



## Development of a highly sensitive and selective optical sensor for determination of ultra-trace amount of silver ions

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### ABSTRACT

A new selective membrane optical sensor was prepared for the determination of ultra-trace amounts of silver(I). The optical sensor was prepared using a recently synthesized ionophore, 7-(1H-indol-3-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine 3,11(4H,12H)-dione, as an ionophore and ETH-5294 as a chromoionophore in a PVC membrane. The influence of several parameters on the preparation of the optical sensor and the determination of Ag(I) was studied and optimized. The optical sensor has a wide linear dynamic range ( $2.27 \times 10^{-11}$  to  $1.13 \times 10^{-3}$  mol L<sup>-1</sup>) with a low detection limit of 9.5 pmol L<sup>-1</sup> Ag(I). The response time of this sensor was 210 s. The optical sensor could be regenerated several times using 0.2 mol L<sup>-1</sup> HCl solution. The influence of potential interference ions on the Ag(I) determination was studied. The results showed that the prepared optical sensor was very selective to silver ions so that it had no significant response to common ions such as Mn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, and Co<sup>2+</sup>. The sensor was also applied successfully for the determination of silver ions in different real samples such as Zayandehrood river water, two polymetallic ores, and silver sulfadiazine (1.0%) topical cream.

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## 1. Introduction

Silver ion, as a heavy metal ion, in comparison with cadmium, chromium, copper, and mercury, is among one of the most poisonous categories of toxic ions [1]. Given the growing application of silver in medicine and industry, its entrance in the environment has been increased [2,3]. Silver can be assimilated from the lungs, gastrointestinal tract, mucous membranes, and skin [4]. There is a very low concentration of silver in the human body but it does not have any physiological or biochemical role within the body [5]. In the body, silver creates conditions such as argyria, which is produced when the silver is accumulated in the blood and soft tissues, especially skin [5]. Several methods for the measurement of silver have been reported, including ion selective electrodes [6–8], differential pulse anodic stripping voltammetry [9], dispersive liquid–liquid microextraction coupled with UV–vis spectrophotometric [10], inductively coupled plasma [11], microextraction based on ionic liquid [12,13], and mass spectrometry [14]. Most of these techniques have important limitations and problems that are related

to sample preparation, time consuming, expensive and/or complicated analysis systems, boring, and hard operation.

Optical sensors have received considerable attention in recent decades. Optical sensors have many advantages such as ease of production, cheapness, good selectivity and sensitivity, high dynamic concentration range and also low detection limit [15–18]. As yet, several reviews and papers have been reported for the measurement of silver by optical sensors based on colorimetric and/or fluorimetric methods [19–30].

In the present work, based on a recently synthesized ionophore [31] in PVC membrane, a highly selective optical chemical sensor is designed. This sensor is without any pre-concentration steps and can detect very low concentrations of silver ions. The detection limit and selectivity of this optical sensor is superior to all reported optical sensors based on colorimetric method. Furthermore, no serious interference is observed (see Tables 5 and 6).

## 2. Experimental

### 2.1. Chemicals

Analytical reagent grade chemicals (with the highest degree of purity available, free of silver ions) and tetrahydrofuran (THF), all from Merck, and deionized water were used throughout. ETH-5294, polyvinyl chloride (PVC) high molecular mass, was obtained

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from Fluka. Dioctyl sebacate (DOS), dibutyl phthalate (DBP), dioctyl phthalate (DOP), and sodium tetraphenylborate (NaTPB), all from Aldrich, were used.

Buffer solution of pH 6.5 was prepared from nitric acid and potassium citrate.

A stock solution of  $0.010 \text{ mol L}^{-1}$   $\text{Ag(I)}$  ions was prepared by dissolving an appropriate amount of  $\text{AgNO}_3$  into a 100-mL standard flask and diluting it to the mark with the deionized water. Lower concentrations were prepared by appropriate dilution of the stock solution with citrate buffer of pH 6.5.

7-(1H-indol-3-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine-3,11(4H,12H)-dione,  $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}_4$  (MW: 422.477), was used as an ionophore and prepared according to the reported method [31]. The ionophore is a white powder with m.p. of 190–191 °C. The IR spectra (KBr) showed: 748(s), 818(m), 1049(s), 1126(s), 1219(s), 1257(s), 1439(m), 1504(s), 1535(s), 1597(m), 1686(vs), 2804(w), 2928(w), 3271(m), 3414(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz):  $\delta$ =2.75 (t, 4H,  $J$ =5.3 Hz), 3.54 (t, 4H,  $J$ =5.3 Hz), 3.85 (s, 2H), 4.41 (s, 4H), 6.70 (t, 2H,  $J$ =7.4 Hz), 6.85–7.04 (m, 4H), 7.08 (s, 2H), 7.30 (d, 1H,  $J$ =8.1 Hz), 7.61 (s, 2H), 7.63 (d, 1H,  $J$ =7.3 Hz), 8.60 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$ =35.6, 46.6, 51.9, 67.6, 110.7, 111.3, 118.9, 119.5, 122.2, 122.5, 124.1, 127.3, 136.4, 146.5, 167.5. Mass  $m/z$  (%): 423( $\text{M}^+$  +1, 0.2), 422( $\text{M}^+$ , 0.5), 421(0.1), 420(0.3), 349(0.8), 306(0.4), 293(0.6), 292(1.5), 280(1.5), 245(1.1), 225(20.2), 167(10.3), 130(100.0), 102(27.7), 85(48.4), 69(82.9).

## 2.2. Apparatus

A double beam UV–vis spectrophotometer (Cary-500 Scan, Varian, Palo Alto, CA, USA) with 1.0 cm quartz cells was used for the absorbance measurements. pH measurements were taken by model 827 pH/ion meter (Metrohm, Herisau, Switzerland) equipped with a combined glass electrode.

Atomic emission measurements were taken by Inductively Coupled Plasma (Perkin–Elmer, OPTIMA 7300–DV).

## 2.3. Membrane preparation

A typical membrane consisted of 31.0 mg PVC, 62.0 mg DOP, 3.0 mg NaTPB, 2.5 mg ionophore, and 1.5 mg ETH-5294, all dissolved in 1.0 mL of THF. The mixture was stirred with a magnetic stirrer for 15 min to achieve a homogeneous solution. A glass slide with 9 mm  $\times$  50 mm was selected and cleaned with 1.0 mol  $\text{L}^{-1}$  sulfuric acid and sodium hydroxide solutions, respectively; then it was washed with water and dried in an oven at 110 °C for 1 h.

The membrane was cast by pipetting a 20  $\mu\text{L}$  aliquot of the membrane solution onto the glass slide, and spread rapidly using a capillary glass tube. The membrane was allowed to stand in room temperature to dry for 4 h.

## 2.4. Measurement procedure

The sensor was placed in a 1.0 cm quartz cell containing  $\sim 3$  mL of the citrate buffer solution (pH 6.5). After three min, its absorbance was measured at  $\lambda_{\text{max}}$  660 nm. Then, the cell was filled with  $\text{Ag(I)}$  standard solution (where it was buffered at pH 6.5 with the buffer solution) and after 210 s, the absorbance of the sensor was measured. After measuring all of the standard solutions, the optical sensor was regenerated in 0.2 mol  $\text{L}^{-1}$  HCl solution for 420 s. Following that, the cell was filled with  $\text{Ag(I)}$  sample solution and after 210 s, the absorbance of the sensor was measured again. The calibration curve was plotted; subsequently, the concentration of sample was found.

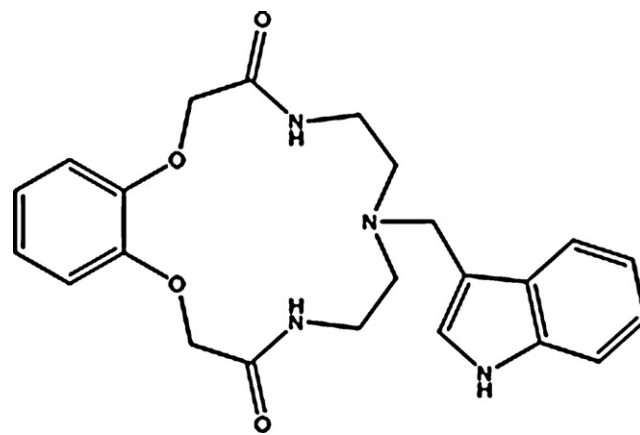


Fig. 1. Structure of the ionophore.

## 2.5. Real sample preparation

Acid digestion method was used for preparation of polymetallic ore samples [32]. A suitable amount of the sample (less than 0.5 g) was transferred into a 15 mL polytetrafluoroethylene (PTFE) crucible. Then, 3.0 mL of concentrated HF, 3.0 mL of concentrated HCl, 3.0 mL of concentrated  $\text{HNO}_3$  and 0.5 mL of concentrated  $\text{HClO}_4$  was added. The mixture was evaporated to almost complete dryness under gentle heating on a hot-plate at 120–150 °C. After cooling to room temperature, the residue was dissolved in water on a hot plate. The final solution was made up to 100 mL. Then, 1.0 mL of the solution was diluted to 25 mL with the citrate buffer (pH 6.5) in a 25-mL volumetric flask prior to the measurement.

Determination of silver content in silver sulfadiazine 1% topical cream was done by burning to ash a certain amount of the cream in oven and then dissolving its ash in concentrated  $\text{HNO}_3$ . Next, the solution was filtered and this was followed by dilution with distilled deionized water to prepare a primary solution. Concentration of the sample is reduced by gradual dilution of the primary solution with deionized water. The prepared solution in the last stage of dilution is then buffered with the citrate buffer (pH 6.5) prior to the measurement.

Zayanderood river water was collected in polyethylene bottle and two drops of nitric acid was added. The sample was filtered to remove any solid particles before analysis. Then 1 mL of the citrate buffer (pH 6.5) was added to 9.0 mL of the sample in a 10-mL volumetric flask prior to the measurement.

## 3. Results and discussion

### 3.1. Principle of the operation

The ionophore, 7-(1H-indol-3-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine 3,11(4H,12H)-dione, has  $-\text{NH}$  and suitable cavity (Fig. 1). The cavity size has an important effect on the membrane selectivity, because an especial ion could fit to the cavity and has contact mode interaction. It seems that the cavity size is suitable for  $\text{Ag}^+$  ions. It can, therefore, interact with  $\text{Ag}^+$  ions. The organic membrane contains ionophore, chromoionophore (acid–base indicator), and anionic additive stabilized in polyvinylchloride (which is plasticized by DOP). By contacting the membrane sensor with an aqueous solution containing silver ions, these ions interact with the membrane and form complex with the ionophore. Therefore, the charge balance is annihilated. By renewing the charge balance,

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