

## Flow Injection Potentiometric Determination of Silver(I) in Photographic Film Developing Solution Samples by Polyvinylchloride Membrane Silver(I) Selective Electrode

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**Summary:** A polyvinylchloride (PVC) membrane silver(I) selective electrode was developed for the determination of silver(I) ions in photographic film developing solutions. The electrode was embedded into a home-made flow cell and successfully used as a potentiometric detector in a flow injection potentiometric (FIP) system. Under the optimized flow injection conditions, the electrode exhibited a non-Nernstian slope of  $67.20 \pm 0.80$  mV in the linear range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  mol/L ( $R^2=0.9961$ ) and the lowest value for limit of detection (LOD) was calculated as  $7.1 \times 10^{-6}$  mol/L. The electrode displayed good sensitivity, selectivity, repeatable and rapid response towards silver(I) ions. Lifetime of the electrode was determined as at least two months in FIP system. The electrode was also successfully applied for the potentiometric determination of silver(I) ions in photographic film developing solution samples in FIP system. The results attained from FIP system were compared with the atomic absorption spectrophotometry (AAS) results by using student's *t*-test at 95 % confidence level and relative deviation (RD) between the two methods was  $< 8\%$ .

**Keywords:** Silver(I) selective electrode, Flow injection potentiometry, Photographic film developing solution, Potentiometric analysis.

### Introduction

Ion selective electrodes (ISEs) offer very attractive properties such as simplicity of apparatus and ease of use, low cost, fast response, high selectivity and sensitivity, high reproducibility and especially miniaturization capability [1]. Because of this properties, ISEs have been utilized as detectors in flow injection analysis (FIA) systems and a lot of automated clinical analyzers for the correct and fast analysis of diverse ionic species (such as  $\text{Li}^+$ ,  $\text{VO}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{ClO}_4^-$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  etc.) during the past decades [2-8].

Silver is used widely in the photographic film paper surface, radiological film surface, alloys, jewellery, manufacture of electrical apparatus, certain cream and production of dental amalgams [9]. As a result of the use of silver in photographic process and due to involving of high amounts especially as silver(I) ions, its monitoring in environment and water resources becomes a must. Trace amounts of silver is not harmful, even can be useful due to its antibacterial properties, but it shows toxic effects when taken in large quantities. Therefore, silver's

fast, accurate and reliable analysis is important to environment and human health.

Many methods including atomic absorption spectrometry (AAS) [10, 11], inductively coupled plasma mass spectrometry (ICP-MS) [12, 13], colorimetric solid-phase extraction (CSPE) [14], discontinuous flow analysis (DFA) [15] for the determination of silver(I) ions have been reported in literature. Some of these methods require expensive apparatus and are time consuming, whereas determination of silver(I) ions with potentiometric methods are both low cost and simple [16]. Especially potentiometric systems combined with flow injection analysis systems can be used in potentiometric analysis due to their great properties such as working in a small sample volumes, continuous washing of detector, simple instrumentation and wide linear working range [17-19]. Additionally, the transient nature of the signal in FIA may help to eliminate interference effect if the electrode response to interfering ions is slower than that to the main ion [20]. Although its excellent advantages, there are only a few reports in literature

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describing the flow injection potentiometric determination of silver(I) ions [16, 32].

In our previous work, we proposed a solid state PVC membrane silver(I) selective electrode based on the newly synthesized [N,N'-ethylenebis-(3-methoxy salicylaldehyde)] as an electroactive membrane ingredient. In the cited work, potentiometric performance characteristics and applications of the offered electrode in batch mode were tested [21]. In the current study, the utilization of the previously developed silver(I) selective electrode for the determination of silver(I) ions were investigated in flow injection potentiometric (FIP) mode. Besides, this work deals with the flow injection potentiometric (FIP) application of this electrode for the determination of silver(I) ions in photographic film developing solution samples. The currently proposed flow injection potentiometric system for silver(I) determination offers high-speed analysis due to the high degree of automation provided by the flow injection system.

## Experimental

### Reagents and Solutions

High molecular weight polyvinylchloride (PVC), graphite, tetrahydrofuran (THF), *o*-nitrophenyl ether (NPOE), sodium tetraphenylborate (NaTPB) and potassium tetrakis(4-chlorophenyl)borate (KTPCIPB) were purchased from Sigma Aldrich. The nitrate salts of cations used for preparation of standard and stock solutions were obtained from Sigma Aldrich. Epoxy (TP3100) and hardener (Desmadur RFE) which was used in the preparation of solid state were obtained from Denlaks A.Ş. (Gaziantep, Turkey). Distilled de-ionized water was used in the preparations of standard and stock solutions throughout experiments. All standard and stock solutions were prepared from analytical grade nitrate salts of the related cations. Photographic film developing solution samples assured from local photo studios were used for the analysis either directly or diluted with de-ionized water.

### Apparatus

The potentiometric measurements in dynamic mode were carried out with a laboratory-made computer-controlled high-input impedance multi-channel potentiometric measurement system. The data output was recorded via a home-made software program. Throughout all the measurements, Ag/AgCl reference electrode (which was purchased from Gamry) was used. The FIA system consisted of

LAMBDA VIT-FIT model programmable syringe type pump and VICI model two position injection valve (25 µL) with interconnecting teflon tubing and a home-made flow cell. A UNICAM 929 model flame atomic absorption spectrophotometer with a deuterium-lamp background correction was used for the determination of silver in reference to the potentiometric method. The measuring conditions were as follows: UNICAM hollow cathode lamp, 10 cm 1-slot burner, air-acetylene flame (fuel gas flow-rate of 1.50 L/min), 0.1 nm spectral bandwidth, and 7 mm burner height. The wavelength and the lamp current of silver were 328 nm and 4 mA, respectively [21].

### Preparation of PVC membrane silver(I) selective electrodes

Silver(I) selective electrodes were prepared by following the same steps in our previous work [21]. The electrodes were prepared in two steps. At the first step, a mixture of conductive material consisting of 50 % (w/w) graphite, 35 % (w/w) epoxy and 15 % (w/w) hardener was prepared by dissolving in sufficient tetrahydrofuran (THF). When the appropriate viscosity was reached, a shielded copper wire with the length of 5.0 cm and radius of 0.5 mm was immersed into this mixture a few times to obtain a solid-state contact with coating thickness of about 0.2 mm. The coated wire was kept at 30 °C overnight. At the second step, a membrane cocktail consisting of 4.0 % (w/w) ionophore (12.0 mg), 33.0 % (w/w) PVC (99.0 mg), 62.0 % (w/w) NPOE (186.0 mg), 1.0 % (w/w) KTPCIPB (3.0 mg) was prepared in 3.0 mL THF. The surface of the conductive material was coated with this membrane by dipping into the cocktail for 4-5 times until about 0.2 mm membrane thickness was obtained. Then the coated electrode surface was left to be dried in laboratory conditions overnight. Prior to use, silver(I) selective electrodes were conditioned for at least 6h by soaking in a  $1.0 \times 10^{-1}$  mol/L silver(I) nitrate ( $\text{AgNO}_3$ ) solution. All measurements were made at room temperature (25 °C).

### Fabrication of the flow-through PVC membrane silver(I) selective electrode

For the flow injection measurements, a home-made with a low-dead volume flow cell was designed and silver(I) selective electrodes were conveniently embedded into this cell. Pump, injection valve and flow cell were connected with teflon tubing. A schematic diagram of flow injection potentiometric (FIP) system used in the measurements is shown in Fig. 1. As a carrier

solution, a  $1.0 \times 10^{-1}$  mol/L potassium nitrate solution was used. Standard solutions and samples were injected into the carrier solution by using a two-position injection unit which has 25  $\mu\text{L}$  sample loop. Flow injection analysis (FIA) signals were recorded by a multi-channel potentiometric measurement system.

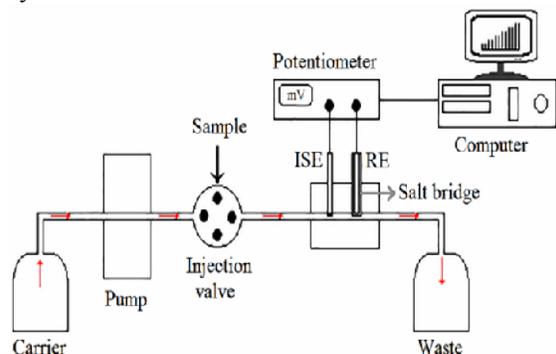


Fig. 1: A schematic representation of the FIP system.

## Result and Discussion

### Optimization of flow injection potentiometric system

The flow conditions such as flow rate, tubing length, concentration of carrier solution and injection volume were investigated in order to optimize the performance of the FIP system [22-25]. Firstly, the length of flow-line between the injection valve port and flow cell was built as short as possible in order to reduce dispersion and dilution. It was studied  $1.0 \times 10^{-2}$  mol/L standard silver(I) solution and so maximum tubing length was determined as 15 cm with respect to peak heights.

To obtain the best peak heights and the ideal peak width, the flow rate as an important parameter was investigated in the FIP system [26-28]. As the flow rate increased, peaks became narrower and reached a maximum at a flow rate of about 1.5 mL/min. But, at higher flow rates, the peak height was decreased slightly. The results obtained are shown in Fig. 2. Therefore, a flow rate of 1.5 mL/min was selected as an optimum value and then it was studied in rest of the experiments.

In the flow injection potentiometric analysis systems, sample volume or injection volume is also a significant factor in order to obtain optimum peak heights. When the studied sample volume is high, higher peak heights are obtained. But, this case requires greater consumption of sample and a longer time to reach the baseline [29, 30]. In this study,

injection volume effect was studied in various sample volumes from 10 to 50  $\mu\text{L}$  at flow rate of 1.5 mL/min. The peak heights were increased with the increase of sample volume. However, any increments in the peak heights were not observed at the sample volumes higher than 25  $\mu\text{L}$ . Thus, 25  $\mu\text{L}$  sample volume was selected as the optimum sample volume.

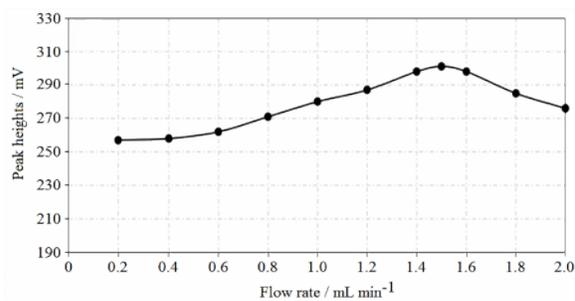


Fig. 2: Influence of different flow rates on the response of silver(I) selective electrode in FIP mode.

Generally, in FIP systems, the response of the ion selective electrodes was affected by the composition of carrier solution with regard to baseline stability. In the optimum conditions (1.5 mL/min flow rate and 25  $\mu\text{L}$  sample volume), the best flow injection potentiometric performances such as selectivity, sensitivity, fast and linear response were attained with the use of 0.1 mol/L potassium nitrate solution. Before the measurements, the silver(I) selective electrodes embedded suitably in the FIP system were conditioned by passing the carrier solution through the flow-cell for 20 minutes.

The sampling rate is a significant parameter in the flow injection potentiometric analysis systems in terms of duration of analysis. The proposed potentiometric FIP system displayed sampling rate of about 80 injections per hour.

### Influence of pH in FIP system

The influence of pH on the potential of silver(I) selective electrodes in FIP system was tested with the injection of  $1.0 \times 10^{-4}$  mol/L and  $1.0 \times 10^{-3}$  mol/L solutions of silver(I) which were prepared at different pHs ranging between 2.0 and 10.0. The pH adjustment of silver(I) solutions were made by adding small volumes of 0.1-1.0 mol/L nitric acid and sodium hydroxide solutions [1]. Solutions of 25  $\mu\text{L}$  silver(I) at different pHs were injected into the carrier solution and respective peaks were recorded. As can be seen from the results shown in Fig. 3, any

notable change in the peak heights were not observed in the pH range of 4.0-8.0. But at lower and higher pH values, potential of electrode was affected by the pH. The observed decline in the peak heights at higher pH values from pH 8.0 could be because of the occurrence of some hydroxyl complexes of silver(I). At lower pH values from pH 4.0, electrode probably responded to hydrogen ions

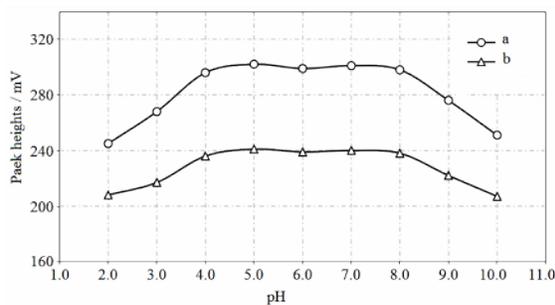


Fig. 3: Influence of pH on the silver(I) selective electrode response [a:  $1.0 \times 10^{-3}$  M  $\text{Ag}^+$ , b:  $1.0 \times 10^{-4}$  M  $\text{Ag}^+$ ]

#### Potentiometric behaviors of silver(I) selective electrode in FIP mode

In the optimized conditions, firstly standard silver(I) solutions were injected into the carrier solution in order to determine calibration graphic and linear concentration range. The obtained peaks and related calibration plot were given in Fig. 4. These results showed that silver(I) selective electrode in the FIP system had over-Nernstian behavior with the slope of  $67.20 \pm 1.09$  mV and a linear potentiometric response over the concentration range of  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-1}$  mol/L. Limit of detection (LOD) and limit of quantification (LOQ) of the silver(I) selective electrode were calculated as  $7.1 \times 10^{-6}$  mol/L and  $1.80 \times 10^{-4}$  mol/L respectively [31]. Linear relation between silver(I) activity and potential response is given below and  $R^2$  is determined as 0.9961.

$$\Delta E = (509.40 \pm 2.38) + (67.20 \pm 1.09) \log a_{\text{Ag}^+}$$

The selectivity coefficients of the silver(I) selective electrode in the FIP system were calculated according to the separate solution method (SSM). The obtained selectivity coefficient values are given in Table-1 as a comparison with those of the batch mode. As can be seen obviously in Table-1, silver(I)

selective electrode in the FIP system has high selectivity to silver(I) ions over the alkaline earth metal and transition metal ions. But,  $\text{Fe}^{3+}$  ions cause some interference. In addition,  $\text{Cr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  ions did interference hardly. When the selectivity coefficient values both in batch and FIP modes were compared, some differences between them were observed. These observations may be related partly with the transient nature of signal in the FIP system [32].

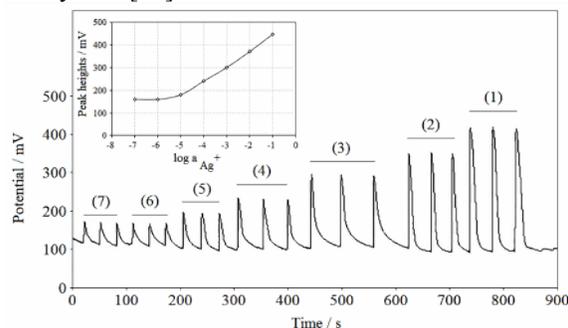


Fig. 4: Under optimum conditions, the obtained peaks with the injections of silver(I) standard solutions at various concentrations and related calibration plot [(1):  $1.0 \times 10^{-1}$  M  $\text{Ag}^+$ , (2):  $1.0 \times 10^{-2}$  M  $\text{Ag}^+$ , (3):  $1.0 \times 10^{-3}$  M  $\text{Ag}^+$ , (4):  $1.0 \times 10^{-4}$  M  $\text{Ag}^+$ , (5):  $1.0 \times 10^{-5}$  M  $\text{Ag}^+$ , (6):  $1.0 \times 10^{-6}$  M  $\text{Ag}^+$ , (7):  $1.0 \times 10^{-7}$  M  $\text{Ag}^+$ ].

Table-1: Potentiometric selectivity coefficients calculated with separate solution method (SSM) in both batch and the FIP mode.

Interferent Ion	Selectivity Coefficients / $\log K_{\text{Ag}^+, \text{B}}^{\text{Pot}}$	
	In batch mode	In FIP mode
$\text{Mg}^{2+}$	-4.80	-4.62
$\text{Sr}^{2+}$	-4.00	-3.87
$\text{Ni}^{2+}$	-4.80	-4.68
$\text{Ba}^{2+}$	-4.51	-4.55
$\text{Zn}^{2+}$	-4.87	-4.70
$\text{Fe}^{3+}$	-0.95	-0.90
$\text{Cd}^{2+}$	-3.75	-3.61
$\text{Al}^{3+}$	-4.81	-4.82
$\text{Pb}^{2+}$	-3.63	-3.48
$\text{Na}^+$	-3.68	-3.52
$\text{Ca}^{2+}$	-3.70	-3.71
$\text{NH}_4^+$	-4.27	-4.10
$\text{Li}^+$	-4.00	-3.87
$\text{Co}^{2+}$	-4.57	-4.58
$\text{Mn}^{2+}$	-4.60	-4.47
$\text{Cr}^{3+}$	-5.14	-5.01
$\text{Cu}^{2+}$	-4.79	-4.65

Table-2: The comparison of some performance characteristics of the proposed flow injection potentiometric silver(I) selective electrode with those of the others available in the literature.

References	Slope (mV/decade)	Linear working range (mol/L)	Limit of detection (mol/L)	Sampling-rate (injection/hour)
16	65.90±1.00	1.0×10 <sup>-6</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-6</sup>	-
32	57.50±0.30	1.0×10 <sup>-6</sup> - 1.0×10 <sup>-2</sup>	-	≈20
This paper	67.20±0.80	1.0×10 <sup>-5</sup> - 1.0×10 <sup>-1</sup>	7.1×10 <sup>-6</sup>	≈80

Table-3: The determined amounts of silver(I) by the proposed FIP system, AAS method and batch mode along with the relative deviations (RD) and calculated *t*-value.

Sample	The determined amount of silver(I) / mg/L			RD / %	<i>t</i> -test <sup>b</sup>	
	Batch mode <sup>a</sup>	FIP mode <sup>a</sup>	AAS <sup>a</sup>		<i>t</i> <sub>table</sub>	<i>t</i> <sub>experimental</sub>
P1	2.78±0.03	-7.17	2.46±0.05	2.65±0.01	-7.17	
P2	3.81±0.04	-4.65	3.49±0.07	3.66±0.01	-4.65	
P3	11.22±0.07	6.83	11.57±0.12	10.83±0.02	6.83	4.303
P4	3.06±0.02	-5.41	2.97±0.08	3.14±0.01	-5.41	0.214

<sup>a</sup>Values are mean values for n=3.<sup>b</sup>*t*-test was applied between FIP mode and AAS for three measurements at 95% confidence level

### Comparison of potentiometric performance of some silver(I) selective electrodes in FIP system

The number of described flow injection potentiometric silver(I) selective sensor in the literature is limited. Some analytical parameters of the two reported flow injection potentiometric silver(I) selective electrodes were compared with the currently proposed one in terms of limit of detection, slope, linear working range and sampling-rate. Their potentiometric performance characteristics were summarized in Table-2. The linear range and sampling rate of the current system is considered to be satisfied. However, the detection limit is seen slightly higher than those of the electrodes reported in literature. The most intriguing property of the current system seems to allow rapid determination of silver(I) ions.

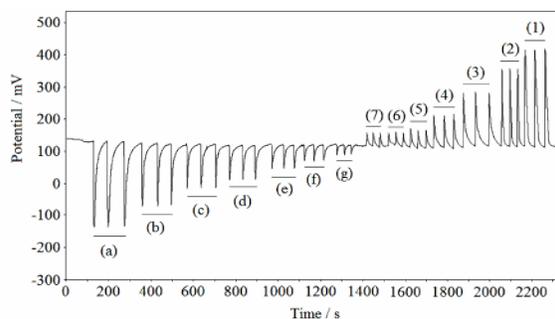


Fig. 5: The silver(I) selective electrode response against both iodide ions and silver(I) ions in the proposed FIP system [(1): 1.0×10<sup>-1</sup> M Ag<sup>+</sup>, (2): 1.0×10<sup>-2</sup> M Ag<sup>+</sup>, (3): 1.0×10<sup>-3</sup> M Ag<sup>+</sup>, (4): 1.0×10<sup>-4</sup> M Ag<sup>+</sup>, (5): 1.0×10<sup>-5</sup> M Ag<sup>+</sup>, (6): 1.0×10<sup>-6</sup> M Ag<sup>+</sup>, (7): 1.0×10<sup>-7</sup> M Ag<sup>+</sup>; (a): 1.0×10<sup>-1</sup> M I<sup>-</sup>, (b): 1.0×10<sup>-2</sup> M I<sup>-</sup>, (c): 1.0×10<sup>-3</sup> M I<sup>-</sup>, (d): 1.0×10<sup>-4</sup> M I<sup>-</sup>, (e): 1.0×10<sup>-5</sup> M I<sup>-</sup>, (f): 1.0×10<sup>-6</sup> M I<sup>-</sup>, (g): 1.0×10<sup>-7</sup> M I<sup>-</sup>].

### Analytical applications

Silver(I) selective electrodes offer reversible and selective responses against the halide ions. Because of these properties, it can be utilized as an indicator electrode in potentiometric titrations [33]. In the proposed FIP system, the potentiometric response against iodide ions of silver(I) selective electrode were obtained by using standard iodide solutions in the concentration range of 1.0×10<sup>-7</sup> mol/L to 1.0×10<sup>-1</sup> mol/L. As it is seen in Fig. 5, silver(I) selective electrode exhibited a reversible response against iodide ions, and may have a potential use in potentiometric titrations of halide ions in FIP mode.

In real sample analysis, photographic film developing solutions supplied from local photo studios were examined. Firstly, the FIP system was calibrated by using standard silver(I) solutions in the concentration range from 1.0×10<sup>-7</sup> mol/L to 1.0×10<sup>-1</sup> mol/L. By using the peak heights obtained from the injections of standard silver(I) solutions, the calibration plot was created. Later, each photographic film developing solution samples were injected three times into the FIP system. In this way, reproducibilities of the responses were tested. The amounts of silver(I) in each sample were calculated from the average peak height (Fig. 6). The results for the determination of silver(I) obtained from the proposed FIP system, together with the results taken from atomic absorption spectrometric (AAS) are summarized in Table-3. The results of the FIP system and the results obtained from atomic absorption spectrometry (AAS) were evaluated statistically by applying *t*-test (for comparing accuracy of the two methods). When the null hypothesis was not installed on a significant difference between the two methods, experimental *t* value was calculated as 0.214 at % 95 confidence level for n=3. As the calculated value of *t*<sub>experimental</sub> (*t*<sub>(0.05, 2)</sub> = 0.214) was smaller than the value of *t*<sub>table</sub> (*t*<sub>(0.05, 2)</sub> = 4.303), the null hypothesis remained

as true [34]. As a result, it was determined that there is no important difference between the accuracy of the analysis achieved by both methods. Table-3 indicates the sample analysis results with their relative deviations. The silver(I) selective electrode was successfully applied for the potentiometric determination of silver(I) ions in flow injection potentiometric system.

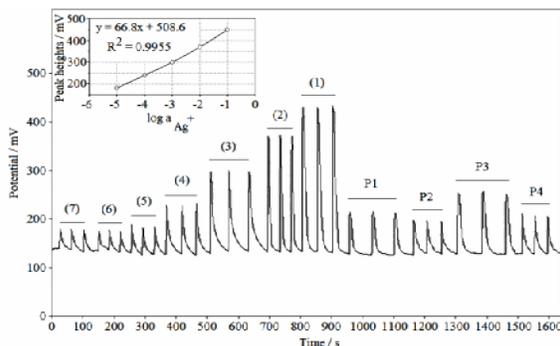


Fig. 6: The analysis of photographic film developing solution samples in the proposed FIP system.

### Conclusions

In this work, PVC membrane silver(I) selective electrode was prepared and suitably embedded in a home-made low-dead volume flow cell for the use as a potentiometric detector. In this way, a novel flow injection potentiometric system for the potentiometric determination of silver(I) ions have been developed and optimized. The results of the FIP measurements show that the presently proposed FIP system can be successfully used to determine the amount of silver(I) ions in photographic film developing solutions. The most important advantages of the proposed FIP system are its fast response against silver(I) ions, high selectivity, good sensitivity, high sampling rate, applicability over a wide pH range and low-cost. In addition, it can be studied at very low sample and standard solution quantities. Further advantages are that the proposed FIP system is suitable for routine analysis of silver(I) ions, and does not require expensive equipment and time consuming pre-treatment process.

### References

1. A. Dadkhah, M. K. Rofouei and M. H. Mashhadizadeh, Synthesis and Characterization of N,N -bis(benzophenone imine)formamidine as Ionophores for Silver-Selective Electrodes, *Sens. Actuators, B.*, **202**, 410 (2014).
2. H. Karami, M. F. Mousavi, M. Shamsipur, New Flow Injection Potentiometric Graphite Coated

- Ion-Selective Electrode for the Determination of  $\text{VO}_2^+$  ions, *Anal. Chim. Acta.*, **481**, 213 (2003).
3. F. Coldur, M. Andac and I. Isildak, Flow-Injection Potentiometric Applications of Solid State  $\text{Li}^+$  Selective Electrode in Biological and Pharmaceutical Samples, *J. Solid State Electrochem.*, **14**, 2241 (2010).
4. N. A. Chaniotakis, J. K. Tsagatakis, E. A. Moschou, S. J. West, X. Wen, Magnesium Ion-Selective Electrode: Optimization and Flow Injection Analysis Application, *Anal. Chim. Acta.*, **356**, 105 (1997).
5. S. H. M. A. Almeer, I. A. Zogby and S. S. M. Hassan, Novel Miniaturized Sensors for Potentiometric Batch and Flow-Injection Analysis (FIA) of Perchlorate in Fireworks and Propellants, *Talanta.*, **129**, 191 (2014).
6. H. Karami, M. F. Mousavi, M. Shamsipur, Flow Injection Potentiometry by a New Coated Graphite Ionselective Electrode for the Determination of  $\text{Pb}^{2+}$ , *Talanta.*, **60**, 775 (2003).
7. X. Yang, D. B. Hibbert, P. W. Alexander, Flow Injection Potentiometry by poly(vinyl chloride)-Membrane Electrodes with Substituted Azacrown Ionophores for the Determination of Lead(II) and Mercury(II) Ions, *Anal. Chim. Acta.*, **372**, 387 (1998).
8. M. Shamsipur, A. S. Dezaki, M. Akhond, H. Sharghi, Z. Pazirae and K. Alizadeh, Novel PVC-Membrane Potentiometric Sensors Based on a Recently Synthesized Sulfur-Containing Macrocyclic Diamide for  $\text{Cd}^{2+}$  Ion. Application to Flow-Injection Potentiometry, *J. Hazard. Mater.*, **172**, 566 (2009).
9. V. K. Gupta, M. R. Ganjali, P. Norouzi, H. Khani, A. Nayak and S. Agarwal, Electrochemical Analysis of Some Toxic Metals by Ion-Selective Electrodes. *Crit. Rev. Anal. Chem.*, **41**, 282 (2011).
10. G. Chakrapani, P. L. Mahanta, D. S. R. Murty, B. Gomathy, Preconcentration of Gold, Silver and Palladium on Activated Carbon and its Determination in Geological Samples by Flame AAS After Wet Ashing, *Talanta.*, **53**, 1139 (2001).
11. S. Dadfarnia, A. M. Haji Shabani, M. Gohari, Trace Enrichment and Determination of Silver by Immobilized DDTC Micro Column Flow Injection Atomic Absorption Spectrometry, *Talanta.*, **64**, 682 (2004).
12. K. Chiba, I. Inamoto, and M. Saeki, Application of Isotope Dilution Analysis-Inductively Coupled Plasma Mass Spectrometry to the Precise Determination of Silver and Antimony in Pure Copper, *J. Anal. At. Spectrom.*, **7**, 115 (1992).

13. C. Chang, H. Kui, S. Jiang, Bandpass Reaction Cell Inductively Coupled Plasma Mass Spectrometry for the Determination of Silver and Cadmium in Samples in the Presence of Excess Zr, Nb and Mo, *Anal. Chim. Acta.*, **493**, 213 (2003).
14. M. P. Arena, M. D. Porter and J. S. Fritz, Rapid, Low Level Determination of silver(I) in Drinking Water by Colorimetric-Solid-Phase Extraction, *Anal. Chim. Acta.*, **482**, 197 (2003).
15. A. J. Dole, T. J. Cardwell, R. W. Cattrall, R. Giacomo, C. G. Rodrigues and G. R. Scollary, The Determination of Silver in Photographic Emulsions by Discontinuous Flow Analysis, *Electroanalysis*, **10**, 21 (1998).
16. H. Ibrahim, Carbon Paste Electrode Modified with Silver Thimerosal for the Potentiometric Flow Injection Analysis of Silver(I), *Anal. Chim. Acta.*, **545**, 158 (2005).
17. F. Mizani, M. Shamsipur, M. R. Yaftian and D. Matt, Flow-Injection Potentiometry by Poly(vinyl chloride)-Membrane Electrodes with Diphosphoryl-dicarboxylic acid-p-tert-butylcalix[4] arene Ionophore for the Determination of Th(IV) Ions, *Anal. Sci.*, **29**, 361 (2013).
18. F. Coldur and M. Andac, A Flow-Injection Potentiometric System for Selective and Sensitive Determination of Serum Lithium Level, *Electroanalysis*, **25**, 732 (2013).
19. M. F. M. Shamsipur, M. F. Mousavi, N. Alizadeh, K. Alizadeh, H. Eshghi, H. Karami, A Novel Flow Injection Potentiometric Graphite Coated Ion-Selective Electrode for the Low Level Determination of Uranyl Ion, *Anal. Chim. Acta.*, **589**, 22 (2007).
20. S. S. Beheshti, M. K. Amini, A Simple and Selective Flow-Injection Potentiometric Method for Determination of Iodide Based on a Coated Glassy Carbon Electrode Sensor, *Int. J. Electrochem. Sci.*, **2**, 778 (2007).
21. C. Topcu, F. Coldur, M. Andac, I. Isildak, N. Senyuz, H. Bati, Ag<sup>+</sup>-selective poly(vinyl chloride) Membrane Electrode Based on [N,N-ethylenebis-(3-methoxy salicylaldehyde)], *Curr. Anal. Chem.*, **7**, 136 (2011).
22. Y. M. Issa, H. Ibrahim, H. M. Abu-Shawish, Carbon Paste Electrode for the Potentiometric Flow Injection Analysis of Drotaverine Hydrochloride in Serum and Urine, *Microchim. Acta.*, **150**, 47 (2005).
23. H. Ibrahim, Chemically Modified Carbon Paste Electrode for the Potentiometric Flow Injection Analysis of Piribedilin Pharmaceutical Preparation and Urine, *J. Pharm. Biomed. Anal.*, **38**, 624 (2005).
24. Y. M. Issa, S. B. Sayed, A. A. Mutair, Ion-Selective Electrodes for Potentiometric Determination of Ranitidine Hydrochloride, Applying Batch and Flow Injection Analysis Techniques. *Anal. Sci.*, **21**, 1443 (2005).
25. M. Andac, H. Eren and F. Coldur, Determination of Nitrate in Leafy Vegetables by Flow Injection Analysis with Potentiometric Detection, *J. Food Drug Anal.*, **19**, 457 (2011).
26. S. S. M. Hassan, H. E. M. Sayour, S. S. Al. Mehrezi, A Novel Planar Miniaturized Potentiometric Sensor for Flow Injection Analysis of Nitrates in Wastewaters, Fertilizers and Pharmaceuticals, *Anal. Chim. Acta.*, **581**, 13 (2007).
27. Z. L. Chen, P. Grierson, M. A. Adams, Direct Determination of Phosphate in Soil Extracts by Potentiometric Flow Injection Using a Cobalt Wire Electrode, *Anal. Chim. Acta.*, **363**, 191 (1998).
28. G. S. Kanberoglu, F. Coldur, O. Cubuk, C. Topcu, B. Caglar, A novel flow-injection potentiometric detector for determination of tamoxifen in anticancer drug formulations, *Sensor Lett.*, **14**, 59 (2016).
29. S. Nellaiappan, A. S. Kumar, Selective Flow Injection Analysis of Iodate in Iodized Table Salts by Riboflavin Immobilized Multiwalled Carbon Nanotubes Chemically Modified Electrode, *Electrochim. Acta.*, **109**, 59 (2013).
30. S. S. M. Hassan, I. H. A. Badr, H. S. M. Abd-Rabboh, Potentiometric Flow Injection Analysis of Anionic Surfactants in Industrial Products and Wastes. *Microchim. Acta.*, **144**, 263 (2004).
31. M. M. Ardakani, H. Dehghani, M. Jalayer, and H. R. Zare, Potentiometric Determination of Silver(I) by Selective Membrane Electrode Based on Derivative of Porphyrin, *Anal. Sci.*, **20**, 1667 (2004).
32. Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda, and S. Amemiya, Potentiometric selectivity coefficients of ion-selective electrodes. Part I. Inorganic cations (technical report), *Pure Appl. Chem.*, **72**, 1851 (2000).
33. Ł. Tymecki, E. Zwierkowska, S. Głab, R. Koncki, Strip Thick-Film Silver Ion-Selective Electrodes, *Sens. Actuators, B.*, **96**, 482 (2003).
34. C. M. F. Ribeiro, C. D. Matos, M. G. F. Sales and M. C. V. F. Vaz, Citrate Selective Electrodes for the Flow Injection Analysis of Soft Drinks, Beers and Pharmaceutical Products, *Anal. Chim. Acta.*, **471**, 41 (2002).