameters to reach the highest sensitivity and reproducibility, (ii) statistically evaluate the reliability of the method in terms of accuracy and precision, and (iii) comparatively analyze the real time samples by matrix-matched calibration or standard addition method. In this study, details of the optimization process for triplicate measurements of 100 μg L<sup>-1</sup> Ag<sup>+</sup> by using one-variable-at-a-time method, analytical figures of merit and some statistical evaluations are as follows:

##### 3.3.1. Effect of pH and buffer concentration

It is of highly importance to select appropriate chelating agent and metal ions to form a hydrophobic complex when metal ions are extracted by the UA-CPE. The complex is extracted to surfactant phase. The extraction efficiency depends on the acidity of the solution as the pH has an impact on the overall charges of the analyte, thus affecting the generation of the complex between the metal and the surface active functional groups.

The complex formation and its chemical stability are the two important factors involved in the separation and pre-concentration of metal ions by UA-CPE. They need to present sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase. The pH plays a critical role on complex formation and subsequent extraction and has been a significant parameter for UA-CPE. Thus, extraction efficiency depends on the pH at which complex formation is investigated. The UA-CPE of Ag<sup>+</sup> ions as a function of pH and calibration sensitivity at concentration levels of 2.5, 25 and 100 mg L<sup>-1</sup> were carried out in the pH range of 3.0–10.0. The results are shown in Fig. 1 (a–b). The recovery for Ag<sup>+</sup> ions sharply increased with increasing pH from 3.0–5.0, and reached a maximum with pH at 5.0. At low pHs, the low recoveries for Ag<sup>+</sup> ions were observed owing to the incomplete complex formation among reagents in reaction media. When the pH is in a range of 5–10, it could be a problem for the hydrolysis of Ag<sup>+</sup> ions due to sharp decrease in sensitivity. At lower and higher pHs than 5.0, the low recoveries for Ag<sup>+</sup> ions were observed owing to the incomplete CT complex formation among reagents in reaction media, hydrolysis of Ag<sup>+</sup> ions and inhibition of efficient proton coupled CT among reagents with increasing pH. At higher pHs than 5.0, another cause can be base catalyzed Cannizzaro disproportionation of formaldehyde chosen as reductant in this study, 2CH<sub>2</sub>O + H<sub>2</sub>O → CH<sub>3</sub>OH + HCOOH where both cyclic imide structure and histidine moiety act as a base, so as to lead to a modification in complexation based on CT among Ag<sup>+</sup> ions and reagents. Taking into

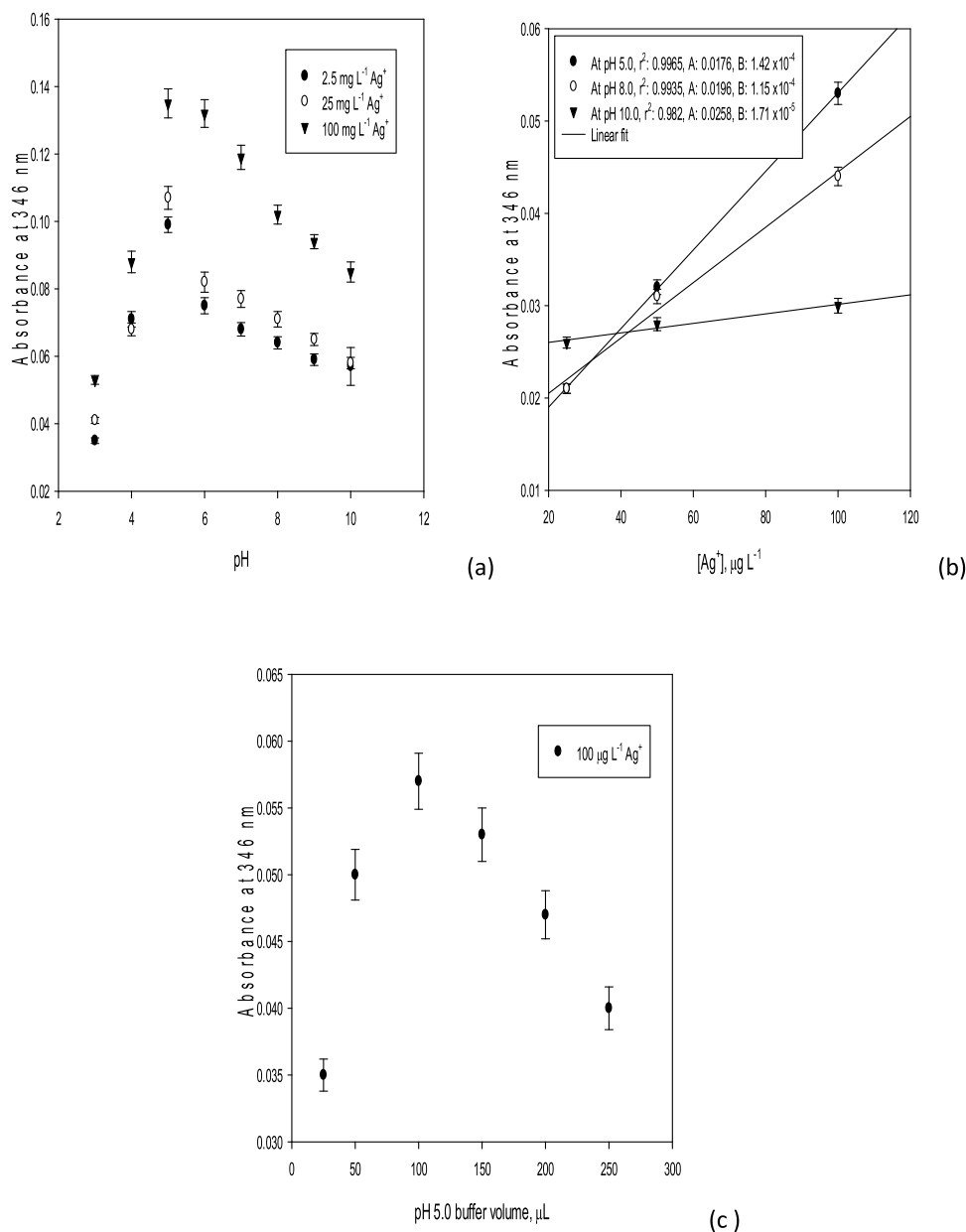


Fig. 1. Effect of (a) pH, (b) linear dependence of calibration sensitivity to pH for concentration levels of 25, 50 and 100 mg L<sup>-1</sup> Ag<sup>+</sup> at 346 nm and (c) pH 5.0 buffer volume on absorbance of 100 µg L<sup>-1</sup> Ag<sup>+</sup> ions as a measure of calibration sensitivity.

account all these factors, a pH value of 5.0 as a result of participation of carbonyl, nucleophilic Tris-N moiety on cyclic Tris-modified-copolymer into the complexation, and pH and CT sensitive imidazole group of histidine in presence of formaldehyde and SDS in terms of an extractable complex formation of Ag<sup>+</sup> ions at tetrahedral geometry was chosen to be optimal for further studies.

The effect of buffer concentration at pH 5.0 on the sensitivity in Fig. 1 (c) was also studied in volume range of 25–250 µL of B–R buffer solution at 0.04 mol L<sup>-1</sup>. The best sensitivity was obtained at a volume of 100 µL for Tris-modified imidic copolymer. At lower and higher buffer volumes, the sensitivity for Ag<sup>+</sup> ions were gradually decreased. Perhaps, this may be due to the reducing nature of citric acid as a component of the buffer and its competitive nature with the complexing ligands available. Therefore, a buffer volume of 100 µL for selective extraction of Ag<sup>+</sup> ions was adopted as optimal for further studies.

### 3.3.2. Effect of Tris-modified imide copolymer concentration

Chelating agent is one of the important factors influencing the

extraction efficiency. As can be seen in Fig. 2, the extraction of Ag<sup>+</sup> ions was carried out in the Tris-modified copolymer concentration ranging from 50 to 350 µL. The sensitivity as a measure of quantitative extraction of Ag<sup>+</sup> ions sharply increased with increasing chelating copolymer matrix concentration in range of 50–250 µL of its solution at 0.1 g/100 mL in THF, and reached a maximum at a volume of 250 µL. However, when copolymer solution volume in THF is higher than 250 µL, the sensitivity gradually declines. This decrease in sensitivity could be due to formation of extractable ion-associate by intermolecular interactions (like weak hydrogen bonding and π-π stacking) among excess Tris-modified chelating copolymer (in fact, containing pH- and concentration-dependent functional groups such as C=O, cyclic tertiary-N and -OH, including phenyl ring) and other reagents in absence of Ag<sup>+</sup> ions at pH 5.0, so as to lead to an increase in sample blank. Therefore, the optimal volume for Tris-modified imide copolymer was considered to be 250 µL in THF for further studies.

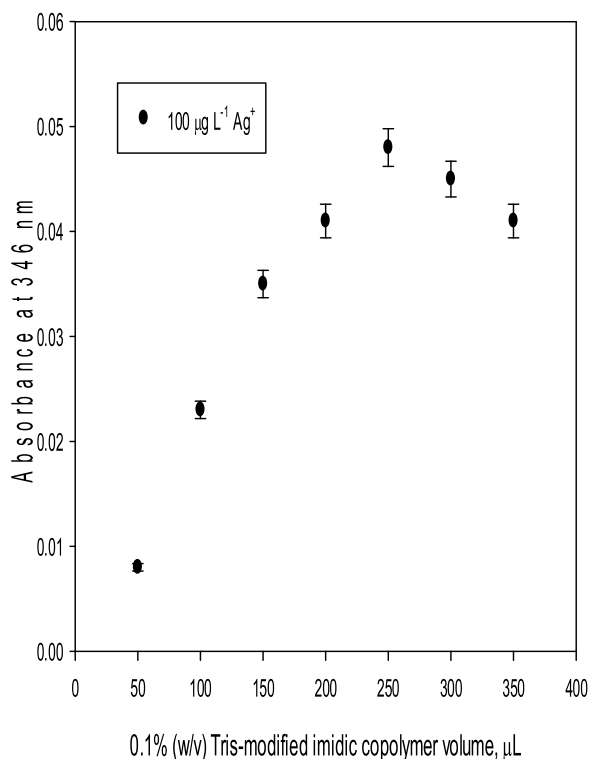


Fig. 2. Effect of 1.0% (w/v) Tris-modified imidic copolymer volume in THF on absorbance as a measure of sensitivity.

### 3.3.3. Effect of histidine and formaldehyde concentrations

Histidine is a pH sensitive coordination ligand for soft metal ions such as  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^+/\text{Cu}^{2+}$  and  $\text{Au}^+/\text{Au}^{3+}$  with  $\text{pK}_a$  values of 1.8 ( $-\text{COOH}$ ), 6.0 (imidazole) and 9.18 ( $-\text{NH}_2$ ), including  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions where L-histidine shows absorption maximum at 309 nm by  $n-\pi^*$  transition in UV region, but 321/420 nm, and 372/390 nm by inter-ligand charge transfer (ILCT) and metal to ligand charge transfer (MLCT) under ligand field effect in presence of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions in pH range of 4.0–10.0, respectively (Medvidović-Kosanović et al., 2018; Czoika et al., 2008; Kipp et al., 2004; Sun and Kirschenbaum, 2018). Also, it is a cyclic

amino acid with isoelectric  $\text{pH}_{\text{pzc}}$  of 5.49 in zwitterion structure, which can be easily oxidized by pH controlled CT in redox environment. Imidazole group is particularly one of suitable elements for pH sensitive molecular switches. Imidazole forms the side chain of histidine and its  $\text{pK}_a$  (6.10) is well in near to neutral pHs. Furthermore, the protonated and the non-protonated forms of imidazole are chemically very different. The non-protonated form has essentially a hydrophobic and aromatic character whereas the protonated form is hydrophilic and positively charged. Consequently, the nature of chemical interactions differs significantly at pHs above or below the  $\text{pK}_a$ . At pH 5.0 the imidazole group is protonated, and prefers a hydrophilic environment. Thus, an ion-association pair of consisting of histidine and another hydrophobic residue (herein, chelating cyclic imide copolymer matrix and mixed surfactant, SDS-Triton X-114 plus Triton X-100) could function as a pH-sensitive “His button.” It “closes” tightly at lower and higher pHs than 5.0, but selectively “opens” at pH 5.0 especially in presence of synergistic SDS with opposite charge to facilitate oxidation by CT, because hydrophobic species are repelled by the charged form of histidine (Katarina et al., 2006; Hosoba et al., 2009a,b). Because of all these reasons, histidine concentration as a promoter can also be considered to be one of the important factors influencing the extraction efficiency. As can be seen in Fig. 3 (a), the extraction of  $\text{Ag}^+$  ions was carried out in the histidine volumes ranging from 25 to 1500  $\mu\text{L}$  at a concentration of  $0.02 \text{ mol L}^{-1}$ . The sensitivity as a measure of quantitative extraction of  $\text{Ag}^+$  ions sharply increased with increase in histidine volume from 25 to 100  $\mu\text{L}$ , and reached a maximum at a volume of 100  $\mu\text{L}$ . However, when its volume is higher than 100  $\mu\text{L}$ , the sensitivity gradually decreases. This decrease in sensitivity could be due to an increase in blank signal in absence of trace  $\text{Ag}^+$  ions. Another cause can be an imine adduct formation between increasing histidine concentration and formaldehyde based on Schiff base formation,  $\text{CH}_2=\text{N}-$ , by condensation in presence of  $\text{Ag}^+$  ions at pH 5.0. Therefore, it is concluded that a volume of 100  $\mu\text{L}$  is optimal for further experiments.

The effect of formaldehyde concentration on extraction efficiency was investigated at volumes ranging from 50 to 350  $\mu\text{L}$  at a concentration of 0.1% (v/v). As can be seen in Fig. 3(b), the extraction efficiency linearly increased with increasing volume in 50–250  $\mu\text{L}$ , and reached a maximum sensitivity at a volume of 250  $\mu\text{L}$ . However, when its volume is higher than 100  $\mu\text{L}$ , the extraction efficiency gradually decreases. This decrease in signal could be due to an increase in blank signal in absence of trace  $\text{Ag}^+$  ions. Another cause can be an imine adduct formation

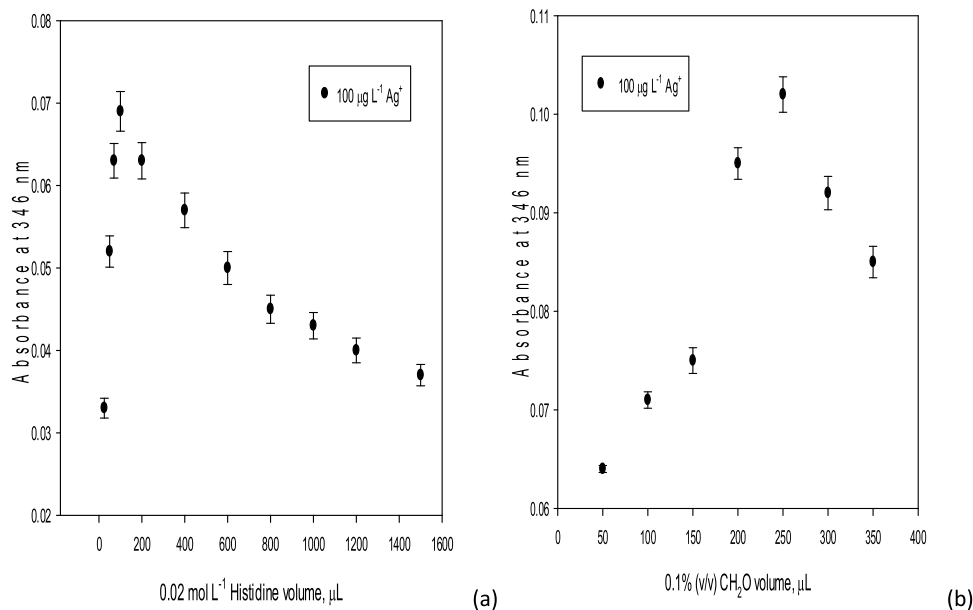


Fig. 3. Effect of (a)  $0.02 \text{ mol L}^{-1}$  Histidine volume (b) 0.1% (v/v)  $\text{CH}_2\text{O}$  volume on absorbance as a measure of sensitivity.

between increasing histidine concentration and formaldehyde based on Schiff base formation,  $\text{CH}_2=\text{N}-$ , by condensation in presence of  $\text{Ag}^+$  ions at pH 5.0. Therefore, it is concluded that a volume of 100  $\mu\text{L}$  is optimal for further experiments.

### 3.3.4. Effect of SDS, and the mixed Triton X-114 plus Triton X-100 concentrations

The concentration of ionic and non-ionic surfactants used in the UA-CPE plays key roles in extraction process. In presence of mixed non-ionic surfactants, Triton X-114 and Triton X-100 (4:1, v/v) as extractant in pre-concentration of trace  $\text{Ag}^+$  ions, at initial the ionic surfactant, SDS in volume ranges of 20–200  $\mu\text{L}$  at 4.0% (w/v) was adopted as a synergistic auxiliary ligand in extraction step. The sensitivity in Fig. 4 (a) sharply increased in range of 20–50  $\mu\text{L}$  for Tris-modified imidic copolymer, poly (SMIm), reached to a maximum at 50  $\mu\text{L}$  and gradually decreased at higher volumes than 50  $\mu\text{L}$ . At low SDS concentrations, this sharp increase in sensitivity may be due to synergistic relationship between pH and SDS concentration in microheterogeneous environment. In fact, it is believed that this is resulted from sharp decrease in critical micelle concentration (CMC) of SDS in presence of 4  $\text{mmol L}^{-1}$  KCl as electrolyte at pH 5.0 where the CMC of SDS is ranged from 8.08 to 1.99 in unbuffered (in water) and buffered media (50  $\text{mmol L}^{-1}$  phosphate buffer, pH 7.0), respectively (Fuguet et al., 2005; Thongngam and McClements, 2005; Mobin et al., 2013). However, the decrease in sensitivity at higher concentrations may be due to increase in analyte blank as a result of extractable ion-pair formation between SDS and protonated poly(SMIm) and histidine ligands via pH-sensitive carbonyl and imidazole groups in absence of  $\text{Ag}^+$  ions. Therefore, SDS volume of 50  $\mu\text{L}$  (equivalents to a concentration of 0.139  $\text{mmol L}^{-1}$ ) was considered to be enough in this study.

Triton X-114 is one of the non-ionic surfactants extensively used in UA-CPE as extractant due to its advantages such as commercial availability with high purity, low toxicity and cost as well as high density of the surfactant-rich phase thus promoting the phase separation by centrifugation, relatively low cloud point temperature and low CMC in combination with Triton X-100. In order to be able to monitor very low levels of silver in beverage matrices such as beer and wine, such a mixture was conceived and implemented to achieve low analyte blank and high calibration sensitivity. As a result, different volumes of Triton X-114-Triton X-100 mixture (4:1, v/v) in Fig. 4(b) were investigated ranging from 0.25 to 1.5 mL at a concentration of 5.0% (4:1, v/v) for

checking the extraction efficiency. As can be seen in Fig. 4(b), The sensitivity for 100  $\mu\text{g L}^{-1}$   $\text{Ag}^+$  ions linearly increased with an increase in mixed surfactant volume from 0.25 to 1.25 mL for poly(SMIm), and reached to a maximum at nearly a volume of 1.25 mL. The recovery gradually decreases when the concentration of Triton X-114 is higher than 1.25 mL. Such observations can be ascribed an increase in volume and viscosity of the micellar phase. Thus, a volume of 1.25 mL of the mixed non-ionic surfactants at 5.0% (v/v) was adopted to be optimal for further studies in order to achieve the highest sensitivity in spectrophotometric detection of  $\text{Ag}^+$  ions at 346 nm.

### 3.3.5. Effect of incubation time and temperature

The largest analyte pre-concentration factor is possible when the UA-CPE process is performed with equilibration temperature well above the cloud point temperature of the mixed micellar system. Therefore, the incubation temperatures ranging from 20 °C to 65 °C and time between 1 and 20 min in ultrasonic bath (300 W, 40 kHz) were studied. From the results, it has been observed that an equilibration time and temperature of 12 min and 45 °C is enough to reach the best sensitivity with maximum recovery for Tris-modified imide copolymer.

### 3.3.6. Effect of centrifugation time at 3000 rpm

Effect of centrifugation time on the UA-CPE procedure was investigated in range of 1–20 min for fast phase separation. From the results, it has been observed that the phase separation is completed in a centrifugation time of 5 min at 3000 rpm, and found to be enough for complete UA-CPE.

### 3.3.7. Effect of the ionic strength

In general, the addition of salt could decrease the solubility of aqueous sample phase and lead to enhancement of the dispersion of the analyte into the surfactant rich phase by the “salting-out effect” phenomenon. The presence of salt can increase the incompatibility between the water structures in the hydration shells of analyte and surfactant macromolecules, which can reduce the concentration of “free water” in the surfactant-rich phase and, consequently, reduce the volume of the phase (Bezerra et al., 2005). In order to investigate the effect of ionic strength on the extraction efficiency, various experiments were performed by adding different amounts of KCl (in range of 25–250  $\mu\text{L}$ , 2.0  $\text{mol L}^{-1}$ ) in a centrifugation tube of 50-mL. Other experimental conditions were kept constant during the analysis. The results show that

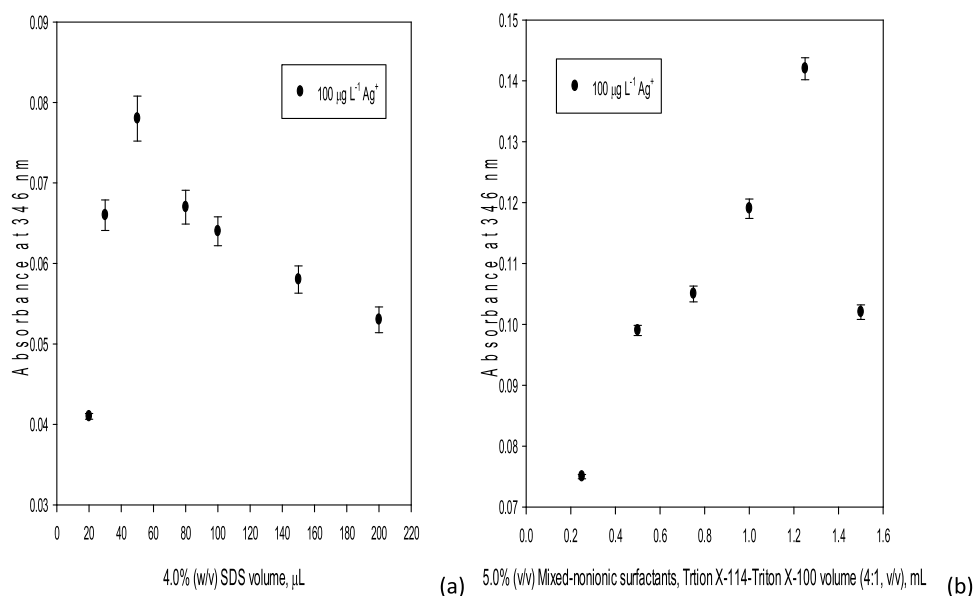


Fig. 4. Effect of (a) 4.0% (w/v) (SDS volume) (b) 5.0% (v/v) mixed-nonionic surfactants, Triton X-114 plus Triton X-100 (4:1, v/v) volume on absorbance as a measure of sensitivity.

ionic strength has linearly a significant effect on the sensitivity up to a volume of 150  $\mu\text{L}$  (equivalents to a concentration of 4  $\text{mmol L}^{-1}$ ). At higher volumes than 150  $\mu\text{L}$ , there is not a significant increase in sensitivity. Thus, ionic strength was kept constant at a salt concentration of 4  $\text{mmol L}^{-1}$  in order to obtain reproducible and stable analytical signals.

### 3.3.8. Effect of diluents

In order to facilitate the detectability of the sample solution by spectrophotometry, it was necessary to decrease the viscosity of the surfactant-rich phase. Different solvents, such as acetone, acetonitrile, ethanol, methanol, THF and solutions of ethanol and methanol acidified with 0.2  $\text{mol L}^{-1}$   $\text{HNO}_3$ , were tried in order to select the one producing the best results regarding sensitivity, reproducibility, and stability of the signal. The best result was obtained with THF. Aliquot of THF (0.2 mL) was added to the surfactant-rich phase after phase separation, in which the micellar phase (approx. 0.2 mL) is diluted to a volume of 0.4 mL for a pre-concentration factor of 62.5 from pre-concentration of optimal 25-mL sample (in the range of 5–35 mL). This amount of THF was chosen to ensure a sufficient volume of the sample for maximum sensitivity. For smaller volumes, the reproducibility of the signals was very poor, whereas for higher volumes, there was a decrease in the signal due to dilution.

### 3.4. Method validation

Under the optimal conditions, the performance of the method was studied in detail. The method allows a low detection limit of 0.77  $\mu\text{g L}^{-1}$  by the solvent-based calibration curves ( $n$ : 6) in linear range of 2.5–125  $\mu\text{g L}^{-1}$  with determination coefficient of 0.993 while it allows a detection limit of 1.10  $\mu\text{g L}^{-1}$  by the matrix-matched calibration curves ( $n$ : 6) in linear range of 4–160  $\mu\text{g L}^{-1}$  with determination coefficients of 0.992. In order to minimize the possible matrix effect and instrumental signal fluctuations, matrix-matched standard calibrations curves, consisting of ten concentration levels (0, 5, 10, 25, 50, 75, 100, 125, 150 and 200  $\mu\text{g L}^{-1}$ ) for beverage extracts, were set up by spiking these different amounts of analyte into sample extracts. Blanks (samples with zero addition of the analyte) were simultaneously quantified using the standard addition, and the levels of  $\text{Ag}^+$  ions present in the samples were subtracted. To evaluate the performance of the calibration curves, all the samples were also analyzed using a standard addition method based on spiked with three levels of analyte standards (0, 5, 25, 100  $\mu\text{g L}^{-1}$ ) in both solvent and sample extracts. The spiked sample extracts and blanks were run consecutively in the instrument. It has been observed that there is not a significant difference between slopes of calibration curves with a matrix effect of 6.31%, so as to cause enhancement in signal at 346 nm. Also, the two-sided Student's  $t$ -test was also checked to see if there was a matrix effect. For this purpose, from calibration data (each one, for  $n$ : 6) the two average slopes were compared using the formula  $m_1 - m_2 = \pm t \times s_{\text{pooled}} \times (n_1 + n_2/n_1 \times n_2)^{1/2}$  for degrees of freedom of  $(n_1 + n_2) - 2$  and 95% confidence level. From the results, it was observed that the calculated  $t$ -value (1.54) is lower than the critical  $t$ -value (2.23). This indicates that there is no significant matrix effect. Similarly, the confidence intervals of slopes of  $(7.76 \pm 0.14) \times 10^{-4}$  and  $(8.25 \pm 0.17) \times 10^{-4}$  were determined at 95% confidence level for each of the calibration curves where  $t_{(n-2)}$  is 2.78 for degrees of freedom of 4, and it was observed that the confidence intervals coincided with recovery efficiency of 94%. The confidence interval was described as  $m \pm t_{(n-2)} \times s_m$  where  $m$  is the slope and  $s_m$  is the standard deviation of slope. The corresponding regression equation was found to be Abs:  $(7.76 \pm 0.5) \times 10^{-4}C + (3.86 \pm 0.2) \times 10^{-3}$  for calibration in solvent while it was Abs:  $(8.25 \pm 0.6) \times 10^{-4}C + (4.35 \pm 0.3) \times 10^{-3}$  for matrix-matched calibration in sample extracts where Abs is absorbance and  $C$  is the concentration of silver, respectively. The limits of detection and quantification (LODs and LOQs,) calculated by using the expressions at  $3.3 \times s_{\text{blank}}/m$  and  $10 \times s_{\text{blank}}/m$ , respectively where  $s_{\text{blank}}$  is the

standard deviation of twelve replicate measurements of blanks and  $m$  is the slope of the calibration curves, according to ICH (2005) were 0.85 and 2.57  $\mu\text{g L}^{-1}$  for the solvent-based calibration curves where  $\sigma$  is the standard deviation of twelve replicate measurements of the blank and  $m$  is the slope of the calibration curve while these values ranged from 1.21 and 3.67  $\mu\text{g L}^{-1}$  for the matrix-matched calibration curves. The repeatability and intermediate precision (as RSDs) of the extraction process for both calibration approaches were found to be in ranges of 3.5–5.1% and 3.8–5.7%, and 4.1–6.3% and 4.5–7.1% for  $\text{Ag}^+$  ions (5, 25 and 100  $\mu\text{g L}^{-1}$ ,  $n = 5$ ,  $3 \times 5$  for same day and three consecutive days) with a recovery percentage in range of 91.5–98.5%. In fact, regarding repeatability, the RSD values are lower than the maximum allowed RSD value of 21% in the studied concentration range, according to AOAC (2012). In a similar way, regarding intermediate precision in literature (Stöckl et al., 2009), the RSD values below 10% are recommended when analyzing elements. As an indicator of the method accuracy, the recovery percentages (92.1–98.5% and 91.5–96.7% for two calibration curves) are also within the acceptable limit values of 60–115% established by AOAC (2012) for the studied concentration range. From pre-concentration of 25-mL sample solution, a pre-concentration factor of 62.5 was obtained with a sensitivity enhancement of 23.2-fold.

Herein, it can be defined as the ratio between the original aqueous matrix sample volume and the surfactant-rich phase volume,  $CF = V_{\text{matrix}}/V_s$ . However, if the mass transfer of metal ions into the micellar phase is not quantitative, it is better represented by the enrichment factor, EF. Thus, EF, which is also described as sensitivity improvement factor, can be calculated by the ratio of the slopes of the calibration curves with and without pre-concentration (Bezerra et al., 2005).

All the analytical parameters related to the pre-concentration system are represented in detail in Table 1.

### 3.5. The selectivity study

The effect of potential interference of some anionic and cationic species on the pre-concentration and determination of  $\text{Ag(I)}$  was studied. In these experiments, aqueous solutions containing  $\text{Ag}^+$  ions (100  $\mu\text{g L}^{-1}$ ) with the addition of interfering ions were treated in tolerance ratios ranging from 1:25 to 1:2000, according to the recommended UA-CPE procedure under the optimal conditions, and the results are given in Table S2. Table S2 depicts the tolerance limits of the diverse ions, i.e. interferent-to-analyte ratios in which the relative error was less than  $\pm 5.0\%$  in terms of a variation in signal. Only an interference at low tolerance ratios (in range of 25–150) has been observed from  $\text{Hg}^{2+}$ ,  $\text{Cu}^+/\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{As}^{3+}$  and  $\text{Sb}^{3+}$  ions forming a stable complex with primary ligand, Tris modified-poly(SMIm) matrix and/or secondary ligand, histidine at pH 5.0. The serious interfering effect of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions up to 250-fold excess over silver was greatly suppressed and improved using 1.5 mL of 0.01  $\text{mol L}^{-1}$  iminodiacetic acid (IDA) solution. Especially, copper is thought to be complex with a similar mechanism. Indeed, copper is present in higher concentrations (with totally a safe limit of 0.3–0.5  $\text{mg L}^{-1}$ ) than silver in beer and wine samples. Moreover, due to a reducing environment, it is clear that copper is in +1 oxidation step in these samples rich in polyphenols and anthocyanin's. Therefore, it is possible to complex selectively with both histidine and cyclic modified imidic copolymer in the presence of SDS at pH 5.0, depending on the concentration, in a similar way to those of  $\text{Ag}^+$  ions. In the literature, in the microextraction of copper with methimazole based on an ionic liquid (IL), it has been observed that in the reduction step by cyclic voltammetry, copper ( $\text{Cu}^{2+}$  or  $\text{Cu}^+$  ions selectively is complexed with both cationic cyclic thioamide, 2-butylthiolonium, [mimSBU<sup>+</sup>] and anionic bis (trifluoromethanesulfonyl) amide, [NTf<sub>2</sub><sup>-</sup>] around pH 5.0 (Reyna-Gonzalez et al., 2010). Similarly, in the presence of SDS depending on its charge and the pH of the environment (at pH 5.5), it was observed that copper forms an ion-associated complex



**Table 1**

Analytical figures of merit of the developed method.

Calibration type	From regression analysis				Precision		Accuracy		
	Linear range, $\mu\text{g L}^{-1}$	Slope $\pm$ SD	Intercept $\pm$ SD	Determination coefficient, $r^2$	$^a$ LOD, $\mu\text{g L}^{-1}$	$^a$ LOQ, $\mu\text{g L}^{-1}$	Repeatability (as RSD% for same day, 5, 25 and 100 $\mu\text{g L}^{-1}$ , n: 5)	Intermediate precision (as RSD% for three consecutive days, 5, 25 and 100 $\mu\text{g L}^{-1}$ , n: 5)	Recovery %
By calibration curve in solvent	2.5–125	$(7.76 \pm 0.5) \times 10^{-4}$	$(3.86 \pm 0.2) \times 10^{-3}$	0.993	0.85	2.57	3.5–5.1	4.1–6.3	92.1–98.5
By matrix-matched calibration curve prepared from beer/wine extracts	4.0–160	$(8.25 \pm 0.6) \times 10^{-4}$	$(4.35 \pm 0.3) \times 10^{-3}$	0.992	1.21	3.67	3.8–5.7	4.5–7.1	91.5–96.7
$^b$ Matrix effect, %	+6.31%								
$^c$ Sensitivity enhancement factor (EF)	23.2								
$^d$ Pre-concentration factor (CF)	62.5								

$^a$  Limits of detection and quantification ((LODs, LOQs) for  $\text{Ag}^+$  ions were determined according to the expressions at  $3.3 \times s_{\text{blank}}/m$  and  $10 \times s_{\text{blank}}/m$ , respectively (where  $s_{\text{blank}}$  is the standard deviation of twelve replicate measurements of blanks and  $m$  is the slope of the calibration curves).

$^b$  Based on comparison of slopes of two calibration curves established in solvent and sample extracts by using formula,  $\text{ME}\% = (1 - m_{\text{solvent}}/m_{\text{matrix-matched}}) \times 100$ .

$^c$  Ratio of slopes of calibration curves established with and without pre-concentration.

$^d$  Ratio of the bulk aqueous sample solution volume to volume of the surfactant-rich phase.

with histidine (for especially  $\text{Cu}^+$ ,  $\beta = 10^{17}$ ) (Venelinov et al., 2006). The interference of  $\text{Sn}^{2+}$  and  $\text{Mn}^{2+}$  ions were suppressed up to 500-fold using 0.2 mL of 0.025 mol  $\text{L}^{-1}$   $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  solution. Also, the interference of  $\text{As}^{3+}$  and  $\text{Sb}^{3+}$  ions was suppressed up to 500-fold after pre-oxidation of  $\text{As}^{3+}$  and  $\text{Sb}^{3+}$  to  $\text{As}^{5+}$  and  $\text{Sb}^{5+}$  with 0.01 mol  $\text{L}^{-1}$   $\text{H}_2\text{O}_2$  solution in alkaline medium. As can be seen from Table S2, it is clear that the developed UA-CPE method is relatively selective in terms of major species present in real samples. The recoveries in the range of 92.0–101.5% with a lower RSD than 3.5% were obtained for different tolerance ratios for  $\text{Ag}^+$  ions. The results indicated that matrix did not affect the absorbance of  $\text{Ag}^+$  ions at 100  $\mu\text{g L}^{-1}$  at any of the studied tolerance ratios.

### 3.6. Accuracy of the method

The accuracy of the method was controlled by analysis of two certified samples, SRM 1643a, d Trace elements in water and natural water via standard addition method based on spiking at levels of 5, 10 and 15  $\mu\text{g L}^{-1}$  before extraction and spectrophotometric analysis. It can be seen that the results found by the present method in Table 2 are statistically in good agreement with their certified values where the experimental t-values are lower than the critical t-value of 2.31 for 4 degrees of freedom at confidence interval of 95%. Also, after spiking, it is clear that recovery and precision levels can be quantitatively accepted with RSDs in range of 2.45–6.10% and recovery rates of 100.8–102.4% for five replicate measurements. The percentage of recoveries (R) of spike standards were calculated as follows:

$$R (\%) = (C_m - C_0)/C_m \times 100 \quad (1)$$

where  $C_m$  is a value of metal in a spiked sample,  $C_0$  the value of metal in a sample, and  $m$  is the amount of metal spiked.

### 3.7. Analytical applications of the method

The proposed method was applied for the determination of low levels of  $\text{Ag}^+$  ions (as total Ag) in beverage samples. The results are shown in Tables 3a and 3b). It was found that total Ag at sub-ppb levels were observed in beverage samples studied. The accuracy of the method was verified in term of statistical evaluation by means of Student's t-test of experimental data based on matrix-matched calibration for two quality control samples and multiple standard addition method after two

**Table 2**

The accuracy and/or validity of the method developed for  $\text{Ag}^+$  ions at pH 5.0 for analysis of total Ag levels in two certified water samples with low and high levels (n: 5).

CRMs	Certified, $\mu\text{g L}^{-1}$	$^a$ Observed, $\mu\text{g L}^{-1}$	RSD %	Recovery %	The one paired t-test $^b$ , $t_{\text{exp}}$
SRM 1643d Trace elements in water	$1.270 \pm 0.057$	$1.30 \pm 0.08$ (n: 10) <sup>c</sup>	6.15	102.4	0.84
SRM 1643a Trace elements in natural water	$8.081 \pm 0.046$	$8.15 \pm 0.20$ (n: 5)	2.45	100.8	0.77

$^a$  The mean plus SD of five replicate measurements using the proposed method.

$^b$  The experimental t-values calculated by using  $t = N^{1/2} (\mu - x_{\text{average}}) / s$  for five replicate measurements at confidence interval of 95% in which the critical t-value is 2.78 for 4 degrees of freedom at confidence interval of 95%.

$^c$  The mean plus SD determined from ten replicate measurements of sample by multiple standard addition method based on spiking with 5, 10 and 15  $\mu\text{g L}^{-1}$   $\text{Ag}^+$  around LOQ of the method, including sample.

sample preparation procedures for selected beer and wine samples, and recovery rates obtained from replicate measurements with and without spiking. The selected food samples were spiked with the target analyte at concentration levels of 10  $\mu\text{g L}^{-1}$  including two quality control samples, before extraction and analysis. Extractions were carried out under the optimized reagent conditions, intra-day and inter-day accuracy and precision measurement results (as the percent recoveries and RSDs, n: 5) are summarized in Tables 3a and 3b). Accuracy (percentage recovery values) from matrix-matched calibration approach and standard addition method were in the range of 96–103% with RSDs lower than 7.1 and 7.7% for two sample preparation procedures. From direct measurement results without spiking via two calibration approaches to compensate for the matrix effect in spectrophotometric analysis, it has been observed that the total Ag levels are in range of 2.7–5.5  $\mu\text{g L}^{-1}$  in wine samples while they are in range of 2.5–4.2  $\mu\text{g L}^{-1}$  in beer samples. It can be seen that total Ag levels in the wine samples, including beer, are agreement with the results (<0.001–4.92, 0.55–12.16  $\mu\text{g L}^{-1}$ ) found in their

**Table 3a**The intra- and inter-day accuracy and precision studies of free Ag<sup>+</sup> levels measured in the selected two quality control samples via matrix-matched calibration curve.

Sample	Added, µg L <sup>-1</sup>	Accuracy/precision					
		Intra-day (n: 5)			Inter-day (n: 3 × 5)		
		<sup>a</sup> Found, µg L <sup>-1</sup>	Recovery%	RSD%	<sup>a</sup> Found, µg L <sup>-1</sup>	Recovery%	RSD%
White wine	–	3.8 ± 0.2	–	5.3	4.1 ± 0.2	–	4.9
	10	14.1 ± 0.5	103	3.5	14.5 ± 0.6	104	4.1
Beer without alcohol	–	2.5 ± 0.12	–	4.8	2.8 ± 0.15	–	5.4
	10	12.7 ± 0.4	102	3.2	13.1 ± 0.5	103	3.8

<sup>a</sup> The mean plus its standard deviation of five replicate measurements obtained by using matrix-matched calibration approach in which 5.0 mL of the pre-treated and extracted-sample solutions were independently analyzed with and without spiking with 5, 10 and 15 µg L<sup>-1</sup> after dilution of 1:5-fold with dilute, 2.0% (v/v) HNO<sub>3</sub>.

**Table 3b**

The analysis results of total Ag levels in beer and wine samples by the developed spectrophotometric method (n: 5).

Sample	Added, µg L <sup>-1</sup>	By the standard addition method						<sup>**</sup> The paired Student's <i>t</i> -test <sup>b</sup> , <i>t</i> <sub>exp</sub>	<sup>**</sup> Variance ratio <i>F</i> -test <sup>c</sup> , <i>F</i> <sub>exp</sub>
		*After extraction with 3.0 mL of 0.02% (w/v) thiourea in 5.0 mL of 2.0% (v/v) HNO <sub>3</sub> for 12 min at 50 °C in ultrasonic bath			*After extraction with 5.0 mL of mixture of 3.0 mol L <sup>-1</sup> HNO <sub>3</sub> and 0.3 mol L <sup>-1</sup> H <sub>2</sub> O <sub>2</sub> (3:2, v/v), and then adding 5.0 mL 1.0 mol L <sup>-1</sup> CH <sub>3</sub> COOH and 2.5 mL of 1.0 mg L <sup>-1</sup> Bi(III) for 7.0 min at 40 °C in ultrasonic bath				
		<sup>a</sup> Found, µg L <sup>-1</sup>	Recovery %	RSD %	<sup>a</sup> Found, µg L <sup>-1</sup>	Recovery %	RSD %		
Red wine <sub>1</sub>	–	5.5 ± 0.3	–	5.4	5.3 ± 0.3	–	5.7	1.05	
	10	15.2 ± 0.7	97	4.6	15.5 ± 0.7	102	4.5	–	
Red wine <sub>2</sub>	–	2.8 ± 0.2	–	7.1	2.6 ± 0.2	–	7.7	1.58	
	10	12.5 ± 0.6	97	4.8	12.7 ± 0.6	101	4.7	–	
Red wine <sub>3</sub>	–	4.2 ± 0.3	–	7.1	4.3 ± 0.3	–	7.0	0.53	
	10	13.8 ± 0.6	96	4.3	14.2 ± 0.6	97	4.2	–	
White wine <sub>1</sub>	–	3.8 ± 0.2	–	5.3	3.7 ± 0.2	–	5.4	0.79	
	10	13.4 ± 0.6	96	4.5	13.5 ± 0.6	96	4.4	–	
White wine <sub>2</sub>	–	2.7 ± 0.2	–	7.4	2.8 ± 0.2	–	7.1	0.79	
	10	12.3 ± 0.6	96	4.9	12.5 ± 0.6	97	4.8	–	
Beer <sub>1</sub>	–	3.5 ± 0.2	–	5.7	3.4 ± 0.2	–	5.9	0.79	
	10	13.2 ± 0.5	97	3.8	13.1 ± 0.5	97	3.8	–	
Beer <sub>2</sub>	–	3.5 ± 0.2	–	5.7	3.4 ± 0.2	–	5.9	0.79	
	10	13.2 ± 0.5	97	3.8	13.3 ± 0.5	99	3.7	–	
Beer <sub>3</sub>	–	4.2 ± 0.2	–	4.8	4.3 ± 0.2	–	4.7	0.79	
	10	13.8 ± 0.5	96	3.6	14.0 ± 0.5	97	3.6	–	

<sup>\*</sup> The mean plus its standard deviation of five replicate measurements obtained by multiple standard addition method (after spiking with 5, 10 and 15 µg L<sup>-1</sup>) via two different sample preparation procedures to ensure from accuracy and precision of results after quantitatively pre-oxidation of colloidal and matrix bound organic/inorganic silver to Ag<sup>+</sup> after (i) extraction with 3.0 mL of 0.02% (w/v) thiourea in 5.0 mL of 2.0% (v/v) HNO<sub>3</sub> for 12 min at 50 °C, and (ii) extraction with 5.0 mL of mixture of 3.0 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.3 mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (3:2, v/v), and then adding 5.0 mL 1.0 mol L<sup>-1</sup> CH<sub>3</sub>COOH and 2.5 mL of 1.0 mg L<sup>-1</sup> Bi(III) as effective solubilizing and releasing agent (from inorganic bound Ag<sub>2</sub>S) for 7.0 min at 40 °C under ultrasonic bath conditions (40 kHz, 300 W) in sample extracts.

<sup>\*\*</sup> The accuracy and precision results based on statistical comparison of results with those obtained by standard addition method after two sample preparation procedures.

<sup>a</sup> The mean plus its standard deviation of five replicate measurements obtained by using two calibration approaches in which aliquot (5.0 mL) of the degassed, acidified, extracted and diluted sample solutions were independently analyzed by the matrix matched calibration and multiple standard addition method after dilution at ratio of 1:5 with dilute HNO<sub>3</sub> to overcome the matrix effect.

<sup>b</sup> The experimental *t*-values were calculated by using  $t = (x_{\text{average},1} - x_{\text{average},2}) / s_{\text{pooled}} \times [(N_1 + N_2) / (N_1 \times N_2)]^{1/2}$  for five replicate measurements at confidence interval of 95% in which the critical *t*-value is 2.78 for 8 degrees of freedom at confidence interval of 95%.

<sup>c</sup> The experimental *F*-values calculated by using  $F_{4,4} = S_1^2 / S_2^2$  for five replicate measurements at probability level of *p* = 0.05 in which the critical *F*-value is 5.05.

selective and sensitive analysis by ICP-OES and/or ICP-MS by two independent author groups in literature (Plotka-Wasylika et al., 2018; Geana et al., 2013). European law fixed at 100 µg L<sup>-1</sup> the maximum acceptable limit for Ag residues in wine, following the treatment with AgCl to eliminate or reduce off-odors (Commission Delegated Regulation (EU), 2015). In this study, the total Ag levels in the wines, including beer analyzed by the present method were well below the European legal limits, therefore, the wine and beer samples appeared to be safe as regards the risk related to the potentially toxic metal intake. Moreover, according to the paired Student's *t*-test, there is not statistically a significant difference between the results obtained by two sample preparation procedures from comparison of two average value. The results clearly show that the proposed UA-CPE method can be successfully applied to accurate and reliable determination of total Ag level in the

selected alcoholic beverage samples, which further indicates the capability of the method in the determination of the trace amounts of total Ag in real time samples containing different matrix components under the optimal conditions.

### 3.8. Comparison of the method with other reported methods

The method was compared with a variety of detection methods that had recently been reported in the literature for extraction, pre-concentration, and determination of Ag<sup>+</sup> ions from sample matrices. The analytical features of the method are given in Table S5. As can be seen from Table S5, it is evident that the method has quantitatively a wide linear working range for the poly(SMIm) matrix functionalized with Tris and Fe<sub>3</sub>O<sub>4</sub> NPs. Moreover, the LODs/LOQs of the method,

0.85/2.57 and 1.21/3.67  $\mu\text{g L}^{-1}$  for the two calibration approaches, is either better than or comparable with that of other methods which even use more sensitive detection techniques such as ET-AAS (or GFAAS) and FAAS after pre-concentration with CPE or different modes of CPE, SPE or different modes of SPE, DLLM and DLLM-SFOD (Ghaedi et al., 2009; Mohammadi et al., 2009; Araújo et al., 2010; Gao et al., 2010; Gürkan et al., 2016; Omidi et al., 2015; Yang et al., 2017; Karimi et al., 2011; Manzoori et al., 2007; Afzali et al., 2011; Fouladvandi and Elhami, 2017; Zengin, 2019). In fact, the sensitive detection techniques like ETAAS (or GFAAS), FI-FAAS require expert user in his/her research area, including expensive, complicated, time-consuming furnace programs and use of matrix modifiers. The more sensitive techniques such as ICP-OES and ICP-MS are costs of equipment, operating (Ar gas) and laboratory set up (air-conditioning), requires multiple high purity gases and high level of staff expertise, and interferences need to be controlled, including memory effect. Shortly, the method, based on sensitive/selective detection of sub-ppb levels of  $\text{Ag}^+$  ions by spectrophotometry at 346 nm, can be evaluated as simple, cost-effective, safe, eco-friendly, accurate, and reliable analytical detection tool with a pre-concentration factor of 37.5-fold from pre-concentration of 35-mL sample because it uses low-volume non-toxic organic solvents, and shows more favorable properties as simplicity, quickness, and relatively low cost when compared to SPE, and different modes of SPE requiring generally longer analysis time, high aqueous sample volume, and manipulation of sample as well as possibility of contamination, loss of analyte, risk of degradation of compounds during long analysis time, and less accuracy and precision. In addition, the method gave comparably accurate and reliable results in terms of linearity, accuracy, and intra-day and inter-day precision and provided an evidence of spectrophotometry's feasibility as an alternative approach to routine quality control of levels of low amounts of silver in other sample matrices.

#### 4. Conclusions

The current study reports for the first time the UA-CPE coupled micro-volume UV-vis spectrophotometry for total Ag determination. Herein, a fast, simple, fast and eco-friendly UA-CPE procedure for the selective extraction of the ion-pair complex based upon efficient CT among reagents (cyclic imidic copolymer matrix, histidine, SDS and formaldehyde) and silver at pH 5.0 before detection by spectrophotometer is presented. The findings represent improvement in micro-extraction methodology, assembling extensive studies on the technique as well as detailed discussion on the mechanism of action unlike the majority of CPE or UA-CPE in literature. The method exhibits high selectivity towards strongly interfering ions such as redox sensitive Cu and Fe exist at higher concentrations than that of Ag in beer and wine matrices. The developed technique represents a powerful tool in accelerating the extraction and separation processes, so as to facilitate pH-dependent coordination and mass transfer between two immiscible phases. Therefore, the results of this approach may bring novel opportunities for the development of sustainable analytical methodologies, and the trend will continue in the future for simultaneous determination of sub-ppb levels of Cu and Ag in edible vegetable oils by our research group despite challenges faced for developing ion-pairing reagents and/or chromophoric CT probes, including ionic surfactant (SDS or CTAB), for sensing various analytes. The current work can be upgraded to sub-ppb levels via pre-concentration through UA-CPE using the modified chelating copolymers in nanoscale. Finally, the present work will set the trend for coupling spectrophotometry with microextraction techniques and will be able to serve as a standard and direction for researchers in the field.

#### Compliance with ethics requirements

Authors have no financial relationship with the organization that sponsored the research.

#### Ethical approval

This article does not contain any studies with human or animal subjects.

#### CRedit authorship contribution statement

**H.B. Zengin:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation. **R. Gürkan:** Validation, Visualization, Writing - original draft, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jfca.2021.103814>.

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