Preconcentration and Voltammetric Determination of Silver Ions On PVF^+Cl^- Modified Platinum Electrode

PVF^+Cl^- Modifiye Platinyum Elektrotlar ile Gümüş İyonlarının Voltametrik Tayini ve Önderiştirmesi

Research Article

Mutlu Sönmez Çelebi[1*], Haluk Özyörük[2], Serdar Abacı[2]
[1]Ordu University, Faculty of Science and Arts, Department of Chemistry, Ordu, Turkey
[2]Hacettepe University, Faculty of Science, Department of Chemistry, Ankara, Turkey

ABSTRACT

Preconcentration of silver (I) ions on poly(vinylferrocenium)/chloride (PVF^+Cl^-) modified platinum electrode prior to differential pulse anodic stripping determination of the metal was reported. At the optimum conditions, a calibration curve having two linear parts with different slopes was obtained at the concentration intervals $1x10^{-3}$ M – $5x10^{-5}$ M and $5x10^{-6}$ M – $1x10^{-8}$ M. The detection limit was determined as $1x10^{-9}$ M. The relative standard deviation was calculated as 9.56 % (n = 6) for 1 x 10^{-6} M Ag^+ solution. Interferences of Hg^{2+}, Fe^{3+} and Pb^{2+} ions which are capable of forming chloride complexes were examined. The modified electrode was applied to determination of silver ions in spiked water samples.

Key Words
Poly(vinylferrocenium), Modified electrode, Pt disc electrode, Silver determination

ÖZET

Gümüş(I) iyonlarının poli(vinilferrosenyum)/klorür (PVF^+Cl^-) ile modifiye edilmiş platin elektrotunda önderiştirilmesi ve diferansiyel puls anodik sıyırma voltametrisi ile tayini çalışıldı. Belirlenen optimum koşullarda $1x10^{-3}$ M - $5x10^{-5}$ M ve $5x10^{-6}$ M - $1x10^{-8}$ M derişim aralıklarında iki adet doğrusal kısmı bulunan bir kalibrasyon eğrisi elde edildi. Tayin sınırının $1x10^{-9}$ M olduğu yöntem için $1x10^{-6}$ M Ag^+ çözeltisiyle bağıl standart sapma 9.56 % (n = 6) olarak hesaplandı. Ayrıca klorür kompleksleri oluşturduğu bilinen Hg^{2+}, Fe^{3+} ve Pb^{2+} iyonları için girişim çalışması yapıldı ve modifiye elektrot, gümüş iyonları eklenmiş çeşme suyunda test edildi.

Anahtar Kelimeler
Poli(vinilferrosenyum), Modifiye elektrot, Pt disk elektrot, Gümüş tayini.

Article History: Received: Oct 9, 2014; Revised: Nov 9, 2014; Accepted: Nov 21, 2014; Available Online: Dec 27, 2014.

Correspondence to: M. Sönmez Çelebi, Ordu University, Faculty of Science and Arts, Department of Chemistry, 52200 Ordu, Turkey.
Tel: +90 452 2345010/1672 E-Mail: mutlucelebi@odu.edu.tr

INTRODUCTION

Silver is an important element in our daily life. It is extensively utilized in the photographic and imaging industry, jewellery, mirrors, dental fillings, and other electrical and electronic applications. These widespread applications caused increased silver content of environmental water. The toxicity of silver ranges through several orders of magnitude depending on the silver forms. Monitoring of this element is crucial due to its potential toxicity even at low concentrations. As for human health, silver is suspected of being a contaminant, while it usually interacts competitively with essential nutrients, especially with selenium, copper, Vitamin E, Vitamin B12 and Ag accumulation in the body may lead to a grayish-blue skin discoloration (known as Argyria) [1]. Therefore, the development of simple and highly sensitive methods to evaluate the Ag levels is required for the sake of its utility as well as toxicity.

Determination of silver ion was widely studied using various methods such as atomic absorption spectrometry (AAS) [2-5], fluorescence spectroscopy [6-10], inductively coupled plasma mass spectrometry (ICP-MS) [11,12] and electrochemical methods. Electrochemical methods generally preconcentrate silver ions by complexation prior to voltammetric determination [11-19]. Preconcentration of silver species without a complexing agent has also been studied [20,21].

Chemically modified electrodes (CMEs) are an active research area in many aspects of science and technology, having potential applications in diverse fields such as electroanalysis, chemical sensors, molecular electronics, and solar energy conversion. The metal surfaces that are coated with polymeric films are examples of chemically modified electrodes. These surfaces were intensively investigated because of the possibilities they offer in the fields of electrocatalysis and electroanalysis. One type of macrostructures which are named as redox or electroactive polymers contain a pair of reduced and oxidized groups and the hopping of electrons between these redox pairs is the reason for the electrical conductance [22]. $PVF^+ClO_4^-$ is a good example for the latter type of conducting materials. In addition to its own electroactivity that is caused by this redox pair, diffusion of other electroactive species through the film and subsequent charge transfer at the metallic surface underneath can also take place. The redox centers in the structure can also act as mediator for the charge transfer from substrate to some depolarizers. The type of the solvent, the nature of the electrolyte and its concentration affect the rates of the electron transfer between the electroactive sites and the diffusion of the other depolarizers through the film [19]. PVF^+ was used in several studies as a sensor platform [23-30].

The aim of this study is to develop a modified surface for detection of low amounts of Ag(I). The electrode was prepared by electrodeposition of $PVF^+ClO_4^-$ film onto the platinum surface and then Cl^- was incorporated into the polymer matrix via anion exchange with ClO_4^-. Ag(I) in the solution reacted with Cl^- to form AgCl. After the Ag(I) accumulation at the modified electrode, silver ions were reduced to metallic silver applying a suitable potential and determined by differential pulse anodic stripping voltammetry (DPASV).

MATERIALS AND METHODS

Apparatus

The cyclic voltammetric and potential controlled coulometric studies were carried out with PAR system, which consists of Model 175 Universal Programmer, Model 173 Potentiostat and Model 179 Digital Coulometer. The differential pulse anodic stripping voltammetric studies were performed with PAR Model 174A Polarographic Analyzer. Cyclic voltammograms and differential pulse anodic stripping voltammograms were recorded with EG&G PAR Model RE0150 X-Y recorder.

A platinum (Pt) disc electrode ($A = 7.85x10^{-3}$ cm^2) was used as the working electrode. Before each experiment, the working electrode was polished with slurry of Cr_2O_3 with water, then rinsed with triple distilled water, cleaned in ultrasonic bath and dried.

In the methylene chloride medium, a Ag/AgCl electrode immersed in a separate compartment containing methylene chloride/0.1 M TBAP solution with a saturated amount of AgCl was used as the reference electrode and a Pt wire in separate compartment containing methylene chloride/0.1 M TBAP solution was used as the counter electrode.

In aqueous medium, saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire electrode with a surface area of 2 cm^2 in spiral form was used as the counter electrode.

Reagents and Solutions

PVF was prepared by chemical polymerization of vinylferrocene (Alfa Product) at 70°C for 24 h using 2,2'-Aso-bis(2-methyl-propionitrile) (AIBN) as the initiator [31]. Methylene chloride (Aldrich), which was used for preparing polymer solutions, was washed with concentrated H_2SO_4 (Merck), triple distilled water, Na_2CO_3 (Merck) (5%), and triple distilled water respectively. Then it was distilled over P_2O_5 (Merck) [32].

Deionized water obtained from NANOpure DIamond Analytical ultrapure water system was used to prepare 10^{-3} M stock solution of Ag^+ from $AgNO_3$ (BDH, 99.8% pure). NaCl solutions were prepared using triple distilled water with NaCl (Carlo Erba). Hg^{2+}, Fe^{3+} and Pb^{2+} solutions were prepared from $HgCl_2$ (BDH, Analar), $FeNO_3$ (Merck) and $Pb(NO_3)_2$ (BDH, Analar) respectively.

Tetra-n-butyl ammonium perchlorate (TBAP) was used as the supporting electrolyte in the polymer solution. TBAP was obtained by the reaction of tetra-n-butyl ammonium hydroxide (40 % aqueous solution, Merck) with perchloric acid (BDH) and recrystallised from the 1:9 mixture of water and ethyl alcohol by volume several times. It was then dried at 120 °C under vacuum for 12 hours. This salt was always kept under nitrogen atmosphere.

NaCl (Carlo Erba) was used as the supporting electrolyte in the electrochemical experiments carried out in aqueous medium without further purification.

The polymer solution and the NaCl solution that used as the supporting electrolyte were deoxygenated by bubbling pure nitrogen gas (BOS).

Procedure

First, $PVF^+ClO_4^-$ film was electrodeposited onto the electrode surface by the electrooxidation of 1.0 mg/mL PVF solution in methylene chloride containing 0.1 M TBAP at +0.7 V vs. Ag/AgCl. The thicknesses of $PVF^+ClO_4^-$ films were controlled by the charge passed during the electroprecipitation. A charge of $1x10^{-3}$ C corresponded to $1.32x10^{-6}$ moles of the oxidized PVF per cm^2 (dry thickness of ~300 μm, which corresponds to about $3x10^5$ layers) [33].

In the second step, chloride ions were incorporated into the film via anion exchange [34], by immersing the $PVF^+ClO_4^-$ coated electrode in NaCl solution at open circuit. However, the concentration of the NaCl solution used in this step was important because it was observed that accumulation of more than a certain amount of Cl^- damaged the film and finally caused the film to rupture.

So-formed PVF^+Cl^- modified Pt disc electrode was rinsed with water and immersed in Ag (I) ion solution at open circuit in order to preconcentrate silver species in the polymeric matrix via complex formation with Cl^-. After the preconcentration step, the electrode was rinsed with water and placed in the electrochemical cell containing 1.0 M NaCl. Finally, a suitable potential was applied to the cell for a few minutes to reduce the silver ions and differential pulse anodic stripping voltammogram was recorded.

RESULTS AND DISCUSSION

$PVF^+ClO_4^-$ is a redox type polymer which may be capable of holding some ions with adsorption. The ability of $PVF^+ClO_4^-$ to preconcentrate Ag (I) was investigated. The electrode was immersed into Ag (I) solution for 15 min, subjected to reduction potential of -0.2 V vs SCE for 5 min and DPASV was recorded. Figure 1a shows the stripping peak of silver. This peak was not good enough to detect low amounts of Ag (I) in solutions. However, when the $PVF^+ClO_4^-$ film was kept in Cl^- solution for 15 min before inserting into Ag(I) solution, it was determined that nearly 20 fold increase was observed in the stripping peak current of silver (Figure 1b).

High stripping current was promising for the use of these surfaces for Ag(I) detection. The mechanism of the process can be proposed as follows. $PVF^+ClO_4^-$ is open to anion exchange [35]. When $PVF^+ClO_4^-$ was kept in Cl^- solution, Cl^- ions entered into polymer matrix. It is also known that, Ag(I) and Cl^- form a complex and this complex enhanced the amount of Ag(I) on the surface, consequently, stripping peak increased. The mechanism can be summarized as follows:

$PVF^+ClO_4^- + Cl^- \rightarrow PVF^+Cl^- + ClO_4^-$ Anion Exchange (1)

$Ag^+ + PVF^+Cl^- \rightarrow PVF^+Cl^- (Ag^+)$ Complexation (2)

$PVF^+Cl^- (Ag^+) \rightarrow PVF^+Cl^- (Ag)$ Reduction (3)

$PVF^+Cl^- (Ag) \rightarrow PVF^+Cl^- (Ag^+)$ Stripping (4)

Several parameters such as polymeric film thickness, Cl^- concentration etc. were investigated to determine the optimum conditions for maximum sensor performance.

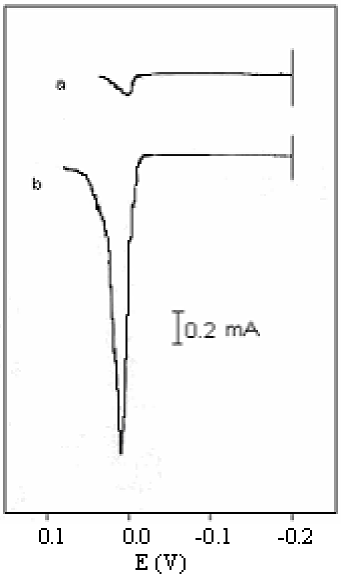

Figure 1. Differential pulse anodic stripping voltammogram of $PVF^+ClO_4^-$ film immersed in $1{\times}10^{-4}$ M Ag^+ solution for 15 min (a), $PVF^+ClO_4^-$ film immersed in 50 mM Cl^- solution for 15 min, then in $1{\times}10^{-4}$ M Ag^+ solution for 15 min, (b) after 5 min cathodic electrolysis at – 0.2 V vs. SCE. v= 5 mV/s.

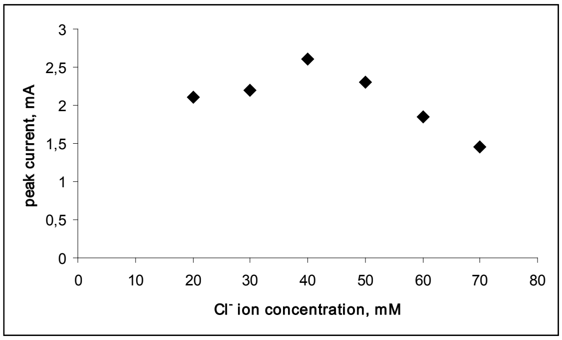

Figure 2. The effect of Cl^- ion concentration on the oxidation peak current for $1{\times}10^{-4}$ M Ag^+ (1.0 mC film thickness, 15 min immersion time in Cl^- ion solution, 15 min preconcentration time, – 0.2 V electrolysis potential, 5 min electrolysis time).

Cl^- Concentration

Cl^- has a critical role in sensor performance as can be seen from mechanism given above. Figure 2 shows the effect of Cl^- concentration on the stripping peak current. Peak current initially increased with Cl^- concentration as expected but decreased surprisingly after 40 mM Cl^- concentration. There was an important visual observation during the experiments with Cl^- concentration greater than 40 mM. Polymeric films were ruptured and this rupture increased up to 80 mM Cl^- concentration and after this value, no surface coating remained. Thus, it was concluded that optimum Cl^- concentration is 40 mM and after this concentration Cl^- initiated pitting and that caused the rupture of the film.

The effect of immersion time in Cl^- solution was also important because the stripping peak current of silver decreased when an immersion time more than 15 min was used. The result supported our claim about the damaging effect of excess Cl^- ions deposited on the surface. Optimum immersion time in Cl^- solution was determined as 15 min.

Polymeric Film Thickness

The effect of polymeric film thickness on the stripping peak current was investigated by changing the charge passed during the electrooxidation of PVF and keeping the other variables constant (Figure 3). As can be seen from Figure 3, peak current increased up to a certain value (0.8 mC), then, started to decrease. This behavior can be attributed to several reasons. One can be damaging effect of excess chloride which was already observed. As the amount of

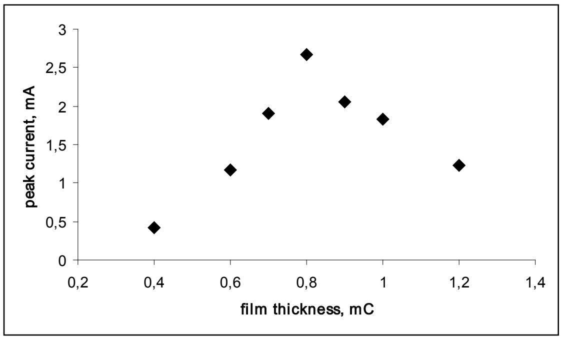

Figure 3. The effect of polymeric film thickness on the stripping peak current for 1×10^{-4} M Ag$^+$ (50 mM Cl$^-$ ion concentration, 15 min immersion time in Cl$^-$ ion solution, 15 min preconcentration time, – 0.2 V electrolysis potential, 5 min electrolysis time).

positively charged PVF$^+$ increased with increasing film thickness, amount of the accumulated Cl$^-$ enhanced, consequently, amount of Ag(I) increased with higher AgCl formation. However, after a certain value, greater amount of Cl degraded the polymeric matrix and decrease was observed. Another reason can be porosity effect. The change in the porosity of the polymer matrix at elevated film thicknesses might have caused observed decrease after 0.8 mC.

Preconcentration time

The change in stripping peak current of silver with increasing preconcentration time was investigated (Figure 4). The stripping peak current remained constant after 10 min because of diffusion limitations. The optimum preconcentration time was chosen as 5 min in order to ensure that the electrode is not saturated with silver ions at this time.

Reduction Potential

The choice of reduction potential for Ag(I) was considerably important. Because, both Ag$^+$ and PVF$^+$ could be reduced during the reduction at constant potential electrolysis. The latter is an unwanted process because when the amount of PVF$^+$ in the polymer matrix decreases, the amount of the negatively charged complex bound to ferrocenium form of the polymer also decreases. Different reduction potentials were applied in the range of 0.2 V to – 0.5 V vs. SCE and it was determined that, -0.2 V is the optimum reduction potential.

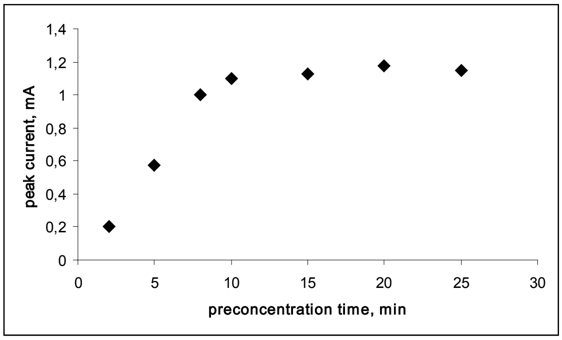

Figure 4. The effect of preconcentration time on the stripping peak current for 1×10^{-4} M Ag$^+$ (0.8 mC film thickness, 40 mM Cl$^-$ ion concentration, 15 min immersion time in Cl$^-$ ion solution, – 0.2 V electrolysis potential, 5 min electrolysis time).

Electrolysis Time

The change in stripping peak current with electrolysis time for reduction of Ag(I) to Ag was also studied to obtain the optimum time needed for reduction of metal ions. Up to 4 min, stripping peak current increased with increasing electrolysis time. However, when the electrolysis time exceeded 4 min, it was thought that the formed neutral metallic species released from the polymer matrix. The effect of this release, which caused the stripping peak currents to decrease, competed with the effect of electrolytic reduction of metal ions. When an electrolysis time was more than 4 min the optimum value is used the release of metallic species became dominant. Optimum electrolysis time was therefore determined as 4 min.

Analytical Characteristics

The change in stripping peak current with Ag(I) ion concentration was investigated applying optimum conditions (0.8 mC polymer film thickness, 40 mM Cl$^-$ ion concentration, 15 min immersion time in Cl$^-$ ion solution, 5 min preconcentration time, - 0.2 V electrolysis potential vs. SCE, 4 min electrolysis time). Every stripping peak current used in the calibration curves was obtained by subtracting the current obtained with PVF$^+$ClO$_4^-$ film from the current obtained with PVF$^+$Cl$^-$ film. Thus, stripping peak currents resulting from complex-formation of the silver ion with Cl$^-$ ion were used (Figure 5 and Figure 6).

At the optimum conditions, a calibration curve having two linear parts with different slopes was

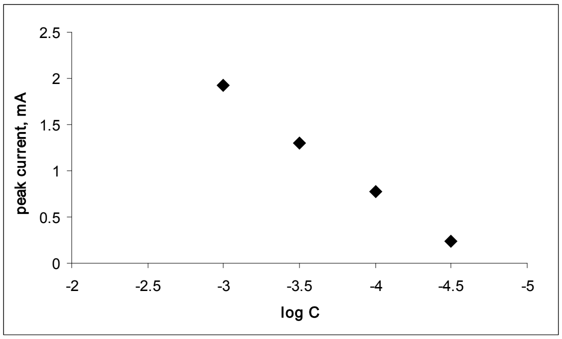

Figure 5. Calibration curve for Ag(I) solution at the concentration interval 1x10^{-3} M - 5x10^{-5} M at optimum conditions (0.8 mC film thickness, 40 mM Cl$^-$ ion concentration, 15 min immersion time in Cl$^-$ ion solution, 5 min preconcentration time, – 0.2 V electrolysis potential, 4 min electrolysis time)

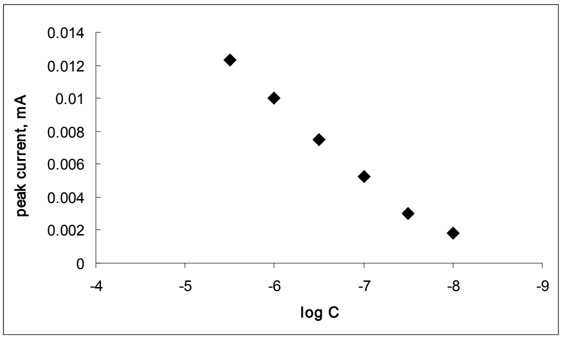

Fig. 6. Calibration curve for Ag(I) solution at the concentration interval 5x10^{-6} M - 1x10^{-8} M at optimum conditions (0.8 mC film thickness, 40 mM Cl$^-$ ion concentration, 15 min immersion time in Cl$^-$ ion solution, 5 min preconcentration time, – 0.2 V electrolysis potential, 4 min electrolysis time).

Table 1. % Interferences of some ions to the response of the electrode in 1:1 and 1:10 concentration ratios with respect to Ag$^+$.

Interfering ion	% Interference	
	1:1	*1:10*
Hg^{2+}	no interference	18.6
Fe^{3+}	89.3	99.0
Pb^{2+}	83.5	98.7

obtained at the concentration intervals 1x10^{-3} M - 5x10^{-5} M (Figure 5) and 5x10^{-6} M - 1x10^{-8} M (Figure 6). The detection limit at the optimum conditions was determined as 1x10^{-9} M for silver(I) ion.

The relative standard deviation was calculated as 9.56 % (n = 6) for 1 x 10^{-6} M Ag$^+$ solution. Interferences of Hg^{2+}, Fe^{3+} and Pb^{2+} ions which are capable of forming chloride complexes on the response of the electrode were examined. For this purpose, the voltammograms of 1x10^{-3} M Ag$^+$ solution were recorded in the presence of ions in 1:1 and 1:10 concentration ratios with respect to Ag$^+$. Results are presented in Table 1.

The proposed modified electrode was tested using water samples by spiking known concentrations of silver to water samples. The results are given in Table 2.

CONCLUSIONS

An easy to prepare, relatively inexpensive and sensitive electrode was developed for silver determination. Ag (I) ions were found to be readily preconcentrated in the polymeric matrix without applying any potential during the preconcentration step. The accumulation of silver ions was due to the formation of negatively charged silver-chloride complexes which should easily be kept in the polymeric matrix. Experimentally, it was shown that the linear response range of the electrode was between the concentration intervals 1x10^{-3} M - 5x10^{-5} M and 5x10^{-6} M - 1x10^{-8} M and the detection limit at the optimum conditions was determined as 1x10^{-9} M. The validity of the method was tested using spiked water samples.

Table 2. Determination of Ag$^+$ ions in spiked water samples.

Sample	Ag$^+$ added (ng mL^{-1})	Ag$^+$ found (ng mL^{-1})	% Recovery
Natural Spring Water	-	n.d.[a]	-
	50	48.6	96.1
Tap water	-	n.d.	-
	50	51.63	103.3

[a] Not detected

References

1. R. Eisler, Silver Hazards to Fish, Wildlife and Invertebrates: A Sypnotic Review, Contaminant Hazard Reviews Report (Biological Report 32, September 1996), Patuxent Wildlife Research Center U.S. National Biological Service.
2. T. Madrakian, A. Afkhami, M.A. Zolfigol, M. Solgi, Separation, preconcentration and determination of silver ion from water samples using silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin, J. Hazard. Mater., B128 (2006) 67-72.
3. J.L. Manzoori, H. Abdolmohammad-Zadeh, M. Amjadi, Ultra-trace determination of silver in water samples by electrothermal atomic absorption spectrometry after preconcentration with a ligand-less cloud point extraction methodology, J. Hazard. Mater., 144 (2007) 458-463.
4. M. Soylak, R.S. Cay, Separation/preconcentration of silver (I) and lead (II) in environmental samples on cellulose nitrate membrane filter prior to their flame atomic absorption spectrometric determinations, J. Hazard. Mater., 146 (2007) 142-147.
5. P. Biparva,M. R. Hadjmohammadi, Selective Separation/Preconcentration of Silver Ion in Water by Multiwalled Carbon Nanotubes Microcolumn as a Sorbent, Clean – Soil, Air, Water 39 (2011) 1081–1086.
6. L. Wang, A.N. Liang, H.Q. Chen, Y. Liu, B. Qian, J. Fu, Ultrasensitive determination of silver ion based on synchronous fluorescence spectroscopy with nanoparticles, Anal. Chim. Acta, 616 (2008) 170-176.
7. M. Soylak, R.S. Cay, Separation/preconcentration of silver (I) and lead (II) in environmental samples on cellulose nitrate membrane filter prior to their flame atomic absorption spectrometric determinations, J. Hazard. Mater., 146 (2007) 142-147.
8. C Yu,, J. Zhang, M. Dingc and L Chen, Silver(I) ion detection in aqueous media based on ‘‘off-on’’ fluorescent probe, Anal. Methods, 4 (2012) 342.
9. F. Wang, R. Nandhakumar, J. H. Moon, K. M. Kim, J. Y. Lee and J. Y., Ratiometric Fluorescent Chemosensor for Silver Ion at Physiological pH, Inorg. Chem. 50 (2011) 2240–2245.
10. X. Zhanga, G. Wang, Luminescent CuS nanotubes as silver ion probes, Spectrochimica Acta Part A 72 (2009) 1071–1075.
11. L. Yang, R.E. Sturgeon, On-line determination of silver in sea-water and marine sediment by inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom., 17 (2002) 88-93.
12. R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Synthesis of a chitosan-based chelating resin and its application to the selective concentration and ultratrace determination of silver in environmental water samples, Anal. Chim. Acta, 558 (2006) 246-253.
13. G.G. Wallace, Y.P. Lin, Preparation and application of conducting polymers containing chemically active counterions for analytical purposes, J. Electroanal. Chem., 247 (1988) 145-156.
14. P. Li, Z. Gao, Y. Xu, G. Wang, Z. Zhao, Determination of trace amounts of silver with a chemically modified carbon paste electrode, Anal. Chim. Acta, 229 (1990) 213-219.
15. E. Lorenzo, H.D. Abruna, Determination of silver with polymer-modified electrodes, J. Electroanal. Chem., J. Electroanal. Chem., 328 (1992) 111-125.
16. Y.H. Li, H.Q. Xie, F.Q. Zhou, Alizarin violet modified carbon paste electrode for the determination of trace silver (I) by adsorptive voltammetry, Talanta, 67 (2005) 28-33.
17. R.K. Shervedani, M.K. Babadi, Application of 2-mercaptobenzothiazole self-assembled monolayer on polycrystalline gold electrode as a nanosensor for determination of Ag(I), Talanta, 69 (2006) 741-746.
18. H. Zejli, J.L. Hidalgo-Hidalgo de Cisneros, I. Naranjo-Rodriguez, K.R. Temsamani, Stripping voltammetry of silver ions at polythiophene-modified platinum electrodes, Talanta, 71 (2007) 1594-1598.
19. A. Mohadesi, M.A. Taher, Stripping voltammetric determination of silver (I) at carbon paste electrode modified with 3-amino-2-mercapto quinazolin-4(3H)-one, Talanta, 71 (2007) 615-619.
20. F. D’Eramo, J.J. Silber, A.H. Arevalo, L.E. Sereno, Electrochemical detection of silver ions and the study of metal-polymer interactions on a polybenzidine film electrode, J. Electroanal. Chem., 494 (2000) 60-68.
21. F.Y. Song, K.K. Shiu, Preconcentration and electroanalysis of silver species at polypyrole film modified glassy carbon electrodes, J. Electroanal. Chem., 498 (2001) 161-170.
22. D.W.M. Arrigan, Voltammetric determination of trace metals and organics after accumulation at modified electrodes, Analyst, 119 (1994) 1953-1966.
23. M. Sönmez Çelebi, H. Özyörük, A. Yıldız, S. Abacı, Determination of Hg^{2+} on poly(vinylferrocenium) (PVF^{+})-modified platinum electrode, Talanta 78 (2009) 405–409.
24. F. Kuralay, A. Erdem, S. Abacı, H. Özyörük, Electrochemical characterization of redox polymer modified electrode developedfor monitoring of adenin, Colloids and Surfaces B: Biointerfaces 105 (2013) 1– 6.
25. F. Kuralay, A. Erdem, S. Abacı, H. Özyörük, A. Yıldız, Characterization of redox polymer based electrode and electrochemical behavior for DNA detection, Anal Chim Acta, 643 (2009) 83–89.
26. F. Kuralay, H. Özyörük, A. Yıldız, Potentiometric enzyme electrode for urea determination using immobilized urease in poly(vinylferrocenium) film, Sensors and Actuators B 109 (2005) 194–199.

27. E. Turkmen, S. Z. Baş, H. Gulce, S. Yildiz, Glucose biosensor based on immobilization of glucose oxidase in electropolymerized poly(o-phenylenediamine) film on platinum nanoparticles-polyvinylferrocenium modified electrode, Electrochimica Acta 123 (2014) 93–102.
28. B.C. Özer, H. Özyörük, S.S. Çelebi, A. Yıldız, Amperometric enzyme electrode for free cholesterol determination prepared with cholesterol oxidase immobilized in poly(vinylferrocenium) film, Enzyme and Microbial Technology 40 (2007) 262–265.
29. M. Gündoğan-Paul, S.S. Çelebi, H. Özyörük, A. Yıldız, Amperometric enzyme electrode for organic peroxides determination prepared from horseradish peroxidase immobilized in poly(vinylferrocenium) film, Biosensors and Bioelectronics 17 (2002) 875-881.
30. G. Aydın, S.S. Çelebi, H. Özyörük, A. Yıldız, Amperometric enzyme electrode for L(þ)-lactate determination using immobilized L(þ)-lactate oxidase in poly(vinylferrocenium) film, Sensors and Actuators B 87 (2002) 8–12.
31. C. Aso, T. Kunitake, T. Nakashima, Cationic polymerization and copolymerization of vinylferrocene, Macromol. Chem., 124 (1969) 232-239.
32. D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, 1980.
33. P.J. Peerce, A.J. Bard, Polymer films on electrodes: Part II. Film structure and mechanism of electron transfer with electrodeposited poly(vinylferrocene), J. Electroanal. Chem., 112 (1980) 97-115.
34. H. Gülce, H. Özyörük, A. Yıldız, Electrochemical Response of Poly(vinylferrocenium)-Coated Pt Electrodes to Some Anions in Aqueous Media, Electroanal., 7 (1993) 178-183.