Determination of Ag⁺ and Cu²⁺ ions in mixture samples obtained in the microwave assisted polyol process by differential pulse anodic stripping voltammetry (DPASV) method

Abstract: A simple and selective differential pulse anodic stripping voltammetry (DPASV) method for the determination of Ag⁺ and Cu²⁺ ions in mixture samples obtained in the microwave assisted polyol process was developed and validated. Analytical methods for the preparation of the reaction mixture for voltammetric analysis (dilute samples in the supporting electrolyte) were worked out and optimized. All measurements were conducted in three-electrode cell system equipped with glassy carbon electrode (GCE) as a working electrode, silver/silver chloride (Ag|AgCl|KCl (sat.)) as a reference and platinum wire as a auxiliary electrode. The optimal conditions for quantitative determination were obtained in an mixture Britton–Robinson buffer at pH 4.1 / ethylene glycol (100/1; v/v). The calibration curves of analysed compounds are linear within the range of concentration: 0.032 − 0.420 μg mL⁻¹ and 0.075 − 0.960 μg mL⁻¹ for Ag⁺ and Cu²⁺, respectively. Good linear behaviour over the investigated concentration ranges were observed with the values of $r^2$ higher than 0.996 for the silver and cooper ions. The accuracy of analytical determinations ranged from 0.4 to 3.6%. The levels of analysed ions in the reaction mixture can be successfully determined using this developed method with no matrix effect.

Keywords: Differential Pulse Anodic Stripping Voltammetry, Silver Ion, Cooper Ion, Polyol Process

1 Introduction

Silver and copper nanoparticles play very important roles in many different areas. Among the various metal nanoparticles, silver and copper nanoparticles have been widely investigated because they exhibit unusual optical, electronic, and chemical properties [1-3].

The traditional way to fabricate silver or copper nanoparticles (NPs) is the chemical reduction of Ag⁺ or Cu²⁺ ions in water or organic solvents in the presence of a stabilising agent (e.g. polyvinylpirrolidone). Silver and copper nanoparticles with various sizes were synthesized by the polyol process. The general polyol process involves the dissolution of a protecting agent or stabilizer in a polyol medium. The overall process can be summarized as follows:

$$\text{CH}_2\text{OH-CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$$

$$2\text{nCH}_3\text{CHO} + 2\text{Me}^{n+} \rightarrow 2\text{Me} + 2\text{nH}^+ + \text{nCH}_3\text{COCOCOCH}_3$$

Several methods have been reported for the quantitative determination of Ag⁺ and/or Cu²⁺ in different matrices including AAS (Atomic Absorption Spectrometry) [4-6], UV-Vis spectroscopy [7], ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) [8], fluorescence spectroscopy [9,10], RP-HPLC (Reversed Phase High Performance Liquid Chromatography) [11], MC-SPE (Multiplexed Colorimetric Solid Phase Extraction) [12], volumetric titration [13], potentiometric [14,15], gravimetric [16] or voltammetry [17-20]. Most of these methods requires the separation of ions from the nanoparticles.

Voltammetric methods are the most favourable techniques for the analysis of metal ions because of its low cost as well as high sensitivity. The content of...
silver and cooper nanoparticles in the reaction mixture exiting the microwave applicator is analysed indirectly by determining the content of other cations Ag⁺ and Cu²⁺ by differential pulse anodic stripping voltammetry (DPASV) method. The developed method enables the determination of Ag⁺ and Cu²⁺ ions in the reaction mixture at each stage of the process without having to separate the ions and nanoparticles.

A knowledge of product or substrate concentration is an important factor from the viewpoint of scaling up or determination of process kinetics. In the open literature that refers to the silver nanoparticles synthesis relatively small number of quantitative data are available on yield or final product concentration. Yields for the studied ions in the other protocols ranged from about 43 to 99% [4, 5,10,11,13].

In the present study, beside the basic researches referring elaboration conditions of determination nearby above-mentioned ions, also the application for reaction mixture was investigated. The procedure was successfully applied to the determination of Ag⁺ and Cu²⁺ ions. The main advantages of the proposed method are related to its rapidity, simplicity, and low cost. The aim of this work was to establish a simple, and sensitive method for determination of Ag⁺ and Cu²⁺ in reaction mixture samples.

2 Experimental procedure

2.1 Chemicals, reagents and solutions

Silver nitrate (min. 99.9% purity) was obtained from POCH (Gliwice, Poland). Silver acetate (anhydrous, 99% purity) and copper(II) acetate (monohydrate, 98.0-102.0% purity) were purchased from Alfa Aesar GmbH & Co KG, A Johnson Matthey Company (Karlsruhe, Germany). Polyvinylpyrrolidone K 25 (extra pure) was bought from Carl Roth GmbH + Co KG (Karlsruhe, Germany). Acetic acid (CH₃COOH), o-boric acid (H₃BO₃), o-phosphoric acid (H₃PO₄), and sodium hydroxide (NaOH), were purchased from POCH (Gliwice, Poland). Ethylene glycol (min. 99.0% purity) was obtained from CHEMPUR (Piekary Śląskie, Poland). All reagents and solutions used in this work were of analytical grade.

2.2 Buffers and solutions preparation

Britton–Robinson (BR) buffer solution at pH 4.1 was prepared by mixing 25 mL 200 μM NaOH solution with 100 mL of a mixed acid that contains 40 μM of each of o-boric, o-phosphoric and acetic acids (H₃BO₃-H₃COOH-H₃PO₄). The pH of the solutions was adjusted by mixing buffer components and was verified before each measurement.

Separate stock solutions of analysed compounds (silver and copper ions) at concentrations 1 mg mL⁻¹ were prepared in 10 mL volumetric flasks by dissolving the appropriate amount of reference substance in water.

Solutions of lower concentrations were prepared by dilution of stock solution in a mixture of BR buffer at pH 4.1/ethylene glycol (100/1, v/v).

Mixed standard solutions containing investigated compounds were prepared by mixing the appropriate amount of individual stock solutions and diluting these mixtures with mixture of BR buffer at pH 4.1/ethylene glycol (100/1, v/v).

All the solutions were prepared using double distilled water. Stock solutions were prepared at the beginning of the study and were stored at 4ºC. All solutions were kept in darkness.

2.3 Instrumentation

All voltammetric measurements were carried out using a potentiostat µAUTOLAB Type III (Eco-Chemie, The Netherlands); with glassy carbon electrode (GCE) as a working electrode (1.5 mm diameter), that was polished with 0.03 μm Al₂O₃ (Buehler), then ultrasonicated in a distilled water and finally rinsed with methanol. A platinum rod was used as a counter electrode, Ag|AgCl|KCl(sat.) electrode was used as a reference electrode (all electrodes purchased from Cypress Systems, Lawrence, USA). Voltammetric measurements were carried out in a 3 mL glassy electrochemical cell. All the measurements were automated and controlled through the programming capacity of the apparatus. Nitrogen was used for the removal of dissolved oxygen from the measured solutions. The pH of the buffered solutions was measured by an ELMETRON (Zabrze, Poland), Model CP-401 pH meter using a combined glass electrode. UV–vis spectra of silver or cooper nanoparticle suspensions were recorded using UV–vis spectrophotometer HITACHI U-2800A.

2.4 Optimization of parameters for analysed Ag⁺ and Cu²⁺

The potentials of oxidation cited in this article were measured relative to the Ag|AgCl|KCl(sat.) electrode.
The glassy carbon working electrode and platinum auxiliary electrode were polished manually to a mirror finish using an alumina (0.03 µm particle sizes) paste and thoroughly rinsed with purified methanol and deionized water between measurements. In the glass electrochemical cell 3 mL of analysed sample were placed. In the aim of removal oxygen, the solution was purged with pure nitrogen for 10 min (and for 30 s before each measurement).

After equilibrating time of 10 s the voltammetric curve was recorded in the potential range from −0.75 to +1.25 V (vs. Ag/AgCl/KCl (sat.)) for Ag⁺ and Cu²⁺ at a scan rate of 50 mV s⁻¹.

After the registration of the voltammograms for a specific sample, an appropriate amount of either a single-reagent or mixed standard solution was added to the electroanalytical cell by means of a micropipette. Each measurement was repeated six times using fresh sample solution to ensure reproducibility of the results. All of the electrochemical experiments were carried out at ambient laboratory temperature (22 ± 2ºC). Between experiments, the cell was treated with concentrated nitric(V) acid and then washed with water. Ag⁺ and Cu²⁺ ions were then analysed using the optimized voltammetric procedure. During the measurements, the solution in the cell was neither stirred nor aerated.

2.5 Calibration curves for analysed Ag⁺ and Cu²⁺ ions

The calibration curve method was applied to quantitative determination of analysed ions in model solutions. Calibration curves for Ag⁺ and Cu²⁺ were prepared separately. Working standard solutions, which were used for calibration curves preparation were prepared by adding to 2 mL mixture of BR buffer at pH 4.1 / ethylene glycol (100/1, v/v) adequately quantity of individual or mixing standard solutions. The calibration curves were measured six times. The obtained data were subjected to a regression analysis, and correlation coefficients were calculated for each compound using Excel.

2.6 Procedure of reaction mixture preparation

In order to check, the possibility of applying the proposed methods for the determination of Ag⁺ or Cu²⁺ in a reaction mixture was also tested. The developed method enables the determination of silver or copper ions without the need to develop two different methods (one for the silver ions and the other for the copper ions). Silver and copper ions have different peak potentials, and the standard addition method was applied for the determination of examined ions in reaction mixture samples.

Silver nanoparticles (Ag NPs) were fabricated in the microwave assisted polyol process that was realized in a flow system. In the experiments, temperature at the outlet of tubular reactor was kept as constant and ranged from 90 to 170°C. The final product was gathered in the chilled vessel and then examined. In the aforesaid method an ethylene glycol was used as reducing agent, silver acetate (AgOAc) as the Ag NPs precursor and polyvinylpirrolidone (PVP) with average molar weight ca. 24 kDa as stabilizing agent. Molar ratio Ag : PVP (in terms to monomer) was constant in all tests and equal to 1:7.

Cooper nanoparticles (Cu NPs) were prepared in a similar manner as the silver nanoparticles. In experiments, the temperature at the outlet of the tubular reactor was about 196°C (close to the boiling point). In the aforesaid method an copper(II) acetate Cu(OAc)₂ was used as (Cu NPs) precursor and PVP with average molar weight ca. 24 kDa as stabilizing agent. Molar ratio Cu : PVP (in terms to monomer) was constant in all tests and equal to 1:7. The process was realized in a flow system (25 L h⁻¹).

2.7 Separation of analysed ions from reaction mixture by diluting

A reaction mixture (1 mL) was poured into 10 mL glass flask and 9 mL of mixture Britton–Robinson buffer at pH 4.1 / ethylene glycol (100/1; v/v) was added. The mixture was then stirred for one minute.
3 Results and discussion

3.1 Development of DPASV method

DPASV was used in the voltammetric measurement due to its very good sensitivity as well as resolving power. DPASV technique is suitable for the simultaneous determination of mixtures of ions. A small difference in half-wave potentials of the analyzed compounds is sufficient for their simultaneous determination. The peak current depends on the concentration, chemical composition of the buffer solution, pH of the medium and instrumental parameters. Optimization of the proposed procedure was carried out to investigate the conditions that may affect on the obtained results.

When the potential was scanned in the range from -0.75 to +1.5 V, no oxidation peak was observed in the absence of silver ion. In the presence of silver ions, an oxidation peak appeared at about +0.3 V. The case was similar for the copper ions determination.

Representative voltammograms from determination of analysed ions (Ag⁺ and Cu²⁺) in mixture samples obtained in the microwave assisted digestion are presented in Fig. 5, showing an absorption peaks at 408 nm for silver and 591 nm for cooper nanoparticles.

Spectrophotometric measurements were carried out in 10 mm quartz cells with an integration time of 1 s. Absorbance values are corrected to Δλ = 10 nm path length. Spectra were recorded in the range 280 – 800 nm. Scan speed was 800 nm s⁻¹.

3.2 Calibration curves and linearity

The calibration curves were performed and evaluated by the least squares linear regression method. Calibration curves (y = ax + b) for analysed ions in model solutions were constructed by plotting the intensity of current (y) versus the concentrations (x) of the calibration standards. Concentrations of analysed ions were determined by calculation of the intensity of current and interpolation of the respective calibration curve. The calibration curves show linear response over the whole range of concentration used in the assay procedure. This allows the development of a calibration curves, which is used to determine the concentration of Ag⁺ and Cu²⁺ in the real samples. Calibration curves for silver and copper ions have the following form:

\[ y = 2.173 \times 10^{-8}x - 6.300 \times 10^{-10} \text{ for } Ag^+ \]
\[ y = 2.440 \times 10^{-8}x + 5.850 \times 10^{-10} \text{ for } Cu^{2+} \]

These calibration curves had a reliable reproducibility for the standard concentrations across the calibration range. High correlation coefficient values (\( r^2 \geq 0.997 \)) were achieved in relatively wide concentration ranges for the analysed ions. The height of peak current vs. concentration dependence was recorded in concentrations range 0.032 – 0.420 μg mL⁻¹ and 0.075 – 0.960 μg mL⁻¹, respectively. These calibration curves had a reliable reproducibility for the standard solutions. The results of regression analysis on calibration curves are reported in Table 1.

The peak current is proportional to the concentration of silver ion in the range from 0.032 to 0.420 μg mL⁻¹, with a detection limit of 0.01 μg mL⁻¹ and cooper ion in the range from 0.075 to 0.960 μg mL⁻¹, with a detection limit of 0.024 μg mL⁻¹.

3.3 Analytes recoveries

Dilution experiments were performed using standard solutions. The determination of the recovery rates was carried out from spiked ion-free supporting electrolytes. The absolute recovery was calculated for each analyte.
Obtained recovery results of spiked supporting electrolyte samples are given in Table 2.

The coefficient of variation for six successive determinations of \( \text{Ag}^{+} \) at 0.29 \( \mu \text{g mL}^{-1} \) concentration is 0.62\% and of \( \text{Cu}^{2+} \) at 0.56 \( \mu \text{g mL}^{-1} \) concentration is 1.06\%.

### 3.4 Limits of detection and quantification

The limits of detection (LOD) and limits of quantification (LOQ) for the analysed ions were calculated on the peak current using following equations: LOD = 3 x S.D./a and LOQ = 10 x S.D./a. Both LOD and LOQ values confirmed the sensitivity of the proposed methods.

The limit of quantification (LOQ) was between 0.031 \( \mu \text{g mL}^{-1} \) and 0.072 \( \mu \text{g mL}^{-1} \) for the analysed compounds (Table 1).

All the values of precision and accuracy including LOQ were within the specified ranges and therefore acceptable. Both LOD and LOQ values confirmed the sensitivity of the proposed methods.

### 3.5 Application of the method to reaction mixture

The developed DPASV methods for the \( \text{Ag}^{+} \) and \( \text{Cu}^{2+} \) ions determination were applied to reaction mixtures. Conditions of \( \text{Ag}^{+} \) and \( \text{Cu}^{2+} \) determination in reaction mixture were elaborated. Methods of reaction mixtures

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**Table 1:** Analytical parameters of calibration curves of examined ions in model solutions (n = 6).

| Ion  | Linear range (\( \mu \text{g mL}^{-1} \)) | \( A^1 \)   | \( B^2 \)   | \( r^{2.3} \) | LOD\(^4\) (\( \mu \text{g mL}^{-1} \)) | LOQ\(^5\) (\( \mu \text{g mL}^{-1} \)) |
|------|------------------------------------------|------------|------------|------------|---------------------------------|---------------------------------|
| \( \text{Ag}^{+} \) | 0.032 – 0.420                             | 2.173E-8   | -6.300E-10 | 0.999      | 0.010                           | 0.031                           |
| \( \text{Cu}^{2+} \) | 0.075 – 0.960                             | 2.440E-8   | 5.850E-10  | 0.997      | 0.024                           | 0.072                           |

\(^1\)Slope; \(^2\)Intercept; \(^3\)Correlation coefficient; \(^4\)Limit of detection; \(^5\)Limit of quantification.

**Table 2:** Results of recoveries examination for \( \text{Ag}^{+} \) and \( \text{Cu}^{2+} \) from samples (n = 6).

| Ion  | Concentration added (\( \mu \text{g mL}^{-1} \)) | Concentration found (\( \mu \text{g mL}^{-1} \)) | S.D.\(^1\) (\( \mu \text{g mL}^{-1} \)) | C.V.\(^2\) (%) | Sx\(^3\) (\( \mu \text{g mL}^{-1} \)) | L\(^4\) (\( \mu \text{g mL}^{-1} \)) | Recovery (%)   |
|------|-----------------------------------------------|-----------------------------------------------|----------------------------------------|----------------|----------------------------------------|---------------------------------|----------------|
| \( \text{Ag}^{+} \) | 0.291                                          | 0.289                                          | 0.002                                  | 0.692          | 0.0008                                 | 0.289 ± 0.004                   | 99.31                       |
| \( \text{Cu}^{2+} \) | 0.560                                          | 0.562                                          | 0.007                                  | 1.064          | 0.002                                  | 0.658 ± 0.010                   | 100.36                      |

\(^1\)Standard deviation of concentrations found, \(^2\)Coefficient of variation of concentrations found, \(^3\)Standard deviation of the mean, \(^4\)Confidence interval (\( \alpha = 0.05 \), \( t = 4.303 \)).

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**Figure 4:** Differential pulse anodic stripping voltammograms obtained for determination of \( \text{Ag}^{+} \) and \( \text{Cu}^{2+} \) in mixture of BR buffer at pH 4.1 / ethylene glycol (100/1, v/v) on glassy carbon electrode.

**Figure 5:** UV–vis absorbance spectra of two nanoparticle solutions: \( \text{Ag} \) NPs (\( \lambda = 408 \text{ nm} \)) and \( \text{Cu} \) NPs (\( \lambda = 591 \text{ nm} \)).

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Determination of Ag⁺ and Cu²⁺ ions in mixture samples obtained in the microwave assisted polyol process.

The data proved the suitability of only diluting procedure for the determination of investigated compounds from reaction mixtures. Representative voltammograms of reaction mixture samples analysis are presented in Figs. 6 and 7.

The developed method allows the determination of Ag⁺ or Cu²⁺ ions in the reaction mixtures at any stage of the reaction.

3.6 Specificity

On voltammograms obtained for real samples no interfering peaks were observed near the peak potentials of the tested analytes (Figs. 6 and 7). To evaluate the specificity of the method analyzed Ag⁺ and Cu²⁺ ions in spiked reaction mixture samples.

4 Conclusion

We have developed and validated a new and reliable DPASV method for determination of Ag⁺ and Cu²⁺ ions and apply the method both to standard solutions and to reaction mixture samples. Developed by our method for determination of Ag⁺ and Cu²⁺ ions can be used as an alternative method to the existing spectrophotometric methods. Simple and effective sample preparation for analysis makes it an easy decision about applying the method for the determination of Ag⁺ and Cu²⁺ ions in model solutions and reaction mixture samples. Received very good separation of the analyzed analytes, enabling them to simultaneous determination. The good validation criteria results of the method allowed its use in the quantification of these compounds. In conclusion, the DPASV assay method, developed in this study using a glassy carbon electrode was proved to be acceptable for assaying Ag⁺ and Cu²⁺ ions in reaction mixture samples. Acceptable recovery (99.3 – 100.4%) shows that the proposed method can be used for the determination of Ag⁺ and Cu²⁺ ions in reaction mixture obtained in the microwave assisted polyol process.

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