# Ion selective electrodes are not suitable for measurements of silver ion concentrations in alkaline carbonate media

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An ion selective electrode (ISE) for determination of the labile silver ion concentration in carbonate containing solutions of pH 10 was seen to give incorrect results due to shifts in the $Ag|Ag^+$ equilibrium. This drawback was not the case for the differential pulse anodic stripping voltammetry (DPASV) method.

## Introduction

Silver is a subject of emerging environmental concern due to the documented high toxicity of silver ions towards aquatic organisms, *e.g.* fish.[1] Its use in consumer products, such as clothes, sportswear, socks and food containers, is rapidly increasing on the market in which silver is commonly added as silver nanoparticles (Ag NPs) with the aim to impart antimicrobial properties.[2] Large knowledge gaps related to their potential adverse effects stress a growing environmental concern and the necessity of accurate measurements.[3] Ag NPs may be transported into different compartments of the hydrosphere and may release silver ions during their lifetime depending on their surface and colloidal properties and on environmental interactions often related to the water chemistry. Washing of clothing is an important source of silver that may have environmental implications. It was previously shown that the amount of Ag NPs released during the laundry cycle varies strongly, but may be of very significant concentrations.[4,5] Accurate determinations of the labile fraction, meaning free ions and weak complexes of silver released from Ag NPs in fabrics during *e.g.* the laundry cycle are important as well as any release of Ag NPs, since the chemical speciation of the released silver is essential for its bioavailability and environmental interaction and fate.[6]

As the ion-selective electrode (ISE) is used in many applications to estimate the ion activity of metals in environmental settings,[7] it is important that the ISE measurements are robust and trustworthy in these media. In general, interfering ions and other problems such as potential drift of the ISE are well-documented and reported.[8,9] Even though the ISE has previously been used to monitor the release of silver in the laundry cycle,[4,5] few or no studies have addressed the effect of carbonates in alkaline electrolytes (media of relevance for the laundry cycle) on the ISE measurements. Another method able to determine electro-active silver, *i.e.* free silver ions and/or the weak complexes (the labile fraction), able to dissociate in the electrical double layer under certain settings,[10] is differential pulse anodic stripping voltammetry (DPASV).[11] The DPASV technique is regarded superior to the ISE methodology when measuring low metal ion concentrations,[10–12] but lacks the operating range and convenience of the ISE.

The aim of this communication is to demonstrate some limitations of ISE determinations of silver in varying carbonate concentrations of alkaline media. For comparison, DPASV measurements have been employed in parallel.

## Materials and methods

DPASV measurements were conducted using an integrated system (797 VA Computrace, Metrohm, Sweden) employing a three-electrode cell consisting of a 2 mm diameter glassy carbon working electrode (GCE) on a rotating stand (Metrohm, Sweden), a platinum counter electrode, and a 3 M KCl Ag/AgCl reference electrode with 2 M $KNO_3$ used as a bridging electrolyte. All potentials are reported *versus* this reference. The surface of the GCE was prepared by polishing using clean alumina (0.3 mm, Struers, Sweden), washing with water and gently drying with tissue. Electrochemical preparation of the GCE surface involved cyclic voltammetry (CV) of the electrode from +0.5 V to −2.20 V at 1.0 V s$^{-1}$ in a 0.025 M $Na_2CO_3$ electrolyte adjusted to pH 10.0 ± 0.05. Cathodic current densities at the peak potential during this preparation were 1.0 to 5.0 mA cm$^{-2}$. Electrodes were stored in 0.025 M $Na_2CO_3$ at pH 10 overnight before use. DPASV measurements were conducted using an electrolyte volume of 10 mL being de-aerated for 3 min by argon-bubbling prior to each measurement. The oxygen reduction reaction was used to confirm the time of de-aeration. For calibration, the pH was buffered using 0.025 M $Na_2CO_3$ adjusted with nitric acid

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(13%) to pH 10.0 and justified by the fact that $Na_2CO_3$ is used ubiquitously in laundry formulations.[13] The electrode was held at +0.45 V for 60 s prior to the measurements to remove any silver from the surface. Deposition potential, sweep rate, voltage step and pulse amplitude and width were optimised. Deposition was conducted at −0.40 V for 120 s while the electrode was rotated at 2000 rpm. Stripping was conducted on a stationary electrode by sweeping the potential from 0.00 V to +0.50 V at 0.040 V s$^{-1}$ using a voltage step of 0.004 V. A differential pulse was applied with an amplitude of 0.050 V and length of 0.040 s. The total measurement time was 380 s from start of de-aeration to the end of stripping. The diameter of the GCEs was 2 mm and the GCEs were purchased from Metrohm (Sweden) with production numbers 10705999, 10706048, 00791592, 01095155, and 01095187. Current densities were calculated using the GCE area (0.031 cm$^2$). A deposition time of 120 s represents a compromise between a practical measurement time and a limit of detection as low as possible.

A silver ISE (Metrohm, Sweden) was used with a low flow double junction 3 M KCl Ag|AgCl reference electrode (Metrohm, Sweden) with 2 M $KNO_3$ as a bridging electrolyte. Potentials were measured using a high impedance ion meter (713 pH meter, Metrohm, Sweden). The solution was stirred continuously during all measurements. Measurements were conducted until the drift was below 1.0 mV min$^{-1}$. The silver ISE was gently polished using 0.3 μm $Al_2O_3$ powder and, prior to use, soaked in 2000 ng silver/10 mL with 0.1 M $KNO_3$ solution. Calibration was performed in 0.1 M $KNO_3$ and 0.025 M $Na_2CO_3$. Using this electrolyte, the ionic strength was essentially constant when adding Ag ions, thus avoiding possible effects of changes in Ag activity.

Chemicals were of the cleanest possible grade, puriss p.a., obtained from Sigma-Aldrich, Sweden.

## Results and discussion

Calibration curves are presented in Fig. 1 for DPASV (left) and ISE (right) at pH 10 and in 0.025 M $Na_2CO_3$. Note that the scales of the DPASV and ISE are different given that the DPASV current responds linearly to concentration, whereas the ISE potential varies logarithmically with concentration. The concentration range covered in this figure is essentially the same for ISE and DPASV. The pH was adjusted to 10 in order to be relevant for solutions containing laundry detergent[13] and did not change during the measurements due to the buffering effect of carbonate.

According to Fig. 1, the calibration was linear down to approximately $10^{-6.7}$ M silver for the ISE, a sensitivity similar to the reported values from the manufacturer and the scientific literature.[14] DPASV enabled a detection limit of $10^{-8}$ M that was lower compared with ISE, Fig. 1 right. A lower limit of detection of DPASV compared to ISE is in line with similar comparisons made for other solutions.[10] It should however be pointed out that the response of DPASV was not linear above 1800 nM silver.

When carbonate was added to a solution containing 1000 nM of silver, the silver concentration measured by ISE varied dramatically, from 2400 to 320 nM (Fig. 2). In contrast, values close to 1000 nM were determined by means of DPASV, although the results started to deviate from 1000 nM at high (>100 mM) carbonate concentrations (Fig. 2). Furthermore, the DPASV peak position of the silver stripping peak shifted when carbonate was added, from 0.32 V while adding 2.5 mM carbonate to 0.26 V while adding 250 mM carbonate.[15] This implies that the addition of $Na_2CO_3$ influences the position of the Ag|Ag$^+$ equilibrium. A large shift in the ISE potential, caused by the presence of carbonate, may hence easily be misinterpreted as a change in silver ion concentration. As sodium carbonate was added to the solution, it was possible that the Ag activity changed, and thus the measured concentration. However, as seen in the DPASV results in Fig. 2 with increasing carbonate concentration, this effect was small compared with the decrease in the measured Ag concentration by ISE. It is not expected that the Na$^+$ ion interferes with the measurement.[8] The exact reason behind the observed shift in silver equilibrium (reflected in the equilibrium potential) is unknown, however possible explanations are surface reactions between carbonate and the $Ag_2S$ membrane of the ISE, and between carbonate and deposited silver in the case of DPASV. Such reactions have been observed to take place for other ions such as Cl$^-$ and Br$^-$, where additional surface species, (AgBr, AgCl) have been reported to form on the $Ag_2S$ membrane of the ISE upon illumination.[16] Chemical equilibrium calculations showed in addition that the
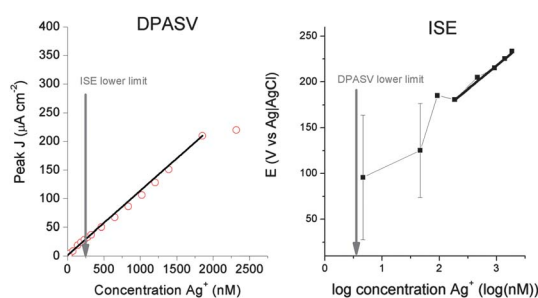


**Fig. 1** Left: calibration curve of DPASV, performed in 0.1 M $KNO_3$ and 0.025 M $Na_2CO_3$ at pH 10. Right: calibration curve of ISE in 0.1 M $KNO_3$ and 0.025 M $Na_2CO_3$ at pH 10. Error bars represent standard deviations of three independent measurements.
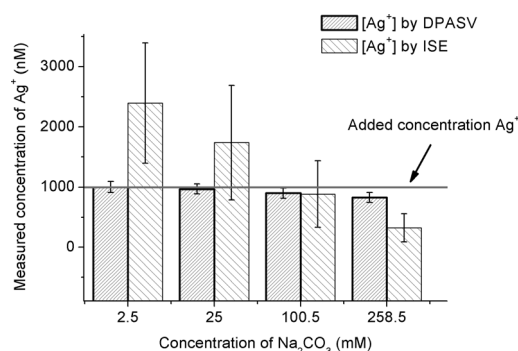


**Fig. 2** Comparison of silver ion concentrations measured by means of DPASV and ISE, respectively, in 0.1 M $KNO_3$ of known silver ion concentration (1000 nM) and varying carbonate concentration (2.5–258.5 mM) at pH 10. Errors were estimated from three (ISE) or two (DPASV) independent measurements.

formation of $Ag_2CO_3$ complexes in solution were not likely to be responsible for observed ISE results. Even though the calibration of the ISE was performed in 25 mM $Na_2CO_3$, measured silver concentrations, presented in Fig. 2, resulted in an overestimation of the results for this carbonate concentration. The measurements were performed in a series starting from low and proceeding to high carbonate concentrations. This procedure clearly affected the performance of the electrode and emphasizes the importance of calibrating and measuring silver concentrations in media of similar carbonate concentrations subsequently.

The generated results have implications for accurate determination of silver ions in carbonate-rich aquatic samples. In laundry detergents the concentration of carbonate is typically around 0.4 g $L^{-1}$ (tens of mM).[17] However, ISE measurements are often conducted in samples of unknown carbonate concentration.[18] The presented results of this study elucidate that largely deviating silver concentrations from the true concentration may be measured by means of the ISE as a consequence of carbonate interferences.

From the pilot investigation conducted at pH 10 follows a need for further investigations on the phenomena of the disturbed $Ag|Ag^+$ equilibrium measured by the ISE upon carbonate addition. For example, surface interactions with carbonates are one possible reason for the observed shift in potential. Such a hypothesis requires however accurate surface analytical studies of the $Ag_2S$ membrane after use in carbonate solutions, not performed in this study. It is furthermore recommended to investigate the effect of carbonates on the measured silver ion concentrations in aqueous solutions of varying pHs, and at other silver concentrations. However, as clearly elucidated, measured silver concentrations in carbonate solutions using the DPASV technique, which do not rely on shifts in $Ag|Ag^+$ equilibrium but rather on the peak height of a stripping peak, are to prefer in carbonate-rich solutions before ISE measurements.

## Conclusions

Differential pulse anodic stripping voltammetry, DPASV, was shown to have significantly higher sensitivity towards silver ions compared with ion selective electrode, ISE, measurements in carbonate containing aqueous solutions of pH 10. The presence of different carbonate concentrations at pH 10 was shown to shift the $Ag|Ag^+$ equilibrium. This effect results in erroneous measurements of active silver (primarily free ions) in carbonate-containing aqueous solutions by means of ISE. The generated results emphasize the importance of parallel determinations of the water chemistry, in particular the carbonate concentration, when measuring the silver concentration by means of an ISE as this largely influences the results, in particular, pronounced at low carbonate concentrations.

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