Carbon composite electrode for potentiometric determination of silver (I)

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Svetlana Shumar [a], Maria Petrova [b] and Elena Kuzminskaya [c]

Tomsk State University, 36 Lenina Avenue, Tomsk 634050 Russian Federation

[a] corresponding author: shumar.svetlana@yandex.ru
[b] mariaanatolevnaa@gmail.com
[c] elanky@mail.ru

Abstract. The possibilities of carbon composite electrode (CCE) as the sensor for potentiometric determination of Ag(I) were investigated. The conditions for potentiometric titration of silver (reagents, pH, supporting electrolyte and working concentration range) using the sensor have been studied and optimized. The precipitation titration curves were processed by the linearization method. The CCE, in comparison with conventional silver electrode is polyfunctional, and it has a lower cost and better performance.

INTRODUCTION

The applications of silver have expanded over recent decades due to its particular physical and chemical properties. Silver alloys are used in various areas of engineering. Chemical resistance and attractive appearance make it an indispensable material in jewelry industry. Also, silver is widely used as a catalyst in organic synthesis, in semiconductor industry and in medicine. The control of amount of silver in different objects is performed by physical and physicochemical methods of analysis, many of which demand the expensive equipment, reagents and additional sample preparation step [1–4]. Electrochemical methods of analysis are advantageous because of their polyfunctional performance, high accuracy, low cost and simplicity. The efficiency of an electrochemical method is determined by the use of appropriate detection system (i.e. indicating electrode or sensor). Therefore, development of new electrode systems and implementation in the routine analysis are prospective areas of analytical chemistry. A new electrochemical sensor, carbon composite electrode (CCE), was previously shown to use in potentiometric determination of some heavy metals [5]. The sensor demonstrates long lifetime and ease working surface renovation; it can be modified (bulk and surface) with conducting or insolating phase; and it also has low cost. The CCE may be used in various electrochemical techniques (e.g. coulometry, voltammetry, potentiometry, etc.) due to its polyfunctional properties.

In this work, the carbon composite electrode has been proposed for the first time as a sensor for the potentiometric titration of Ag(I). The effects of the pH of a solution, precipitate solubility of a forming precipitate, concentration of a potential-determining ion and the composition of supporting electrolyte on Ag(I) potentiometric analytical response were studied. The developed procedure was applied for Ag(I) quantification in some pharmaceuticals.

EXPERIMENTAL PART

Reagents

The working and simulating solutions were prepared with double-distilled water. All the reagents were of analytical grade and were used without further purification except sodium diethyldithiocarbamate (NaDEDC). The titrants for potentiometric titration were the solutions of sodium chloride and NaDEDC. The sodium chloride working solution was prepared from a standard solution. The NaDEDC salt was purified by recrystallization in ethanol before the solution preparation. The concentration of NaDEDC solution remained constant for two weeks when stored in a cool, dark place. The simulating solutions of Ag(I) with concentration

of 1.7×10^{-2} to 1.7×10^{-6} M were prepared by serial dilution of AgNO$_3$ standard solution prior to testing. The solution of 0.1 M KNO$_3$ was used as a supporting electrolyte; the solutions of K-Na tartrate, acetic and ammonia buffer solutions were used as supporting electrolytes and in order to maintained pH constant.

Apparatus

The potentiometric measurements were performed with the pH meter / ionomer Ethan (Russia). The working electrodes were the silver wire and CCE (LTD RPE "Tomanalyt" Russia).The CCE was made of polyethylene concentrate containing 30% carbon with uniform distribution of particles in the bulk of electrode [6]. The electrode has a low weight and small size, higher signal-noise ratio, wide potential detection range, passivation resistance The reference Ag/AgCl electrode was separated from the measurement cell by a salt bridge filled with 10% KNO$_3$ and agar-agar. The titration solution was added to analyt with a pneumatic microburette. The acidity of a solution was measured with pH-meter.

Potentiometric Measurements

The potentiometric titration of Ag(I) was performed according to the following procedure. The 0.2 ml portions of a titrant were added to the analyt. The portions were reduced to 0.03–0.04 ml near the equivalence point. The electromotive force was recorded after each titrant portion and solution stirring until a stable potential is reached. In order to determine the equivalence point, the potentiometric titration curves were processed by the fragmentary linear approximation method with the computational algorithm for the curve processing developed by Mar'ianov [7]. The principle of the method is to use the mathematical model to transform a titration curve into the linear regression, which defines the equivalence point and the reaction equilibrium constant with estimating precision of the least square method. In addition, any region on a titration curve can be used for the process modeling to determine the physicochemical parameters with sufficient accuracy.

## RESULTS AND DISCUSSIONS

Electrode Characteristics

The dependencies $E = f(-lg\ C)$ of Ag(I) calibration curves were investigated in our previous work [8], and the concentration linear ranges of 6×10^{-2} to 6×10^{-7} M and 3×10^{-2} to 3×10^{-7} were found for CCE and silver working electrode, respectively.

In this work, we have determined the electrode characteristics of CCE such as electrode slope and detection limit for Ag(I). The results have shown that the Nernstian slope is 55.64 mV/pC$_{Ag}$ for CCE, and the value for silver electrode is 97.48 mV/pC$_{Ag}$ which is over-Nernstian.

A new polyfunctional sensor has the same short response time (40-60 sec.) comparing to a silver electrode. The disadvantage of a new sensor is a decrease of sensitivity under long-term usage resulting from the accumulation of electrochemical reaction products on its working surface. However, the electrode surface can be easily renovated by cutting. The average performance time without surface renovation is more than one month.

Titrant for Potentiometric Titration of Ag(I)

Dithiocarbamates have gained widespread use in potentiometry among chelating agents for titrimetric determination of metal ions. NaDEDC in particular is widely used in analysis due to its reactivity, simple synthesis and other essential analytical properties. It can form a low-soluble precipitate with Ag(I) ions in the ratio 1:1 in a wide pH range according to Eq. 1:

$$Ag^+ + DEDC^- = AgDEDC\downarrow \tag{1}$$
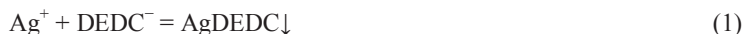
The sensitivity of the CCE and silver working electrode toward DEDC$^-$ ion may be explained by the redox properties of the titrant. The redox pair of oxidized and reductive forms of dithiocarbamate – thiuram disulfide reagent arises in NaDEDC solution (Eq. 2) and the indicator electrode exhibits its redox behavior.

$$2(C_2H_5)_2NCS-S^- \leftrightarrow (C_2H_5)_2NS-S-S-SN(C_2H_5)_2 \tag{2}$$

The solubility product constant, K_{sp}, of a precipitate formed has a sufficient impact on the results of potentiometric titration. When using sodium chloride solution as a titrant, white precipitate of AgCl ($K_{sp} = 1.79 \times 10^{-10}$) [9] is formed according to Eq. 3:

$$Ag^+ + Cl^- = AgCl\downarrow \tag{3}$$

In potentiometric titration, the lowest concentration that can be achieved is limited by the value of the precipitate solubility, which is the square root of K_{sp}, and equals 1.34×10^{-5} for sodium chloride titrant. The lowest Ag(I) determining concentration is decreased by a decade with NaDEDC titrate in comparison with NaCl, because NaDEDC forms a more stable precipitate with Ag(I) (Eq. 1) with lower value of $K_{sp} = 5.8 \times 10^{-20}$. With NaDEDC titrant, the higher jump in potential occurs on a titration curve even in case of extremely dilute Ag(I) solutions, therefore the equivalence point is more correctly determined. However, further dilution leads to the lower jump in potential and increase of error.

The results of Ag^+ potentiometric determination in simulating solutions using the CCE and silver working electrodes, and KNO_3 supporting electrolyte are shown in the table 1. The correctness of measurements was validated by the add-found method.

TABLE 1. The results of Ag(I) potentiometric titration with NaDEDC and NaCl using CCE and silver working electrode
($P = 0.95$; $n = 5$)

Titrant	Added mass Ag(I), m (mg)	CCSE Found mass Ag(I), m (mg)	S_r	Ag Found mass Ag(I), m (mg)	S_r
NaDEDC	18.34	18.45 ± 0.84	0.02	15.24 ± 0.01	0.03
	1.834	1.83 ± 0.09	0.02	1.58 ± 0.01	0.001
	0.184	0.183 ± 0.005	0.01	0.171 ± 0.001	0.05
	0.0184	0.017 ± 0.002	0.005	0.0184 ± 0.0002	0.05
	0.0018	0.0017 ± 0.0001	0.004	—	—
NaCl	18.34	18.77 ± 0.76	0.02	18.3 ± 0.2	0.004
	1.834	1.82 ± 0.03	0.006	1.876 ± 0.04	0.01
	0.183	0.19 ± 0.08	0.02	0.18 ± 0.003	0.01
	0.018	0.017 ± 0.003	0.07	0.016 ± 0.001	0.01

As table 1 shows, the CCE is more sensitive than a silver working electrode, and the data obtained is in good agreement with the expected values within a confidence interval. The lowest concentration levels of Ag^+-ion achieved with NaCl and NaDEDC titrants using CCE were 1.7×10^{-5} M and 1.7×10^{-6} M, respectively, with the maximum error of 4%, which was less than for silver electrode. The titration of very weak Ag (I) solutions leads to the error growth and underestimation of analysis results because of the possible adsorption of Ag^+-ions on chemical glassware.

Analytical Response of Ag(I) on CCE

A typical potentiometric curve for Ag(I) titration with NaDEDC using CCE is shown in Fig. 1a. The titration curve was transformed into a linear plot by the linearization method in order to determine the equivalence point. Since there is a pronounced jump in potential on the titration curve (Fig. 1), the AB region was processed for this purpose.

| (a) | (b) |
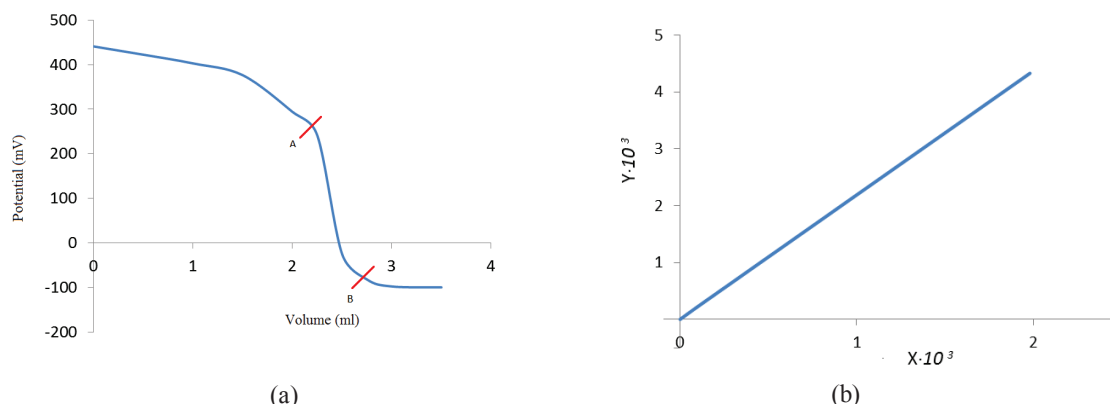
FIGURE 1. (a) Potentiometric titration curve for the simulation solution of 1.7×10^{-3} M Ag(I) with 7.3×10^{-2} NaDEDC using CCE; the aliquot volume is 10 ml; (b) the linear plot for AB fragment of the titration curve

Figure 1b shows the linear plot for AB region, which is approximated by a straight line with good correlation coefficient $r = 0.9999$; the slope V_{eq} (Ag) is 2.494 ± 0.005 ml ($P = 0.95$). This demonstrates good agreement between the titration model and the experimental data.

The experimental solubility product constant of AgDEDC was calculated to be 5.8×10^{-20} using a regression intercept term y_0.

Effect of Supporting Electrolyte

Figure 2 shows the titration curves of Ag^+ simulating solution with NaDEDC with additions of supporting electrolytes. Supporting electrolytes and buffer solutions were used in order to stabilize the ionic strength and to keep pH constant for better reproducibility of analysis results. It is especially necessary to add the supporting electrolyte to very dilute solutions with low conductivity in order to reach the stable electrode potential.

The experimental data obtained with the CCE were compared with those obtained using a silver indicating electrode under the same conditions, and the similar regularities have been found. With the pH increase up to 10 in ammonia buffer solution, the decrease of the jump in potential is observed as a result of the formation of water-soluble coordination complex of $[Ag(NH_3)_2]^+$ chloride. In strong acidic solutions at pH 2, a small growth of an electrode potential is observed on a tail of a titration curve at the end of the silver precipitation. This can be caused by the decomposition of an excess of NaDEDC in acidic solutions and formation of low-soluble diethyldithiocarbamic acid.

The curves with the most pronounced jump in potential were obtained at the pH range from 4 to 6 using KNO_3 supporting electrolyte. The solution of KNO_3 can stabilize the ionic strength and prevent the Ag^+-ion surface adsorption. Due to the screening effect, the supporting electrolyte molecules adsorbed on a precipitate surface reduces the lattice ion adsorption.

Buffer solutions are necessary to prevent the side reactions of Ag^+-ion hydrolysis during the titration in strong alkaline medium. Silver electrode cannot be used in strong acidic solutions at pH<3 because of the possible destruction of the electrode.

The higher jump in potential and good reproducibility in a wider pH range make the CCE a cost-effective alternative to the traditional silver electrode for potentiometric Ag(I) determination.

Effect of Interfering Ions

The NaDEDC titrant can also interact with other metal ions to form stable coordination complexes. As a result, metal ions can affect the potentiometric determination of Ag(I) when they are in a titration solution. The stability of some complex ions of a metal with NaDEDC is as follows [10]:

Hg(II) > Pd(II) > Ag(I) > Cu(II) > Ni(II) > Bi(III) > Co(II) > Pb(II) > Cd(II) > Tl(I) > Zn(II) > In(III) > Sb(III) > Fe(III) > Te(IV) > Mn(II).
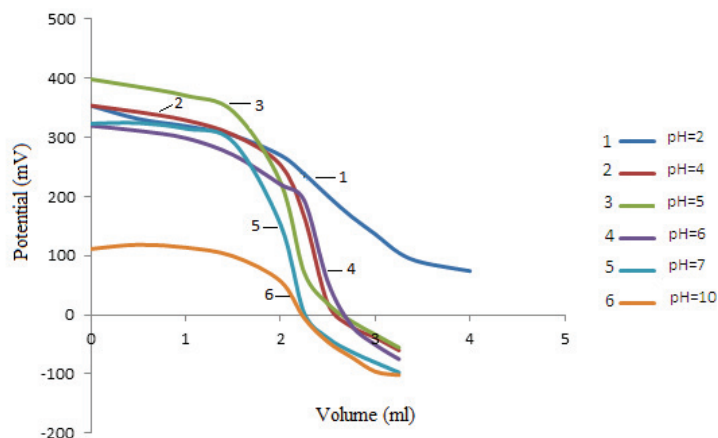
FIGURE 2. Potentiometric titration curves of 10 ml simulating solution containing 1.7×10^{-3} M of Ag(I) with 0.0073 M NaDEDC using CCE; the additions of buffer solutions: (1) HNO$_3$ (pH=2); (2) CH$_3$COOH + CH$_3$COONa (pH=4); (3) KNO$_3$ (pH=5); (4) CH$_3$COOH + CH$_3$COONa + NH$_4$OH + NH$_4$Cl (pH=6); (5) KNaC$_4$H$_4$O$_6$ (pH=7); (6) NH$_4$OH + NH$_4$Cl (pH=10)

The degree of proceeding of a titration reaction [11] can be a useful criterion to estimate the possibility of the separate determination of Ag(I) in a two-component solution containing one of the mentioned interfering ions. In the Fig. 3, two inflections refer to the titration of Ag(I) and interfering ion, respectively. Here, an interfering ion is that which is placed after Ag(I) in the given above series. The degree of proceeding shows which part (in %) of analyt has reacted with the titrant by the time the interfering ion starts to react with it.

For the titration of mixture Ag(I) – M(x) (M = Cu(II), Ni(II), Bi(III), Co(II), Pb(II), Cd(II), Tl(I), Zn(II), In(III), Sb(III), Fe(III), Te(IV) and Mn(II)), the degree of proceeding at a point of inflection in a titration curve was calculated to be 100 % indicating the total conversion of Ag(I) separately from the interfering ion. This confirms the possibility of potentiometric Ag(I) determination when there are interfering ions except Pd(II) in a solution being titrated.
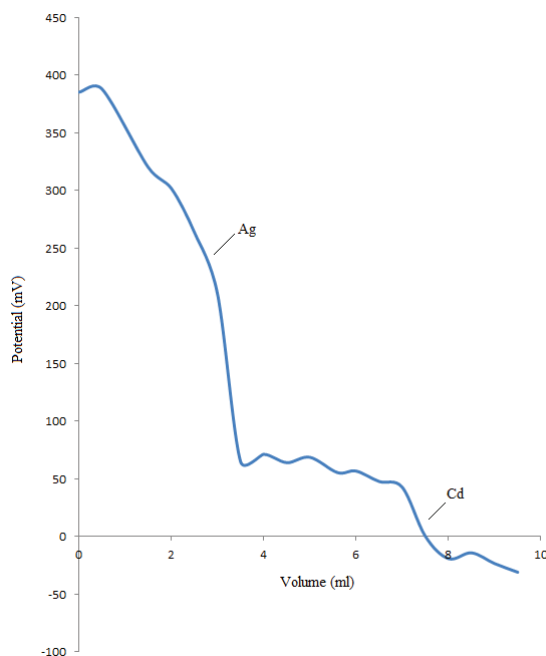
FIGURE 3. Potentiometric titration curve of 10 ml solution containing 1.7×10^{-3} M of Ag(I) and 0.95×10^{-3} M Cd(II) with 0.0005 M NaDEDC using CCE

The interfering effect of Pd(II) can be eliminated by adding a masking agent. The experiment demonstrated the possibility of separate Ag(I) determination in ammonia buffer solution together with disodium EDTA when there is palladium ion in a reaction solution. Palladium ions form more stable ammonia complexes, consequently they do not react with NaDEDC under these conditions. In case of other interfering ions, Ag(I) can be titrated with NaDEDC (Eq. 1) when there is disodium EDTA in a solution, because silver forms weaker complexes with disodium EDTA.

Potentiometric Determination of Ag(I) in Pharmaceuticals

The developed technique has been applied to determine silver in pharmaceuticals such as Sialor®, tablets for solution preparation (active ingredient is silver proteinate) and Argosulfan®, salve (active ingredient is silver sulfathiazole).

Sialor was analyzed according to the following procedure. The tablet of 0.2 g was placed in a beaker and being heated with three-fold excess of nitric acid in water bath until the organic matrix was decomposed and the solution turned from brown to colourless. Then the solution was cooled and placed into a 100 ml measuring flask, and the volume was filled up with double-distilled water.

The 10 ml aliquot of the prepared solution was titrated with NaDEDC using CCE and reference silver chloride electrode. The solution was stirred with a magnet stirrer, and the measuring was done when the stable response was obtained after addition of each portion of a titrant. The results of the potentiometric analysis are shown in the table 2. The correctness of data obtained was confirmed by the comparison with the results of the precipitation titration with visual inspection of the endpoint.

TABLE 2. The results of Ag(I) determination in 2% solution of Sialor® ($P = 0.95$; $n = 3$)

Method of Determination	Found mass Ag(I), g	S_r
Potentiometric Titration	0.0169 ± 0.0005	0.003
Precipitation Titration (visual inspection of endpoint)	0.0171 ± 0.0002	0.02

The sample preparation of Argosulfan for the potentiometric determination on Ag(I) was as follows. The exact quantity of salve (1 g) was placed in a beaker; then, 6 ml of 16 M HNO_3 and 3 ml of H_2O_2 were added and mixed well with the salve under heating. The mixture obtained was placed in a measuring flask together with 5 g of KNO_3 salt, and the volume was filled up to 100 ml with double-distilled water. The titration technique was performed as described above for Sialor. The results obtained by the proposed analytical procedure in comparison with those obtained by the independent methods are shown in table 3.

TABLE 3. The results of Ag(I) determination in 2% cream of Argosulfan® ($P = 0.95$; $n = 3$)

Method of Determination	Found mass Ag(I), g	S_r
Potentiometric Titration	0.019 ± 0.002	0.03
Precipitation Titration (visual inspection of endpoint)	0.017 ± 0.003	0.04
Solid-Phase Spectrophotometry	0.019 ± 0.0025	2.0

As table 3 shows, the results obtained by the proposed technique are in a good agreement with those obtained by spectrophotometric analysis [12]. The results of precipitation titration are underestimated because of the systematic error resulted from imprecise visual inspection of endpoint.

The procedure has high sensitivity and low error and it also needs simple equipment, so it can be proposed for the routine analysis.

SUMMARY

The basic characteristics of a new sensor (concentration linear range, electrode slope and detection limit) for potentiometric analysis have been studying. The response time of the CCE does not exceed 60 sec. so that it can be proposed as a sensor for the routine analysis. The CCE has a wider linear concentration range which is from 1.7×10^{-2} to 1.7×10^{-6} M in comparison with silver working electrode. The conditions for Ag(I) titration in simulating solutions (effects of titrant, composition of supporting solution and pH) have been optimized, and the procedure for Ag(I) determination by potentiometric precipitation titration has been developed. The random error S_r is 0.01–0.05. The developed procedure has been successfully tested in the analysis of pharmaceutical

products with known composition, which has demonstrated that the results meet the expected values within the confidence interval and are confirmed by precipitation titration and solid-phase spectrophotometry.

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