

Effect of ionic-strength adjusters on the detection of silver ion using ion-selective electrode

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Abstract—Ion-selective electrodes (ISEs) are used in a wide variety of applications for determining the concentrations of various ions in aqueous solutions. When compared to many other analytical techniques, ISEs are relatively inexpensive, simple to use, and have an extremely wide range of applications and concentrations. In recent reports, cytotoxicity of silver nanoparticles (AgNPs) showed that AgNPs were ionized in the cells and led to causing cell-death. Thus, the measurement of silver ions in aqueous phase is important. In this work, several sodium and potassium salts were considered as ionic-strength adjusters (ISA) and were used in the calibration step to enhance sensitivity of detection the target ion. The result showed that potassium iodine (0.05 M KI) acted as a very effective ISA, compared to conventional ISA (5 M NaNO₃).

Keywords: Ion Selective Electrode, Silver Ion, Silver Nanoparticles, Toxicity

INTRODUCTION

Silver nanoparticles (AgNP) have a wide array of commercial applications due to their antimicrobial, antifungal, and partially antiviral properties [1]. With widespread use of AgNP containing products, unintentional exposure of AgNP to the environment and humans could induce potential toxic effects of Ag⁺ and AgNP. There is an ongoing debate regarding the role of Ag⁺ released from AgNP and its toxicity against microorganisms [2]. In our previous report [3], *in-vivo* and *in-vitro* cytotoxicity studies showed that AgNPs were ionized in cells and caused cytotoxicity by a Trojan-horse type mechanism. While Ag⁺ and AgNP are all likely to contribute to observed toxicity, ionic Ag generally exhibits the strongest toxic effect [4]. In the recent trend of connecting cytotoxicity to environmental exposure, it is essential to distinguish the toxic effect of Ag⁺ and/or AgNP on the target bio-organisms. Namely, analysis of sole Ag⁺ in AgNP suspension is important issue.

The Ag ion in the AgNP solutions could be measured by using several methods: diffusive gradients in thin films [5], centrifugal ultrafiltration [6], and ion-selective electrode (ISE) [7-11]. Among these, ISE could be used on a real time basis and is suitable in both field and laboratory applications. Haynes and co-workers reported some foundation for the use of fluoros-phase ISE as an *in-situ* nanoparticle characterization tool, addressing a critical technology gap in the field of nanoparticle toxicology [11]. Namely, Ag-ISE is very essential for the study on the silver nanotoxicity. An ISE is a transducer that converts the activity of a specific ion dissolved in solution to an electrical potential that can be measured by a voltmeter

or pH meter [7]. According to the Nernst equation, the voltage is theoretically dependent on the logarithm of the ionic activity, which has a physiological application when used to calculate the potential of an ion's charge *z* across a membrane [12]. The sensing part of the electrode is usually made as an ion-specific membrane.

The use of ISE is limited by interference from other ions and tolerance at very low concentrations of desired ions. No ISE is completely ion-specific; all are sensitive to other ions having similar physical properties, the extent of which depends on the degree of similarity [13]. In some cases the electrode may actually be much more sensitive to the interfering ion than to the desired ion. The outer filling of the reference electrode was 0.1 M KNO₃; thus, the nitrate electrode had various ionic interferences (perchlorate, iodide, chloride, and sulfate) [9]. This problem might be ignored when the interfering ion is present only in relatively very low concentrations, or entirely absent. The other problem is tolerance at very low concentration of target ion. According to the ISE instruction manual [14], the concentration range was 0.01 to 108,000 ppm (10⁻⁷ to 1 M). The calibration curve was constructed from diluted AgNO₃ solutions in the Ag⁺ range 10⁻⁶ to 10⁻³ M, and thus the actual LOD (limit of detection) did not reach the lower detection level. Some researchers reported extending the LOD to the range 10⁻⁹ M by addition of chloride as a ligand [6-8].

Since the free silver ion activity is determined by the logarithm of the solubility product (logK) of the silver anion (i.e., silver-ligand complex), the detection of Ag ion in the low-activity range might be possible with the use of an ionic-strength adjuster (ISA) that has a lower solubility product. Therefore, we used several salts (Na₂SO₄, Na₃PO₄, NaCl, NaI, KBr, KI, and KCl) to investigate the effect of ISAs on the detection sensitivity of silver ion using ISE. The solubility product of Ag₂S is 50.1, but sulfate was excluded due to very strong interference to ion exchange through membrane.

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EXPERIMENTAL

1. Materials

The ion meter was characterized by using three different concentrations of a silver standard with at least three different concentrations along with ISA (5 M NaNO₃ Cole-Parmer, USA). ISE (Cole-Parmer 27502-41) used in this work is a double-junction combination ion-selective electrode that is convenient to use in places where two electrodes will not fit. Solid-state electrodes also have twelve polishing strips. Several different salts of ISA were considered to improve sensitivity and LOD of the ISE for detecting Ag⁺. Herein, several sodium and potassium salts were selected as ISAs; Na₂SO₄ (Duksan, Korea), Na₃PO₄ (Samchun, Korea), NaCl (Samchun, Korea), NaI (Duksan, Korea), KCl (Daejung, Korea), KBr (Samchun, Korea), and KI (Samchun, Korea).

2. Calibration of Silver Ion with ISA

Free Ag⁺ was measured by following Ag-ISE procedures recommended by the operating instructions. Guaranteed concentration range of Ag-ISE was reported as 1 to 10⁻⁷ M silver (108,000 to 0.01 ppm). Ag-ISE was calibrated with concentration of AgNO₃ (Sigma-Aldrich, USA) that varied between 10⁻⁷ to 10⁻³ M. Between samples, the electrode was rinsed with 10% v/v HNO₃ (Duksan, Korea) and de-ionized (DI) water. The calibration curve could be extended to under 10⁻⁹ M by addition of chloride as a ligand [6-8]. Therefore, seven ISAs with different ionic strengths were selected to confirm the linearity over the whole range with a slope of 59 mV/log [Ag⁺] which was evaluated using the Nernst equation [12]. Ag⁺ for all ISAs was measured three times repeatedly.

RESULTS AND DISCUSSION

As shown in Fig. 1, the Ag-ISE was calibrated by measuring the potential of Ag-ISE as a function of the log[Ag⁺] activity. Measurements were performed in DI water with added NaNO₃. Even though the ionic strength of the solutions was not adjusted with ISA, it was

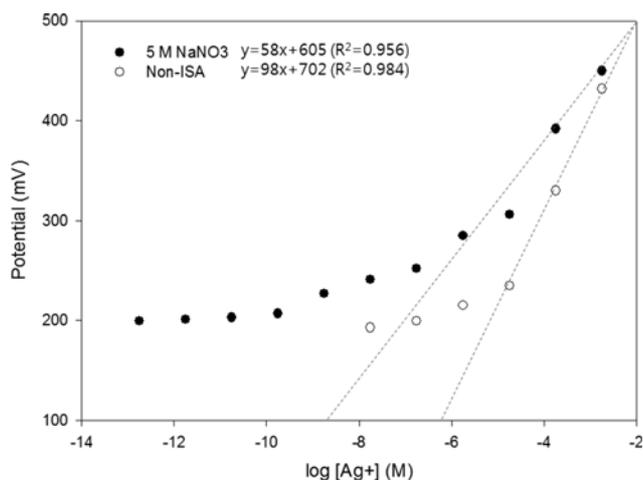


Fig. 1. ISE calibration curve for the measured potential of the Ag-ISE as a function of the log[Ag⁺] activity (black circle): solutions of AgNO₃ with 5 M NaNO₃ as ISA (white circle): solutions of AgNO₃ without ISA.

possible to calibrate the electrode down to 10⁻⁵ M Ag⁺ with good linearity due to the potential change of Ag⁺ in aqueous phase. However, the slope of the Nernstian plot for non-ISA did not match the theoretical value (59.16 mV/log[Ag⁺]) [12]. When the ISE membrane is in thermodynamic equilibrium (i.e., no net flux of ions), the membrane potential must be equal to the Nernst potential. However, in physiology, due to active ion pumps, the areas inside and outside of a cell are not in equilibrium. For samples with high ionic strengths, there are simple methods which can be used to avoid the error introduced by the difference between activity and concentration. The ionic strength in both the calibrating standard solutions and the samples was brought to the same level by adding a suitable ISA. Therefore, in this work, several ISAs were considered.

When 5 M NaNO₃ was used as an ISA, LOD of the Ag-ISE calibration curve went down to 10⁻⁶ M Ag⁺ with a nearly theoretical Nernstian plot (slope=59 mV/log[Ag⁺]). Depending on the charges of the ions, ionic activity of Ag⁺ departs increasingly from concentrations when exceeding 10⁻⁶ M. In dilute solutions, the Nernst equation can be expressed directly in terms of concentrations because activity coefficients are close to unity. However, at very low concentrations of the potential-determining ions, namely, under LOD concentrations, the potential of Ag-ISE was almost at unity due to the effect of cation interference: the exchange current density between Ag⁺ and ISA cation becomes very low.

It was reported that the effect of changing the ionic strength of NaNO₃ in spite of different concentrations (0.01 to 0.1 M) had a minimal impact on the electrode response [8]. However, following the addition of a ligand (Cl⁻, Br⁻, I⁻, SO₄²⁻, and PO₄³⁻) for the Ag⁺, a potential change could be obtained at low-activity range. Since the solubility product of silver-ligand complexes was different with each ligand type, potential values of Ag-ISE changed with concentration of Ag⁺.

As shown in Fig. 2, the ISE calibration curve was obtained with five different electrolytes used as ISAs. The established solubility products of Ag₂SO₄, AgCl, AgBr, AgI, and Ag₃PO₄ are 4.8, 9.8, 12.3, 16.1, and 17.6, respectively. In the case of Na₂SO₄, the lower limit value of potential was almost the same as that of NaNO₃ because

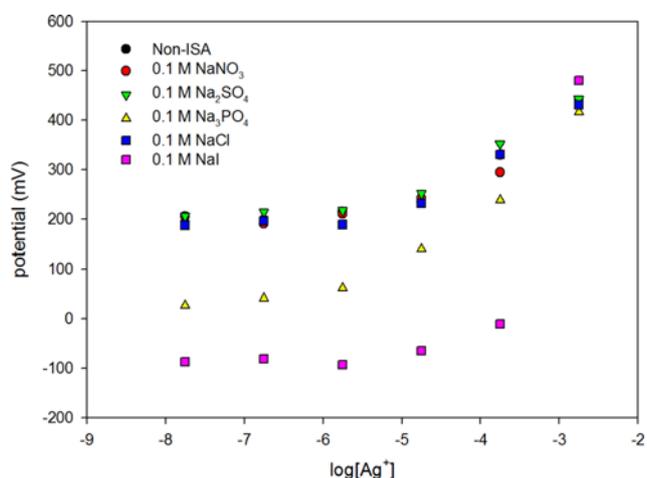


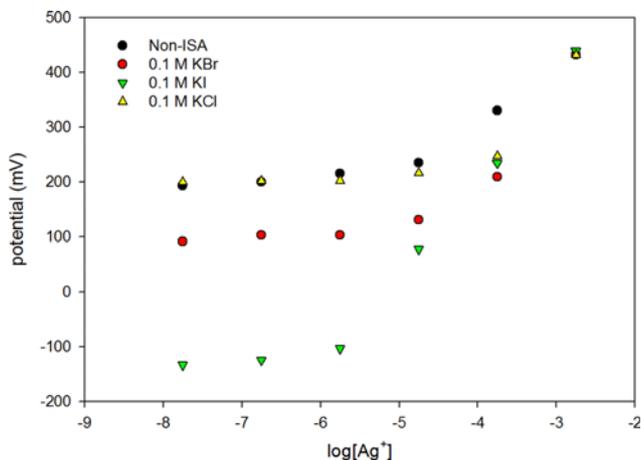
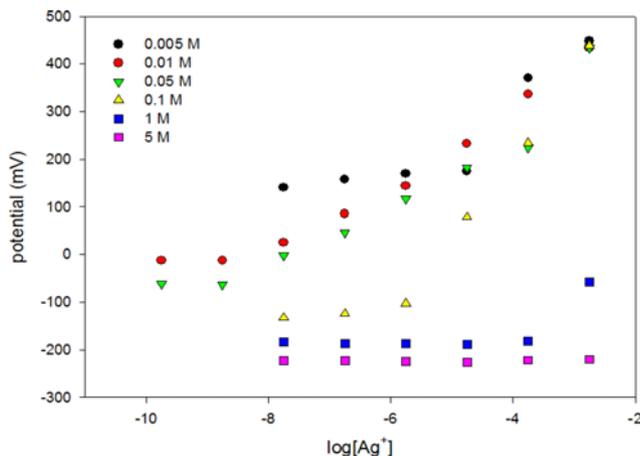
Fig. 2. ISE calibration curve for the measured potential of the Ag-ISE with sodium-form ISAs.

Table 1. LOD and slope of Nernstian plot with type and concentrations of ISAs

Type of ISA	Conc. of ISA (M)	Nernstian slope (mV/log [Ag ⁺])	LOD (log M)
Non-ISA	-	98	-5
NaNO ₃	5	58	-6
Na ₂ SO ₄	0.1	95	-5
Na ₃ PO ₄	0.1	115	-6
NaCl	0.1	82	-6
NaI	0.1	450	-4
KBr	0.1	150	-5
KCl	0.1	160	-5
KI	0.1	178	-6
	0.05	59	-9
	0.01	61	-9
	0.005	136	-5

Ag₂SO₄ has low solubility product and thus is also soluble. However, in the case of ISAs with high solubility product (NaPO₄, NaCl, and NaI), silver cations react quickly with these ligand sources to produce insoluble silver complexes, and thus the potential of silver solutions decreased significantly. In particular, the ISE calibration curve measured with NaI showed lower potential values compared to other ISAs. However, as shown in Fig. 2 and Table 1, the Nernstian slope did not match the theoretical value and the LOD of Ag⁺ did not extend below 10⁻⁶ M. Even though pH membrane was also in interference from Na⁺ and K⁺ at high pH, ISEs in contrast to pH electrode are not entirely ion-specific and can permit the passage of some of the other ions that may be present in the test solution, thus causing problematic ionic interference.

Similar calibration process was carried out with potassium ISAs and the calibration curves are shown in Fig. 3. Since Br⁻ and I⁻ have high solubility product for silver-ligand complex and easily form insoluble silver complexes, potential values were decreased down to 200 mV compared to KCl. Even though Nernstian slopes of all potassium salt of ISAs showed 150-178 mV/M, iodine ligand (KI) showed lowest potential value (-150 mV) and broad range of poten-

**Fig. 3. ISE calibration curve for the measured potential of the Ag-ISE with potassium-form ISAs.****Fig. 4. ISE calibration curve for the measured potential of the Ag-ISE with different concentrations of KI.**

tial change (400 to -150 mV). Therefore, the effect of KI concentration on the Nernstian slope and LOD was further investigated.

With increasing of concentrations of KI, the Nernstian slope deviated from the theoretical value due increasing ionic strength. The logarithmic expression in the Nernst equation is the activity of the measured ion, which is almost same as its concentration in dilute conditions. However, the activity coefficient (γ) at high concentrations was not at unity and thus the Nernst equation did not follow the real potential change due to deviation from ideal behavior. Namely, at higher concentrations, inter-ionic interactions between all ions in the solution (both positive and negative) tend to be less mobile, and thus there are relatively fewer of the measured ions in the vicinity of the membrane than in the bulk solution. Therefore, the measured voltage is less than it would be if it reflected the total number of ions in solution. This causes an erroneously low estimate of the concentration in samples with a high concentration and/or a complex matrix. As shown in Fig. 4, at high concentrations of KI, the decreased dependence of potential with change of Ag⁺ concentration was represented by a low potential value around -200 mV. Namely, the potential change with increasing of Ag⁺ concentration was repressed by the high ionic strength of ISA and then showed unity value.

With decreasing of concentrations of KI, the potential value of the ISE was increased and potential change was dependent on the change of silver concentration. When 0.05 and 0.01 M KI was used as an ISA, the Nernstian slope was well matched with the theoretical value and the detection limit was also enhanced (Fig. 4 and Table 1). At too low of a KI concentration (0.005 M), the LOD and Nernstian slope were not improved compared to 0.05 and 0.01 M KI. Because ISA also acted as a buffer to adjust the ionic strength in measuring the solutions, the ionic strength of ISA should be much higher than that of target ion. Therefore, 0.005 M KI, with small ionic strength (0.005 M), was not an efficient buffer to adjust ionic strength of host solutions.

CONCLUSIONS

In measuring the concentration of silver ion in the aqueous phase,

5 M NaNO₃ was used as conventional ISA. To investigate the effect of ISAs on the detection of Ag⁺ using Ag-ISE, we used several ISAs (sodium and potassium salts) in calibration of the measured potential of the Ag-ISE as a function of logarithm of Ag⁺ activity. When 5 M NaNO₃ was used as ISA in the calibration step, a calibration curve with 10⁻⁶ M LOD was observed with good linearity and nearly matched the Nernstian slope. Iodine ligand showed lowest potential value (-150 mV) in its calibration curve with a broad range of potential change (400 to -150 mV), and thus KI was selected as candidate ISA to investigate the extension of LOD and satisfy the Nernstian slope. The results showed that 0.01-0.05 M KI has 10⁻⁹ M LOD of Ag⁺ and well-matched the Nernstian slope with the theoretical value. Even though some studies report an extension to low-activity range by single point addition of Cl⁻, Br⁻, and I⁻ [6-8], there are no studies that use KI in the full-activity range as an ISA. Therefore, this proposed method using low concentration of KI as ISA might support the enhanced measuring method for detecting of silver ion using Ag-ISE.

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REFERENCES

1. X. Jin, M. Li, J. Wang, C. Marambio-Jones, F. Peng, X. Huang, R. Damoiseaux and E. M. V. Hoek, *Environ. Sci. Technol.*, **44**, 7321 (2010).
2. N. Garcia-Reyero, A. J. Kennedy, B. L. Escalon, T. Habib, J. G. Laird, A. Rawat, S. Wiseman, M. Hecker, N. Denslow, J. A. Steevens and E. J. Perkins, *Environ. Sci. Technol.*, **48**, 4546 (2013).
3. E.-J. Park, J. Yi, Y. Kim, K. Choi and K. Park, *Toxicol. In Vitro*, **24**, 872 (2010).
4. J. Roh, E.-J. Park, K. Park, J. Yi and Y. Kim, *Korean J. Chem. Eng.*, **27**, 1897 (2010).
5. W. Davison and H. Zhang, *Nature*, **367**, 546 (1994).
6. E. Navarro, F. Piccapietra, B. Wagner, F. Marconi, R. Kaegi, N. Odzak, L. Sigg and R. Behra, *Environ. Sci. Technol.*, **42**, 8989 (2008).
7. M. Koch, S. Kiefer, C. Cavelius and A. Kraegeloh, *J. Nanopart. Res.*, **14**, 646 (2012).
8. R. Benoit, K. J. Wilkinson and S. Sauve, *Chem. Central J.*, **7**, 75 (2013).
9. A. Ceresa, A. Radu, S. Peper, E. Bakker and E. Pretsch, *Anal. Chem.*, **74**, 4027 (2002).
10. T. M. Benn and P. Westerhoff, *Environ. Sci. Technol.*, **42**, 4133 (2008).
11. M. A. Maurer-Jones, M. P. S. Mousavi, L. D. Chen, P. Buhlmann and C. L. Haynes, *Chem. Sci.*, **4**, 2564 (2013).
12. D. R. Crow, *Principles and applications of electrochemistry*, Blackie Academic & Professional, New York (1994).
13. N. W. H. Adams and J. R. Kramer, *Aqua. Geochem.*, **5**, 1 (1999).
14. *Operating Instructions of silver/sulfide electrodes*; Cole-Parmer Instrument Company, Illinois (2000).