

## **Analytical application of poly(vinyl chloride-co-vinyl acetate) electrode modified with silver for chloride ions determination in real systems**

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### **ABSTRACT**

Application possibility of new simple Ag-selective electrode for the determination of chloride ions, was investigated in this paper. The poly(vinyl chloride-co-vinyl acetate) electrode modified with silver (PVCAc/Ag) was prepared by simple immersion a glassy carbon rod coated with poly(vinyl chloride-co-vinyl acetate) polymer, which contained plasticizer and lipophilic additive, but without ionophore, into the silver nitrate solution. This simplicity of construction and extensive pH range through remarkable acidic media (pH 0.7 to 7.0), are the advantages of this modified electrode over many of reported silver selective electrodes based on a polymer matrix containing different ionophores. The response of the electrode was linear with a Nernstian slope of 60.25 mV/decade in the concentration range from  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup> Ag<sup>+</sup> and with a detection limit of  $4.25 \times 10^{-6}$  mol/dm<sup>3</sup>. Proposed PVCAc/Ag electrode was applied to the determination of chloride ions in the samples spring waters. The results of chloride ion determination in samples spring waters obtained by proposing electrode and comparative Ag/AgCl electrode were in satisfactory agreement.

*Keywords: silver, electrodes, spring waters, vinyl chloride-co-vinyl acetate, chloride ions*

## **Introduction**

Silver is white, shiny metal of excellent conductivity of electricity and heat, long been known, and due to its characteristics has always attracted attention. It is widely used in electrical industry, electronics, photography, organic synthetic chemistry, and production of fungicides (Smith et al., 1977), batteries, in complex compounds, medicine and other fields. Silver is a non-toxic metal, but its role in physiological processes is not completely understood, so its appearance even in small amounts in the skin, hair (Barrera et al., 1998), gums, cornea, liver, kidneys (Kazuyuki et al., 2001; Wan et al., 1991) are harmful. Also, the presence of soluble silver in wastewater is a problem in many industries. Therefore, there is a need for a fast, sensitive and simple method of determining small amounts of silver ions in different samples. There are different sensitive methods for the determination of silver ions at low levels, such as spectrophotometry (El-Zawawy et al., 1995; Ohshita et al., 1982), atomic absorption spectrometry (Bermejo-Barrera et al., 1996; Chakrapni et al., 2001; Pu et al., 1998; Rahman et al., 2004; Sramkova et al., 1999), inductively coupled plasma mass spectrometry (Chiba et al., 1992), inductively coupled plasma atomic emission spectrometry (Argekar et al 1995), fluorimetry (Kabasakalis, 1994), stripping voltammetry (Damien, 1994).

All these methods require the preliminary preparation of samples, which involves separation from the matrix, preconcentration, and the use of reagents, which are generally expensive. Because of all these methods are complicated and time consuming.

On the other hand, potentiometric sensors, ion-selective electrodes (ISE) have found application as alternative analytical methods because of their precision, sensitivity, selectivity, easy available instruments and low cost.

Nowadays, the majority of ion-selective electrodes are comprised of an organic polymeric membrane into which sensor material based on different ionophores is incorporated. Silver selective electrodes based on crowns (Shamsipur et al., 2002), Schiff-bases (Gupta et al., 2009), calixarenes (Demirel et al., 2006; Lu et al., 2004), *o*-hydroxyacetophenone carbohydrazone (OHAC) (Chandra et al., 2012) as well as other ionophores have been developed.

Most ion-selective electrodes of this type use poly(vinyl chloride) (PVC), a suitable plasticizer as an organic matrix and ionophore as the active part of the sensor (Johnson and Bachas, 2003). Examining the influence of different cations on the PVC matrix, it was found that it is sensitive to concentration changes of some ions, including silver ions. This phenomenon has been elucidated and the possibility of using a simple silver(I) selective electrode based only on a polymeric matrix with a plasticizer and a lipophilic ionic additive, but without ionophores as an active component, has been investigated.

The possibility of applying the proposed PVCAc/Ag potentiometric sensor was tested by determining  $\text{Ag}^+$  ions in ecological water samples and colloidal silver water (Sejmanović et al., 2011). In this study simple Ag- selective electrode was used for determination of  $\text{Cl}^-$  ions by potentiometric titrations in spring water samples.

## Experimental

### Reagents and Solutions

The following reagents were used to prepare the experimental solutions:

1. Silver(I) nitrate ( $\text{AgNO}_3$ ), p.a. "Merck", Darmstadt, Germany.
2. Poly(vinyl chloride-co-vinyl acetate) (Pevikon C870, PVCAc), p.a. "Pevicon", Fostatbolaget, Sweden.
3. Dibutyl phthalate (DBP), p.a. "Fluka", Buchs, Switzerland.
4. Sodium tetraphenyl borate ( $\text{NaTPB}$ ), p.a. "Merck", Darmstadt, Germany.
5. Tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ , THF), p.a. "Merck", Darmstadt, Germany.
6. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), p.a. "Laphoma", Skopje, Macedonia.
7. Sodium chloride ( $\text{NaCl}$ ), p.a. "Laphoma", Skopje, Macedonia.

High purity water (Millipore,  $18\text{M } \Omega \text{ cm}$  resistivity) was used.

The ionic strength of the solution was adjusted using  $\text{NH}_4\text{NO}_3$  solution,  $c(\text{NH}_4\text{NO}_3) = 0.05 \text{ mol/dm}^3$ . Activities were calculated by the Debye-Hückel procedure.

A standard silver nitrate solution was prepared by measuring the required amount of silver nitrate for a solution of concentration  $0.1 \text{ mol/dm}^3$ . This amount (1.6897 g) was dissolved in high purity water and the solution diluted to  $100 \text{ cm}^3$ . The solution was standardized with  $0.1 \text{ mol/dm}^3$  sodium chloride solution. The following standard silver nitrate solution,  $c(\text{AgNO}_3) = 10^{-2} \text{ mol/dm}^3$ , was prepared by pipetting a  $10 \text{ cm}^3$  solution of  $\text{AgNO}_3$  concentration of  $0.1 \text{ mol/dm}^3$  and diluted it with a solution of  $\text{NH}_4\text{NO}_3$  ( $c(\text{NH}_4\text{NO}_3) = 0.05 \text{ mol/dm}^3$ ) in a volumetric flask ( $100 \text{ cm}^3$ ). Solutions of lower concentrations of  $10^{-3} \text{ mol/dm}^3$  to  $10^{-7} \text{ mol/dm}^3$  were prepared by tenfold successive dilution of a standard  $0.01 \text{ mol/dm}^3$  solution of  $\text{AgNO}_3$  with a solution of  $\text{NH}_4\text{NO}_3$  ( $c(\text{NH}_4\text{NO}_3) = 0.05 \text{ mol/dm}^3$ ).

### Apparatus

All potentiometric and pH measurements were performed using the pH meter (Hanna pH-211). The instrument covers an area from pH 2.00 to pH 16.00 (sensitivity  $\pm 0.01$  pH units). When using ion-selective electrodes, the measuring range of the instrument is in the range of +2.000 to -2.000 mV (sensitivity 0.1 mV);

- Magnetic mixer was a product of "VELP Scientifica", set at 4000 rpm;

- Potentiostat PAR Model 273;
- X-Y recorder Model 8033 was a product of “Philips”.

### Electrodes

PVCAc/Ag electrode of our own making, without internal solution and ionophore, is made by simply immersing a glassy carbon (GC) rod coated with a membrane of poly(vinyl chloride-co-vinyl acetate) polymer, plasticizer and lipophilic additive in silver nitrate solution. PVCAc/Ag electrode was used as a working electrode, an Ag(I) ion-selective electrode.

Ag/AgCl electrode was used as a comparative electrode for the determination of chloride in spring water samples. It is obtained by the process of coating a silver strip with melted sensory compound synthesized by pre-deposition from aqueous solutions of a homogeneous mixture (Jovanović et al., 1985).

A double junction saturated calomel electrode (SCEd.j.), produced by Hanna Instruments, with a salt bridge containing  $\text{NH}_4\text{NO}_3$  ( $c(\text{NH}_4\text{NO}_3)=1 \text{ mol/dm}^3$ ), was used as a reference electrode in an electrochemical coupling:

SCEd.j. || standard solutions / sample solution | PVC membrane | GC

### Preparation of PVCAc/Ag electrode

The polymeric membrane contained 39-48% PVCAc, 52-61% DBP and 0.2-1% NaTPB. A total mass of 0.270 g of these reagents was mixed with  $2.5 \text{ cm}^3$  THF. A glassy carbon (GC) ( $\Phi 3 \text{ mm}$ ) (Sigardur-Sigri Electrographite, GmbH, Germany) was directly coated by dipping it several times in this mixture until a bead was formed coating the GC. Electrode prepared in this way was allowed to dry in the air about 12 h. Then, the bead on the glassy carbon was placed into a silver nitrate solution ( $c(\text{AgNO}_3) = 0.01 \text{ mol/dm}^3$ ) for about 30 min in order to condition it before use. This coated GC was used as Ag(I) ion-selective electrode and designated as a PVCAc/Ag electrode. Electrical contact with the instrument was made *via* a cable attached to the end of the undated portion of the glassy carbon.

The surface of the GC stick was washed with THF before being immersed in the mixture of substances, in order to remove traces of grease, carefully polished with 400 grit, then 1200 grit and finally with 2500 grit sandpaper, and afterwards washed with high purity water.

### Sample preparation

For analytical confirmation of PVCAc/Ag ion-selective electrode by determination of chloride ions, the following water samples were used: spring waters sampled from Sjenica territory: source „Česmica“, source „Bazeni“, water from the „Vrelo“, water from the „Jasen“.

The samples of the spring waters were first treated by  $1 \text{ cm}^3$  of  $\text{HNO}_3$   $c= 0.1 \text{ mol/dm}^3$  in a volumetric flask ( $50 \text{ cm}^3$ ), since the working range of the electrode is in very acidic medium, and in

addition eliminates the possible presence of carbonate in the tested waters. The ionic strength in the samples was adjusted with a solution of  $\text{NH}_4\text{NO}_3$  ( $c(\text{NH}_4\text{NO}_3) = 0.05 \text{ mol/dm}^3$ ).

## Procedure

The potentials were measured by varying the concentration of  $\text{AgNO}_3$  in the standard solution within the range from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1} \text{ mol/dm}^3$ . All potentiometric and pH measurements were performed at a temperature of  $25^\circ \text{C}$ . The electrode was prepared as previously described, and placed into  $0.01 \text{ mol/dm}^3 \text{ AgNO}_3$  solution for 30 min.

After the preparation of the water sample, the PVCAc/Ag electrode along with the reference electrode was immersed into the sample and titrated with  $\text{AgNO}_3$  solution. The concentrations of the  $\text{AgNO}_3$  solution for potentiometric titration were:  $1.0 \times 10^{-3} \text{ mol/dm}^3$ ,  $2.5 \times 10^{-3} \text{ mol/dm}^3$ ,  $1.0 \times 10^{-4} \text{ mol/dm}^3$ , and  $5.0 \times 10^{-4} \text{ mol/dm}^3$ . The same increments of the  $\text{AgNO}_3$  solution was added gently up to the end point and continued after it up to few readings. The value of three consecutive potential measurements is accepted as the ultimate. The end point and the amount of  $\text{Cl}^-$  ions in water samples were determined by extrapolation of the three linear portions of the titration plot. The concentrations of  $\text{Cl}^-$  ion in the different water samples were compared by direct potentiometric method, using standard chloride solutions, by  $\text{Cl}^-$  selective on a silver-deposited Ag/AgCl electrode.

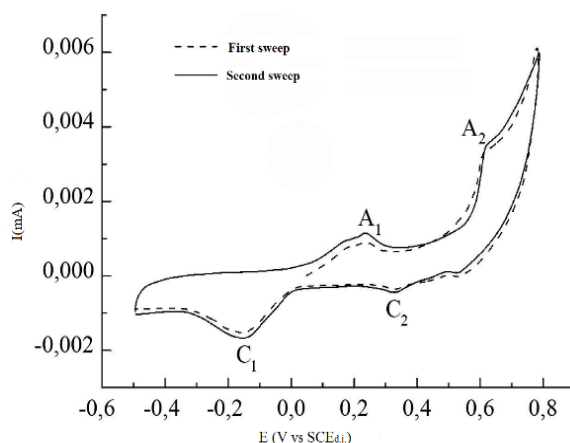
## Results and Discussion

Our previous experiments (Petković et al., 2010) where PVCAc was used as a sensor matrix revealed that this material was highly selective to  $\text{Ag}^+$  with respect to many different cations, with the exception of  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$  ions. The concept of sensor behavior of the PVC matrix without any ionophore, led us to the idea of the simplest construction of a polymer membrane electrode which certainly needed further attention. The similar attempt was performed before, but the analytical performance of the reported electrode was not satisfactory (Malinowska et al., 1994). In the research, a simple sensor was prepared by coating glassy carbon rod with a membrane of poly(vinyl chloride-co-vinyl acetate) polymer, plasticizer (DBP) and lipophilic additive (NaTPB) but without ionophores as the active component.

We showed earlier that GC as well as polypyrrole (PPy) could be modified by silver simply by immersion of the electrode into the silver nitrate solution (Dekanski et al., 2001; Jovanović et al., 2005). The modified membrane was examined by cyclic voltammetry and it was found that cyclic voltammograms of the silver modified PVCAc electrode resemble the voltammograms for a pure silver electrode (Dirkse, 1989). Based on the CV recorded it was concluded that silver was deposited in the

elemental state on the surface and near surface layers of the membrane; similar results were reported for modified polypyrrole and glassy carbon (Figure 1). The operation mechanism of membranes with only PVCAc and DBP can be explained through the red-ox process of the  $\text{Ag}^+/\text{Ag}^0$  couple on the surface of the membrane.

In order to obtain the optimum potentiometric characteristics of the electrode, optimization of the membrane composition by changing the ratio of the membrane component was performed.

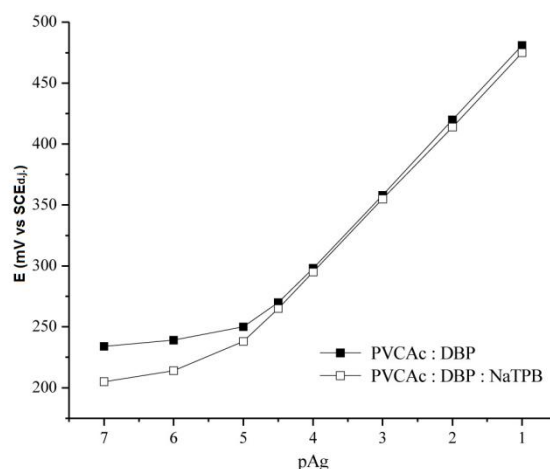


**Figure 1.** Cyclic voltammogram for the GC/PVCAc/Ag electrode in  $0.1 \text{ mol/dm}^3$  NaOH solution (sweep rate  $50 \text{ mV/s}$ ).

## Characteristics of PVCAc/Ag electrodes

### Linear range and limit of detection

The best performance was observed with the membrane optimized electrode composition 44.3%: 55.2%: 0.5% (PVCAc:DBP:NaTPB). The optimized electrode has a linear dependence in the concentration range from  $1.0 \times 10^{-1} \text{ mol/dm}^3$  to  $1.0 \times 10^{-5} \text{ mol/dm}^3$  of Ag(I) with an almost Nernstian slope of  $60.25 \text{ mV/decade}$ , slightly higher than the theoretical value ( $59.16 \text{ mV/decade}$ ), which means that the electrode is highly reproducible. The limit of detection is  $4.25 \times 10^{-6} \text{ mol/dm}^3$  (Figure 2). All the above characteristics make this electrode comparable with ionophore containing electrode reported in the literature (Demirel et al., 2006; Jeong et al., 2011; Shamsipur et al., 2002).



**Figure 2.** Calibration curve of the proposed Ag(I) selective electrode with NaTPB ( ◻ ) and without NaTPB in its composition ( ◼ ).

### Response time

The response time of this electrode was monitored depending on the electrode conditioning time. It was concluded that the shortest response time is 5 to 30 s for standard  $\text{AgNO}_3$  solutions with concentrations of  $1.0 \times 10^{-1} \text{ mol/dm}^3$  to  $1.0 \times 10^{-7} \text{ mol/dm}^3$ , and for the PVCAc/Ag electrode it is achieved after 30 min of conditioning in  $\text{AgNO}_3$  ( $c(\text{AgNO}_3) = 0.01 \text{ mol/dm}^3$ ). After 30 min of conditioning in  $\text{AgNO}_3$  ( $c(\text{AgNO}_3) = 0.01 \text{ mol/dm}^3$ ), the PVCAc/Ag electrode achieves the shortest response time (5 s to 30 s) for a standard  $\text{AgNO}_3$  solution with concentrations of  $1.0 \times 10^{-1} \text{ mol/dm}^3$  to  $1.0 \times 10^{-7} \text{ mol/dm}^3$ .

### Response stability

The response stability of the PVCAc/Ag electrode was evaluated by constant current chronopotentiometry, which is a rapid experimental method and the electrode was found to exhibit a stable potential for a longer than two months.

### Effect of pH

The effect of pH on the potentiometric response of the PVCAc/Ag electrode was studied in solutions with a constant concentration of silver ions ( $c(\text{AgNO}_3) = 0.01 \text{ mol/dm}^3$  and  $0.001 \text{ mol/dm}^3$ ) in the range of pH 0.7 to 9.0. The pH values were adjusted by adding a solution of  $\text{HNO}_3$  or  $\text{NaOH}$  at different concentrations. The potential is independent over the interval from very acidic to neutral medium, *i.e.* from pH 0.7 to 7.0 representing the working range of the sensor. Applicability in a highly

acidic media is a major advantage of this electrode. With increasing pH value, the potential response decreases, which is attributed to the hydroxylation of silver ions. At lower pH value of 0.7 the electrode was not studied because of hydrogen error of the indicator electrode. The advantage of the proposed silver electrode is its applicability in very acidic media, where other electrodes which contain an ionophore in the polymer matrix do not function.

### **Selectivity**

The selectivity of the PVCAc/Ag electrode was evaluated with fixed interference method and matched potential method (Umezawa et al., 1995). The results reveal that the electrode is highly selective for silver ions relative to other ions, and most of the cations tested do not interfere the determination of silver in the potential sample, with the exception of  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$ , which strongly interfere even at  $10^{-2}$  mol/dm<sup>3</sup> concentrations, and their removal from sample is necessary. These ions most likely exhibit their own interactions with the polymeric membrane and their potentiometric response often was not linear and steady under these conditions. The presence of most of the studied cations, such as  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ , would not cause any interference in the estimation of silver ions even if present in concentrations of  $10^{-2}$  mol/dm<sup>3</sup>.  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  ions present at concentrations of  $10^{-2}$  mol/dm<sup>3</sup> in solution have a slight interference.

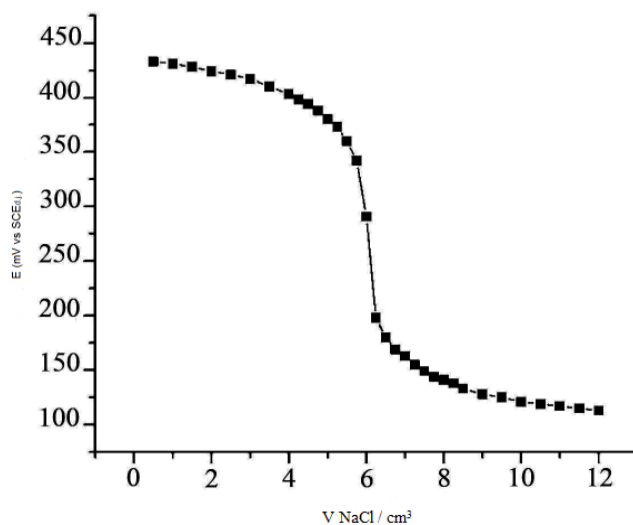
### **Potentiometric titration with sodium chloride**

Proposed optimized PVCAc/Ag electrode composition 44.3%: 55.2%: 0.5% (PVCAc: DBP: NaTPB) was applied as an indicator electrode in the potentiometric titration of silver(I) ions in sodium chloride solution (pH is about 5).

The following diagrams (Figures 3-7) show potentiometric curves when PVCAc/Ag electrode was used as the indicator electrode, with chlorides being titrated.

Potentiometric titration of 6 cm<sup>3</sup> solution of Ag(I) ( $c=1.0 \times 10^{-1}$  mol/dm<sup>3</sup>) diluted with deionized water to a volume of 50 cm<sup>3</sup> with a NaCl ( $c=1.0 \times 10^{-1}$  mol/dm<sup>3</sup>) yielded a sigmoidal (S - curve) curve (Figure 3). The end point of the titration and the amount of  $\text{Ag}^+$  ions in the solution can be accurately determined on the basis of the potentiometric titration curve using the PVCAc/Ag electrode as the indicator electrode.

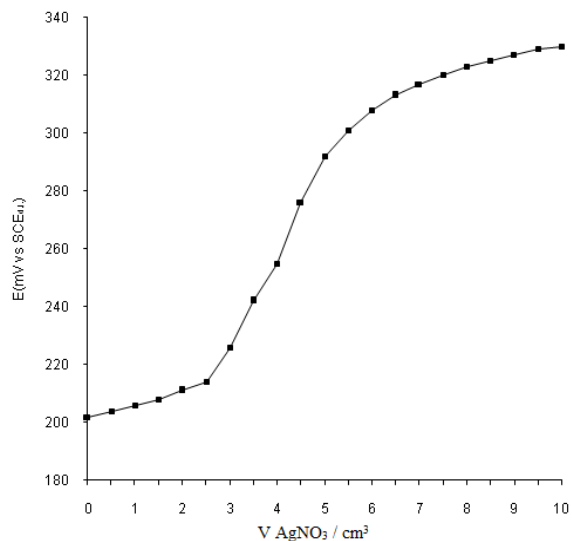




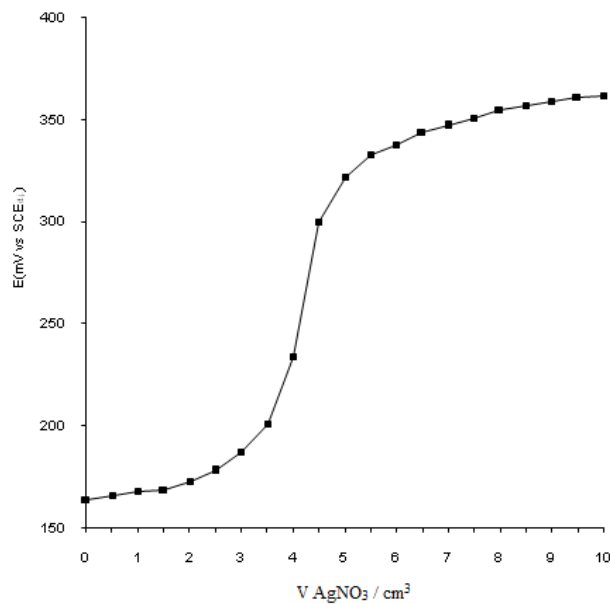
**Figure 3.** Potentiometric titration of  $1.12 \times 10^{-2} \text{ mol/dm}^3$  solution of  $\text{Ag}^+$  ions with  $1.0 \times 10^{-1} \text{ mol/dm}^3$  solution of NaCl with indicator PVCAc/Ag electrode.

### Analytical application in real systems

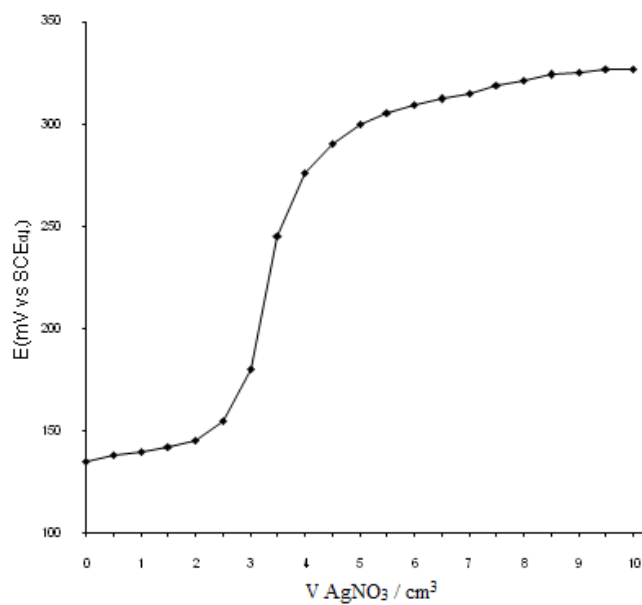
The following diagrams show potentiometric curves of titration of  $\text{Ag}^+$  ions with chlorides when the PVCAc/Ag electrode was used as the indicator electrode. When all chlorides were precipitated, excess of  $\text{Ag}^+$  ions caused the potential jump because the electrode is selective to silver ions.



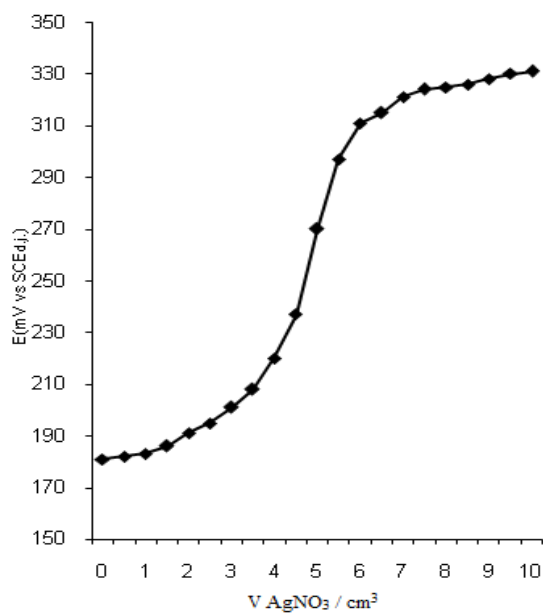
**Figure 4.** Potentiometric titration of Cl<sup>-</sup> ions in a sample of spring water from „Jasen“, with a solution of AgNO<sub>3</sub> ( $c = 2.5 \times 10^{-3}$  mol/dm<sup>3</sup>), using PVCAc/Ag indicator electrode.



**Figure 5.** Potentiometric titration of Cl<sup>-</sup> ions in a sample of spring water from „Česmica“, with a solution of AgNO<sub>3</sub> ( $c = 1.0 \times 10^{-2}$  mol/dm<sup>3</sup>), using PVCAc/Ag indicator electrode.



**Figure 6.** Potentiometric titration of Cl<sup>-</sup> ions in a sample of spring water from „Vrelo”, with a solution of AgNO<sub>3</sub> ( $c = 1.0 \times 10^{-4}$  mol/dm<sup>3</sup>), using PVCAC/Ag indicator electrode.



**Figure 7.** Potentiometric titration of Cl<sup>-</sup> ions in a sample of water from „Bazeni“, with a solution of AgNO<sub>3</sub> ( $c = 5.0 \times 10^{-3}$  mol/dm<sup>3</sup>), using PVCAC/Ag indicator electrode.

The potentiometric curve is sigmoidal in all cases, and the endpoint of the titration is sharp enough. Compare results are shown in Table 1, and it can be considered that the values obtained by the proposed sensor agree well with the results obtained by the comparative method. RSD values for chloride determination in different spring water samples range from 1.48-5.31%.

**Table 1.** Determination of chloride ion in spring water samples using the proposed PVCAc/Ag electrode and the comparative Ag/AgCl electrode.

Sample	Cl <sup>-</sup> (mg/dm <sup>3</sup> )		RSD %
	Found by PVCAc/Ag electrode (n=3)	Found by comparative Ag/AgCl electrode	
Spring water from „Sjenica”			
„Jasen”	7.028±0.2	6.987±0.2	3.22
„Česmica”	27.509±0.4	27.787±0.4	1.48
„Vrelo”	0.232±0.1	0.301±0.2	5.31
„Bazeni”	15.399±0.3	15.612±0.3	1.86

The results reported, our previous studies as well as the results reveal that proposed PVCAc/Ag electrode has been used for the determination of chloride ion concentration in the range of 1.0 to 25.0 mg/dm<sup>3</sup>. At higher concentrations of Cl<sup>-</sup> ions, the water sample solution was used to dilute beginning of the reaction. Water samples that contain lower concentrations of Cl<sup>-</sup> ions than 1.0 mg/dm<sup>3</sup> were concentrated (sample “Vrelo” was concentrated on 1/10 V), because applicability of the proposed method is in the concentration range of 1.0-25.0 mg/dm<sup>3</sup> of chloride ions. The presence of cations in environmental water samples do not interfere the determination of chloride ions by the proposed electrode. Therefore, on the basis of all the above, it can be concluded that the chloride concentration was

successfully determined in spring water samples by potentiometric titration with standard solutions of  $\text{AgNO}_3$  of appropriate concentrations when using the PVCAc/Ag electrode as indicator electrode.

## **Conclusion**

The potentiometric titration curve in all cases is of the typical S-shape, and the end point of the titration is sharp enough. The values obtained agree well with those obtained by the comparative direct potentiometric method. Precision is satisfactory as indicated by the standard deviation values (1.48-5.31%).

Analytical application of poly(vinyl chloride-co-vinyl acetate) electrode modified with silver, without ionophores, of simple construction, is wide because of its characteristics. It is comparable or even better than silver selective electrodes based on a polymer membrane containing different ionophores which are already widely accepted.

Given that the electrode is proven to be reliable throughout this work, a wide concentration and pH range can be used in the analysis of real samples if the interfering ions of  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$  are not present.

## **Conflict-of-Interest Statement**

Authors declare no conflict of interest.

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