Determination of Silver in Rocks and Ores Samples using Modified Voltammetric Technique

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Summary: Novel modified electrochemical method were used to analyze sedimentary, metamorphic, igneous, fined grained, coarse grain granite, granite with feldlaths and ferrogenous sand stone rocks along with boulangerite, stibnite, magnetite and scheelite ores for the presence of silver. Rocks and ores samples were processed through fire assay and acid digestion methods. Effect of various interfering metal ions was studied and it was observed that Hg(I) ions contributed maximum increment in the peak current of Ag(I). Differential pulse anodic stripping voltammetry (DPASV) and cyclic voltammetry (CV) were applied for the determination of silver. Glassy carbon bare and modified electrodes were used as working electrodes. Platinum and saturated calomel electrodes were applied as auxiliary and reference electrodes respectively. The modified method has high affinity, selectivity and sensitivity and can be applied for trace level determination of metal ions. The limits of detection (LDL), quantification (LOQ) and linear regression coefficient (R^2) were found 1.14µg/L, 3.2µg/L and 0.9969 respectively.

Keywords: Voltammetry, Electroanalytical Chemistry, Silver, Electrodes, Rocks, Ores.

Introduction

Silver is termed as precious metal due to its unusual production and greater requirements by community with significant economic values. It has valuable physical and chemical properties along with its industrial and trade uses. It is almost inert in chemical reactivity and possesses very shining properties with soft and flexible nature [1]. The precious nature of silver is due to its inadequate and distinctive production. It exists in combinations with other metals and nonmetals. Thus, the large amounts of less rare metals in the precursors lead to less uptake of silver [2]. Silver has been investigated to allocate its effects on the physiology of humankind and describe its medical advantages. Industrially, silver is highly important metal because more than 85% of the manufactured products involve its use. It has high market value and used as a conductor in various electronic devices, circuits and connectors [3].

Precious Metal Clay (PMC) corresponds to significant developments in the management of silver. PMC consists of very tiny particles of silver or gold floating in an organic binder [4]. Silver has a wide range of applications in jewellary, automobile, chemicals, petrol refineries, electrical, ceramic and glass industries [5-6]. Silver is also used in X–ray photography, medicine (Ag_2O, $AgNO_3$, Argyrols) bactericide/antiseptic, oil and water purifier (Ag_3PO_4), tableware, corrosion control in batteries as well as in stable electrode and medals formation [7]. Pakistan has three significant kinds of rocks e.g. metamorphic, magmas and sedimentary which are used as precursors of precious metals. In these rocks, silver mostly exists in aggregation with gold and other metals. It is usually associated with sulphides of copper, arsenic, iron as well as compounds of selenium and antimony [8].

Some techniques like capillary zone electrophoresis [9], ET-AAS [10], solvent extraction [11-13], kinetic spectrophotometric methods [14-15], Ion-exchange [16], SF-ICP-MS [17], ICP-MS enzymatic [18], colorimetric–solid-phase extraction method [19], vapor generation-inductively coupled plasma atomic emission spectrometry and mass spectrometry [20], spectrophotometric [21], Liquid chromatography [22-23], rotating film per-traction [24], hydrometallurgical [25] and various electrochemical methods [26-28] have been used for the determination of silver.

In this current study, a novel modified, cost effective, robust and highly sensitive voltammetric method was proposed for the determination of silver from its precursors. Different working electrodes

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were used to notice the effect of electrode surface on peak signals.

Experimental

Analytical Techniques

The Waveform Generator PP RI, HI–TEK instruments England, UK with potentiostat, X-Y recorder and cell assembly possessing GCBE/GCME as working electrode, Pt as an auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode were used for voltammetric determination of silver. pH meter, model inoLab of WTW was used for pH measurements. Pipetman Gilson Micropipettes of variable ranges were used for micro volume adjustments of the solutions. Controlled temperature furnace model 810-00-002 was used for fire assay method of the samples. Swiss-made precisa balance model XB 120A was used for weighing purpose. Electric oven model 8559 was used for drying purpose. Atomic Absorbtion Spectrometer (AAS) model Hitachi 180-50, Japan was used for comparative analysis.

Chemicals and Glassware

All chemicals were of high purity analytical grade, purchased from Fluka, Sigma-Aldrich and Fisher Scientific International Company. Standard aqueous solutions of $Ag^+/AgNO_3$, glacial CH_3COOH, KCl, HNO_3, NH_4SCN and potassium hydrogen phthalate (KHP) were prepared in double distilled water respectively. 1% chitosan solution was prepared by dissolving 0.01g chitosan in 1 ml of 2M CH_3COOH. All glassware was kept in a container having 3M HNO_3 solution. These were then washed thoroughly with single distilled water and finally rinsed with double distilled water and dried in an oven for 1hour, cooled to room temperature and used for analytical work.

Sampling Profile

Samples of rocks and ores were collected from different regions of Pakistan. Natures of various sample locations were identified with help of Geology department. Description of various samples is given in Table-1.

Sample Treatment

The ores/ rocks samples were crushed and grinded in a jaw crusher and a ball mills to convert them into powder form. The powdered samples 80micron mesh sizes were then processed by fire assay method to remove the volatile oxides of Pb, Sb and S. After ignition, acid digestion processes were used to treat the ores and rocks samples accordingly. The solution was then concentrated by evaporating the solvent and diluted with double distilled water up to the desired concentrations of silver(I).

Table-1: Rocks and ores samples collected from different areas of Pakistan are given below.

Sample Code	Site of Collection	Physical Appearance	Remarks
R_1	Bakka Khail (NWA)	Brownish	Sedimentary and Metamorphic Basic Rocks
R_2	Miran Shah (NWA)	Purple	
R_3	Mir Ali (NWA)	Dark Gray	
R_4	Karak (K.P.K)	Gray	
R_5	Dara Pezzo (K.P.K)	Dark Brown	
		Samples Collected from PCSIR Laboratories Karachi (Sindh)	
R_6	Jam Khan jo Vandio (Sindh)	Pink	Igneous Rock
R_7		Dark Blue	
R_8		Light Blue	
R_9	Ramji jo Vandio (Sindh)	Dark Green (Maleno Cratic)	Fined Grained Basic Rock
R_{10}		Light Pink (Leuco Cratic)	Coarse Grain Granite Rock
R_{11}		– do –	– do –
R_{12}	Paradaro (Sindh)	Dark Gray	Basic Rocks
R_{13}		Light Gray	
R_{14}		Gray	
R_{15}		– do –	Granite with feldlaths
R_{16}	Mukrio	Dark Green (Hyper Malenium)	Basic Rock
R_{17}	Kasbo	– do –	– do –
R_{18}	On jo Vandio (Sindh)	Dark Red	Ferrogenous sand stone of Barthala formation
R_{19}		Yellow	
R_{20}	Zardari Mine Nagar Parkar	Dark Red	– do –
		Ores Samples Collected from Mineral Testing Laboratories (MTL) Peshawar (K.P.K)	
S.#.	**Ore Sample**	**Composition**	**Color**
1.	Boulangerite	$Pb_5Sb_4S_{11}$	Blue and Grey to Brown
2.	Stibnite	Sb_2S_3	Dark Grey
3.	Magnetite	Fe_3O_4	Purple
4.	Scheelite	$Ca[WO_4]$	Greenish Grey

NWA = North Waziristan agency, K.P.K = Khyber Pukhtunkhwa

Preparation and regeneration of Glassy Carbon Modified Electrode (GCME)

The surface of glassy carbon electrode (GCE) was polished with 0.05 micron alumina slurry for 3-5 minutes, sonicated for 5-10min and rinsed with double distilled water. The electrode was then dried under nitrogen gas to make it ready for voltammetric analysis and modification by organic ligands. A drop of 1% chitosan solution was applied on the cleaned surface of GCE with the help of a dropping capillary. Then it was placed under UV light for 20min in order to get the chitosan dried and firmly attached to the surface of GCE. For new analysis the GCME was regenerated by placing in 2M acetic acid to remove the chitosan and repeat the process from polishing with alumina to drying the chitosan on the surface of glassy carbon electrode.

Methodology

Voltammetric analyses were carried out through a cell assembly containing three electrodes system. A 10mL blank solution only containing supporting electrolytes/buffers was taken in the electrochemical cell and purged with nitrogen gas to remove the dissolved oxygen. It was then electrolyzed under the controlled parameters and background voltammograme was recorded. The aforementioned procedure was also adopted for analyzing the analyte solutions containing Ag(I) ions and same amount of supporting electrolytes/ buffers and thus voltammograms were recorded for Ag(I) ions.

Results and Discussion

Effect of pH on Peak Current of Ag(I)

pH is a very sensitive parameter and causes variation in analytical results. The maintenance of pH by using a proper buffer system is thus highly demanded because small amount of CO_2 can alter the actual pH value of the solution if a single acid/alkali is used for pH adjustment. This may produce disturbance in the peak signal and may increase noise in signal. Fig. 1 represents the change in peak current values with variation in pH of the solution. It can be seen from Fig. 1 that maximum peak current value of 15.7µA is true at a pH value of 4.1. Some researchers [29] have reported 0.1M potassium nitrate for pH adjustment. Some other researchers [30] have studied a pH range of 3.5 to 7.0 for silver determination using modified carbon paste electrode. They used citrate buffer and noticed that pH value 6.0 gives maximum peak current. In current studies 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system with trace amount of 0.005M NH_3 were used for pH adjustments.

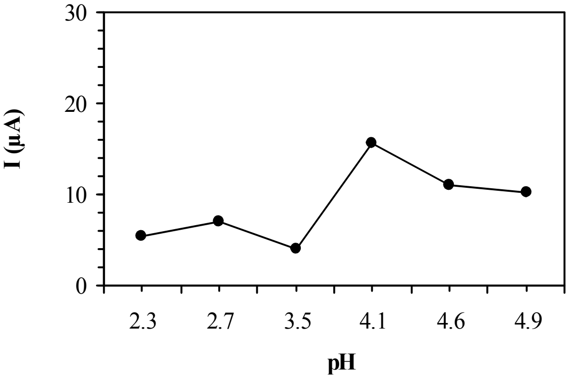

Fig. 1: Effect of pH on peak current of Ag (I): Conc. of Ag (I), 2µg/ ml; scan rate, 100mV/sec; pulse amplitude, 50mV; deposition time, 2min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Effect of Pulse Amplitude on Peak height of Ag(I)

The effect of pulse amplitude was optimized to obtain well shaped peak signals with higher current values. It can be observed from Fig 2 that 100mV pulse amplitude with 100mV/sec scan rate gives maximum peak current for Ag(I). In case of silver determination different pulse amplitudes were reported by various researchers such as 25mV pulse amplitude with 5mV/s scan rate by [31], 10mV pulse amplitude with 100mV/s scan rate by [32] and 250mV pulse amplitude by [33]. The aforementioned pulse amplitude values depend upon nature of electrolytes/ buffer system and type of voltammetry whether DPASV or CV. In current studies, it was also noticed that at very higher scan rates peak signals are distorted due to broadening effect. However, the slower scan rate is advantageous for a higher peak current using DPASV. A scan rate of 100mV/sec for determination of Ag(I) using cyclic voltammetry was also suggested [34].

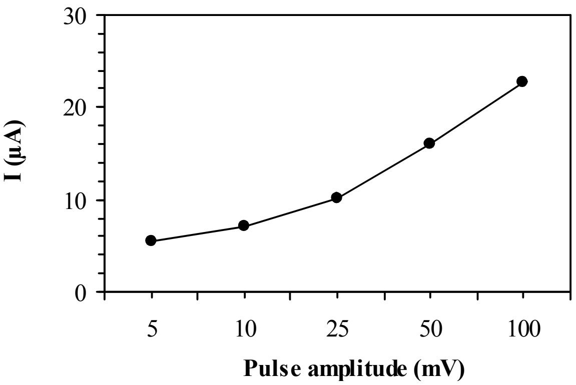

Fig. 2: Effect of pulse amplitude on peak current of Ag (I): Conc. of Ag(I), 2µg/ml; scan rate, 100mV/sec; deposition time, 2min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Effect of deposition time without stirring on Peak Current of Ag(I)

Fig 3 describes the change in peak current with deposition time for Ag(I) standard solution by keeping all other parameters constant. It can be seen from Fig 3 that maximum peak current was obtained at 5min deposition time. This may be due to the maximum pre-concentration of the analyte Ag(I) and its peeling off after deposition which may be due to the solution's affinity. The decrease in peak currents of Ag(I) beyond the optimum deposition time may be due to the formation of oxides and fading of electrode surface as well as degradation of electrolyte contents with the passage of electric current for longer times. In literature [31, 32, 34], optimum deposition time of 3, 5 and 10 min was proposed for the analyses of silver ions. Hence, in current studies the optimum value of deposition time is quite closer to some referenced the literature.

Effect of deposition time followed by stirring on peak current of Ag(I)

Stirring time effect was optimized for maximum peak current response of Ag(I) ions from standard aqueous solutions under the influence of already optimized parameters. It can be observed from Fig 4 that the peak current increases up to some limits with the use of stirring along with deposition time. Stirring offers frequent transfer of metal ions from solution matrix to electrode surface and increase the rate of deposition while decrease the required time for this deposition. In this case the maximum peak current value was obtained with 4 minutes deposition time followed by stirring. Such studies are not common in literature, yet some researchers [31] have described this parameter as a constant value.

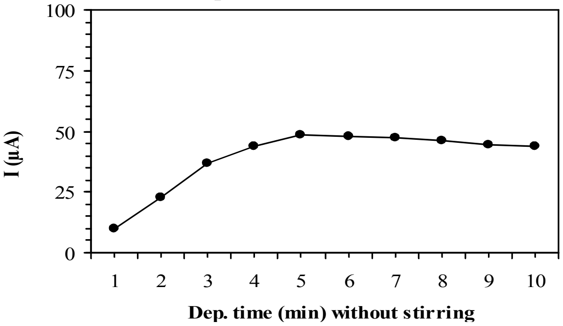

Fig. 3: Effect of deposition time without stirring on peak current of Ag (I): Conc. of Ag(I), 2µg/ml; scan rate, 100 mV/sec; pulse amplitude, 100 mV; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

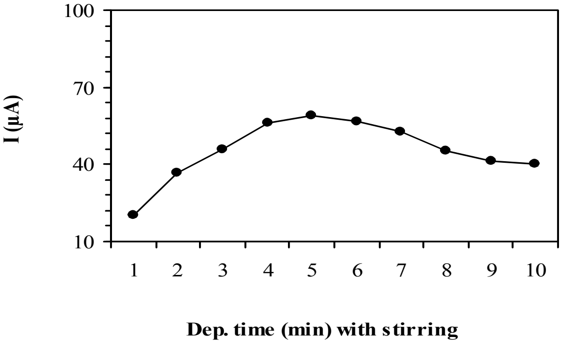

Fig. 4: Effect of deposition time with stirring on peak current of Ag (I): Conc. of Ag(I), 2µg/ml; scan rate, 100 mV/sec; pulse amplitude, 100 mV; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Effect of nitrogen purging time on peak current of Ag(I)

The nitrogen (N_2) or other inert gas is purged to remove oxygen from the solution matrix because oxygen causes noise to signal ratio and distorts peak signals. It is apparent from the Fig. 5 that N_2 purging of 10min followed by 4min electrolysis time gives greater peak current value for silver(I) determination. The N_2 purging was performed to make the peak signals smoother and well resolved. Various researchers [31-32, 35-37] have reported such studies of using inert gas for de-aeration of aqueous solutions containing metal ions.

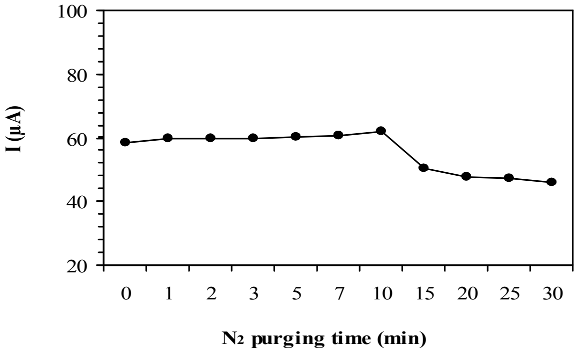

Fig. 5: Effect of N_2 purging time on peak current of Ag (I): Conc. of Ag (I), 2μg/ml; scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10μA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Effect of temperature on peak Current of Ag(I)

Temperature has profound effect on the mobility of ions and internal energy of matter, which accelerate convection. It is evident from Fig. 6 that the peak current increases with increase in temperature from 10–35°C in a nearly linear fashion but decreases thereafter. However, 25°C was selected as optimum temperature because during calibration studies it was noticed that the linear regression value was lesser for 30°C and above as compared to 25°C. The increase of peak current with temperature up to 35°C may be due to the convection phenomenon, which enhances the mobility of ions towards cathode. The decrease in peak current beyond this temperature may be due to the evaporation of electrolytes, which may disturb complex formation and decrease current carrying capacity. Similar findings of temperature effect on peak current have been reported in literature [31].

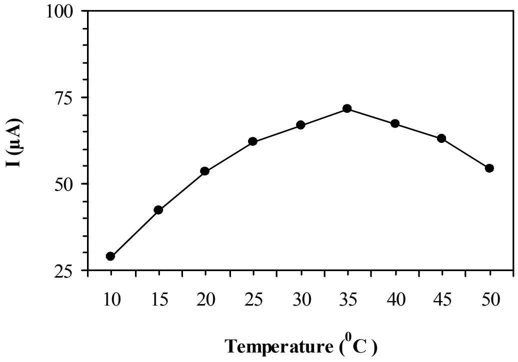

Fig. 6: Effect of solution temperature on peak current of Ag (I): Conc. of Ag(I), 2μg/ml; scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10μA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Effect of Interfering Metals

Although the effect of others interfering metals on electrochemical behavior of silver ions is not essential because the formers can be eliminated as their volatile oxides at higher temperature using fire assay method. The lead button formed after performing the fire assay method was treated with HNO_3. However, interference effect of metal ions was studied to find out a metal which produces highest positive interference for Ag(I) and that could be helpful for lowering the detection limit of Ag(I). Table-2 shows the interference effect of some metals, which may be present with Ag(I) in ores and rocks. Table-2 indicates that Hg(I) ions have the highest positive interference of 85.5% with an enhanced peak current of 115.3μA. Arsenic(III) contributed, the positive interference and Ba(II) ranging from +29.8 to +1.6 respectively while Fe(III) to Cl^{-1} show negative interference ranging from –2.9 to –38.1 respectively. The effect of various metal ions and anions on silver determination was studied [40]. However, they have not reported the use of Hg(I) ions as interfering specie in this study. Interference effect during anodic stripping voltammetry of metals is mainly due to the formation of intermetallics as reported earlier. They studied strong catalytic effect of Au(III) on the slow redox reaction between Ce(IV) and Hg(I) in a sulphuric acid medium at 90°C. Some positive interferon's may also be considered for the enhancement of peak signals of Ag(I) ions but the addition of more metals may result in complication and production of metallic contamination. Usually the interference by metals can be removed with the use of suitable masking agents [38-42] but this may also make the process complicated and costly. Some researchers [28, 43-44] have reported that interfering metals bind the significant analyzing metal due to intermetallic behavior and thus alter its redox properties. Metals with strong intermetallic behavior and less polarizability may result in suppressing the peak signals and metals with soft intermetallic behavior and more polarizability may cause increment in peak signals for Ag(I). In the current studies the positive interference by Hg(I) was used for lowering the LDL for determination of Ag(I) ions by DPASV. In literature, [45] have also explained the interference effect of co-existing substances on the peak current of analyte species. A modified form of Nikolsky-Eisenman equation was used to determine selectivity coefficient (K^{amp}) for the sensor [46-48].

Effect of Hg (I) Conc., on Peak Current of Ag(I)

Fig 7 shows the effect of Hg(I) ions concentration on peak current values of Ag(I) from standard aqueous solutions at others optimized parameters. Studies on the electrochemical behavior of Hg(I) concentration on Ag(I) are not common in the literature. However, a scientist [42] has studied the effect of Hg(I) concentration on Au(III) and reported that at higher concentrations of Hg(I) results become constant. In our case, the intermetallic effect of Hg(I) on Ag(I) follow the same mechanism as described for Au(III). The results in Fig 7 show that there is a gradual increment in the peak current of Ag(I) with increase in the concentration of Hg(I) up to 0.1µg/ml and decreased thereafter. Maximum peak current 153.45µA was recorded at 0.1µg/ml of Hg(I) and 2µg/ml of Ag(I). This decrease in the peak current of Ag(I) may be due to the inhibition effect of higher concentrations of Hg(I), while the increase in peak signals of Ag(I) by addition of Hg(I) may be due to the redox reaction between Ag(I) and Hg(I). Hence, the increment in peak current of Ag(I) may be due to greater reducing effect of Hg(I). The reducing effect of Hg(I) on Ag(I) promotes the accumulation of large amounts of Ag(0) on electrode surface and hence increases the peak signal. Moreover, mercury has the ability to dissolve silver. This is very rapid and independent of time kinetics. Electrolysis provides a favorable medium for more rapid contact between mercury and silver [49]. Oscillations in the current suggest the formation and dissolution of Ag-Hg species. Regarding the Ag-Hg, a passive layer formation begins on the surface of electrode, which lowers currents, while an increment in current values track the dissolution and oxidation processes [50]. The higher concentration of mercury may produce an excess amount of Hg complex instead of Hg(l). This may decrease the chances of intermetallic contacts between silver and mercury. Moreover, an excess amount of mercury may produce strong intermetallics, may cover more area on the surface of working electrode, and reduces peak signal for Ag(I).

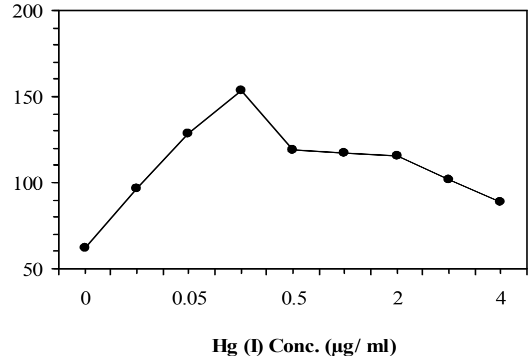

Fig. 7 Effect of Hg (I) Conc., on peak current of Ag (I): Conc. of Ag(I), 2µg/ml; scan rate, 100mV/sec; pulse amplitude, 100 mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min. Glassy Carbon as a working, Platinum as an auxiliary and saturated calomel as a reference electrode are used.

Table-2: Interference effects of various metal ions on peak currents of Ag(I) using DPASV.

Metal ion	**Peak current$^{n=3}$**	**Interference effect**		**Metal ion**	**Peak current$^{n=3}$**	**Interference effect**	
(2µg/ml)	**(µA)^a**	**%**	**K^{amp}**	**(2µg/ml)**	**(µA)^a**	**%**	**K^{amp}**
No ion	**62.0**	**----**	**----**	**Fe^{+3}**	**60.2**	**-2.9**	**-0.029**
Hg^{+1}	**115.3**	**+85.5**	**0.860**	**Pb^{+2}**	**58.0**	**-6.5**	**-0.065**
As^{+3}	**80.5**	**+29.8**	**0.298**	**Ca^{+2}**	**56.8**	**-8.4**	**-0.084**
Ce^{+5}	**75.0**	**+21.0**	**0.210**	**Zn^{+2}**	**56.6**	**-8.7**	**-0.087**
Cd^{+2}	**70.5**	**+13.7**	**0.137**	**Ni^{+2}**	**55.9**	**-9.8**	**-0.098**
Cu^{+2}	**69.7**	**+12.4**	**0.124**	**Sn^{+2}**	**54.1**	**-12.7**	**-0.127**
Hg^{+2}	**68.4**	**+10.3**	**0.103**	**I^{-1}**	**53.0**	**-14.5**	**-0.145**
Au^{+3}	**67.2**	**+8.4**	**0.084**	**Br^{-1}**	**48.2**	**-22.3**	**-0.223**
Cr^{+6}	**66.1**	**+6.6**	**0.066**	**Cl^{-1}**	**38.4**	**-38.1**	**-0.381**
Ba^{+2}	**63.5**	**+1.6**	**0.024**	**----**	**----**	**----**	**----**

Average of Triplicate Analysis (a), Selectivity Coefficient (K^{amp})

Comparison of Voltammetric Signals

Polarization peak signals were recorded for the determination of silver(I) using different working electrodes as shown in Fig. 8. The curve (a) indicates the electrochemical peak signal obtained via GCBE for Ag(I) determination. Curve (b) describes the electrochemical peak signal for Ag (I) using GCME. Curve (c) shows electrochemical peak signal with GCBE for standard aqueous solution containing Ag (I) and treated with an optimum amount of Hg (I) ions. It is evident from Fig 8 that the response of GCBE is obviously higher for Ag(I) standard aqueous solutions treated with an optimum concentration of Hg(I). The peak signals recorded for Ag(I) by using different electrodes systems show different peak potential values. The shift in peak potential may be due to the affinity/force of interaction between Ag(I) ions and the surface where it was deposited. The electrode response for Ag(I) ions treated with controlled quantity of Hg(I) ions is about 3 folds higher than untreated Ag(I) ions. It means that the presence of Hg(I) catalyze the peak signal of Ag(I).

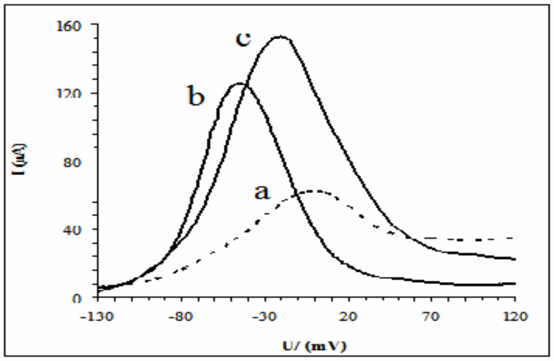

Fig. 8: Comparison of anodic stripping voltammograms (peak signals) obtained with different electrodes settings: (a) GCBE, (b) GCME, for untreated silver standard solutions and (c) GCBE; for silver solutions treated with an optimum concentration of Hg(I) ions; (a,b,c) as working, Platinum as an auxiliary and saturated calomel as a reference electrode are used. Conc. of Ag(I), 2μg/ml; scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10μA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min.

Calibration Curves and Plots

Silver determination was carried out in the concentration range of 0.04–3.0μg/ml with linear regression coefficient of 0.9951 for untreated Ag(I) standard aqueous solutions using GCME (Fig. 9 and 11) and the linear calibration plot for concentration range 0.01–2.0μg/ml with linear regression coefficient of 0.9969 was obtained for standard aqueous solutions of Ag (I) treated with controlled concentration of Hg(I) ions using GCBE (Fig 10 and11). A researcher [36] has reported a detection limit of 2.5×10^{-7}M (26.98μg/L) for silver determination using chemically modified carbon paste electrode. The LDL 1.14μg/ L in our studies is highly comparable and significant to the LDL noticed from the literature e.g. some authors [32] have given the value of LDL 1×10^{-8}M (1.08μg/L) for silver determination using voltammetric techniques. In current studies the lower detection limit (LDL) was calculated as per procedure [51].

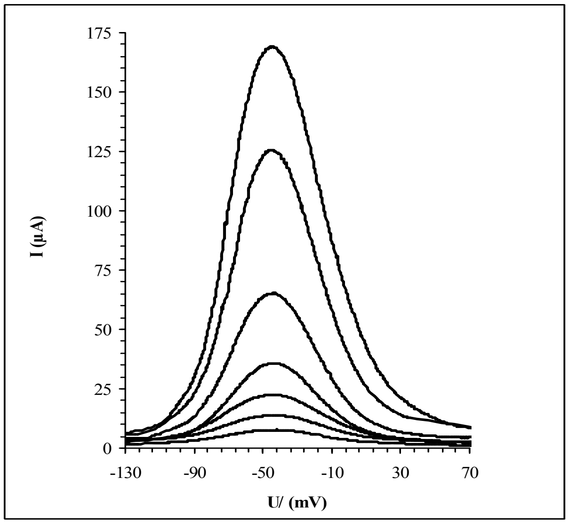

Fig. 9: Calibration curves with GCME as a working, Platinum as an auxiliary and saturated calomel as a reference electrode: untreated standard aqueous solutions of Ag(I) 0.04 – 3.0μg/ml; Scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10μA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min.

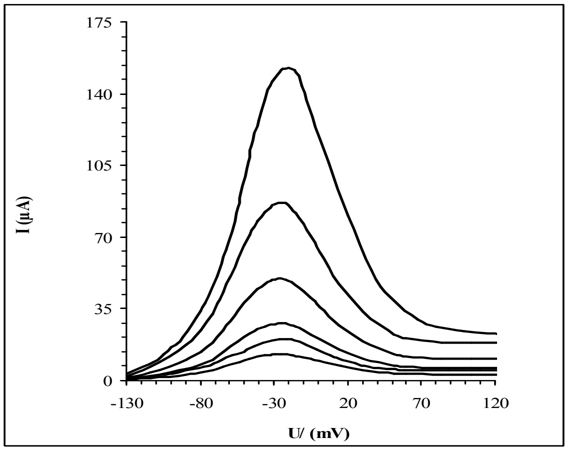

Fig. 10: Calibration curves with GCBE as a working, Platinum as an auxiliary and saturated calomel as a reference electrode: standard aqueous solutions of Ag (I) 0.01 – 2.0µg/ml treated with an optimum concentration of H (I) ions; Scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5 minutes; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min.

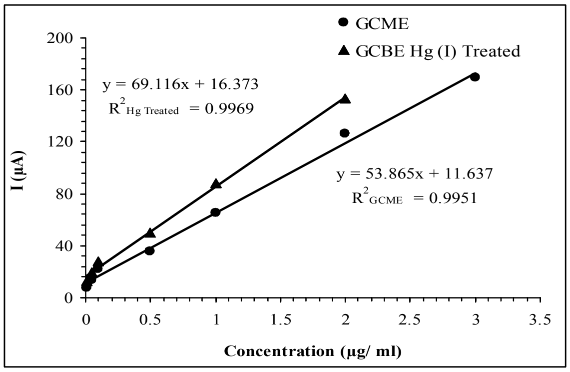

Fig. 11: Calibration plots for Figs 9 and 10: Scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5 minutes; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min. GCBE/GCME as a working, Platinum as an auxiliary and saturated calomel as a reference electrode.

Cyclic Voltammogram

The cyclic voltammogram (Fig12) for Ag(I) shows two peak signals (i) the anodic peak at -20mV and (ii) the cathodic peak at -240mV. The potential difference between the anodic and the cathodic peak signals can be calculated as; $\Delta E = E_p^a - E_p^c = 220$mV and the ratio of peak currents, $I_p^a / I_p^c = 1.8$µA. Thus, 220mV > 59/n mV and 1.8µA > 1µA, hence, all these reveal the quasi-reversible behavior and mechanism of electrode reaction for silver deposition and stripping [52-54].

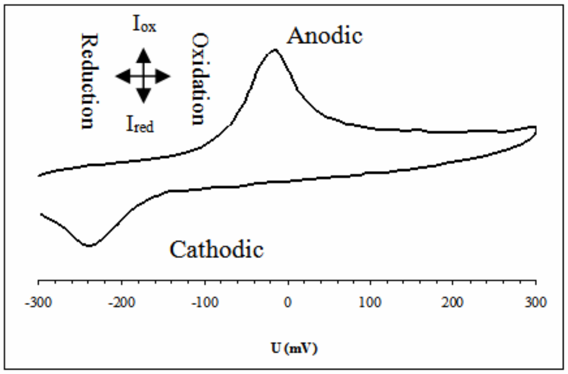

Fig. 12: Cyclic voltammogram showing redox behavior of Ag (I): Conc. of Ag(I), 2µg/ml; scan rate, 100mV/sec; pulse amplitude, 100mV; deposition time with stirring, 5min; electrolytes 0.05M [NH_4SCN and potassium hydrogen phthalate] buffer system and 0.005M NH_3 as supporting electrolytes and pH adjusters; sensitivity, 10µA/cm; potential range, –200 to 200mV; solution temperature 25°C, pH, 4.1; N_2 Purging, 10min. GCME as a working, Platinum as an auxiliary and saturated calomel as a reference electrode.

Sample Analysis

Table-3 shows the results for Ag(I) concentration in various digested ores and rocks samples. The digested samples were diluted up to desired range for voltammetric and spectroscopic analyses (Table-3). The results obtained for Ag(I) by atomic absorption spectroscopy [55] are in close accordance with the results obtained by DPASV, which shows the validity and precision of the developed voltammetric method for Ag(I) determination from its precursors.

Table-3: Application of Method: Comparative results showing presence/absence of Ag (I) in digested ores and rock samples by developed voltammetric method and AAS.

Samples	**Silver (I) Determination (μg/ml)[a]**			
	By new method		**By AAS**	
	(1000 fold) Dilution	**Actual value**	**(250 fold) Dilution**	**Actual value**
Boulangerite	**0.023±0.03**	**22.7**	**0.09±0.09**	**22.1**
Magnetite	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Sheelite	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Rock 1	**0.026±0.11**	**26.4**	**0.11±0.14**	**26.9**
Rock 2	**0.033±0.14**	**33.2**	**0.13±0.25**	**33**
Rock 3	**0.018±0.09**	**17.9**	**0.07±0.19**	**18.5**

Average of Triplicate Analyses (a), Standard Deviation (±)

Conclusion

The surface of glassy carbon electrode modified with chitosan showed high sensitivity for silver ions in comparison to bare surface of the same electrode. Chitosan molecules undergo complexation reactions with metal ions. Hence, the affinity and sensitivity of Chitosan modified surface to silver ions may be higher than the bare surface of carbon. Rock samples (1-3) are first time described as new precursors of silver. However, Boulangerite ore collected from mountains of Pakistan was also found a good source of silver. Glassy carbon modified electrode (GCME) was more optimal and sensitive for trace level determination of Ag(I). However, the addition of Hg(I) ions further increased the peak currents. The more increase in peak currents by addition of Hg(I) may be due to intermetallic effect and reducing behavior of Hg(I) ions. Hg(I) ions can be used for catalytic purpose to lower the limit of detection. Cyclic voltammogram confirmed the redox reactions followed by the deposition and stripping of silver. The modified electrochemical method is robust, sensitive, cost effective and applicable to all kinds of aqueous sample solutions containing Ag(I) ions.

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