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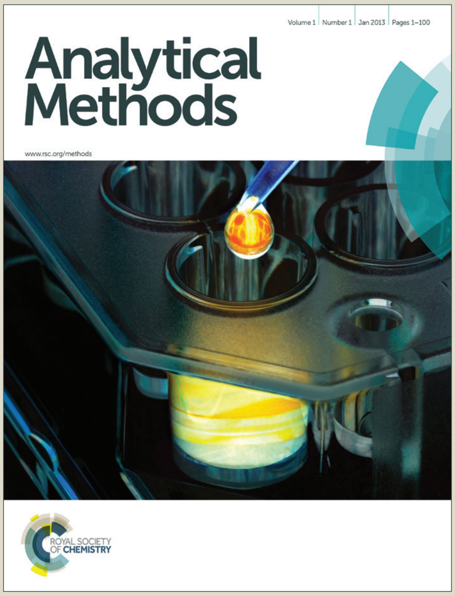

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Silver nanoparticles detection and characterization in silver colloidal products using screen printed electrodes.

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Silver nanoparticles (AgNP) were detected and characterized in several silver colloidal products available in the market. The relationship of diameter of the nanoparaticle with the corresponding peak potential was used to determine the dimensions of the AgNp in real samples. Quantitative analysis was carried out by voltammetry of immobilized particles on screen printed and glassy carbon electrodes. Screen printed electrodes were used prior modification of the reference electrode to attain stable readings of peak potential. The repeatability of the modification as well as the quantitative results were checked and found satisfactory.

Introduction

Silver nanoparticles have been used in all aspects of our day to day life but little care has been paid up to now to what happens to them once they have accomplished their purpose, becoming a waste product. Detection and characterization of nanoparticles in the environment as well as in the daily use products is more necessary than ever.

When dealing with nanoparticles it is necessary to answer three relevant questions, which nature, how many, and which size because their properties and their role as environmental hazards depend on them[1]. Especially size has been proven to be main point since its biotoxicity depends critically on it[2].

Many different attempts have been made involving different techniques to characterize nanoparticles, among the most frequently used are Transmission Electron Microscopy (TEM), Dynamic Light Scattering, (DLS), X- Ray Difraction (XRD) and many others described and compared in the previous literature[3] and more recently field flow fractionation (FFF)[4]. FFF exhibits remarkably features when it is coupled with ICP Mass Spectrometry (ICP-MS)[5] that allows a concentration and size determinations at very low level and down to 10 nm particle diameter. ICP-MS has also proven to be an interesting tool for the detection of single nanoparticles, in particular silver nanoparticles (AgNP) and to distinguish them from Ag(I). It also goes one step further by offering data about particle size and the polydispersity of the sample[6] .

Anodic particle coulometry (APC) is a methodology developed in 2011 by Compton and co-workers based on the measurement of the Faradaic charge transfer when a nanoparticle hits the electrode surface set on an adequate potential at which the metallic nanoparticle is destructively and quantitatively oxidized[7]. It is an alternative tool since it provides information about the size and size distribution of nanoparticles and their concentration. It also provides a view of the behaviour of the nanoparticles, their aggregation and evolution in the solution[8-10] .

Voltammetry of Immobilized particles (VIP) developed by Sholz in the 90's[11] and adapted for the study of nanoparticles oxidation on an electrode has been used to study the relationship between size and peak potential[12-14]. Few microliters of a sample containing nanoparticles are cast on a graphite electrode surface and allowed to dry. Then the electrode is transferred to a suitable supporting electrolyte and the voltammogram is obtained. The oxidation potential of an isolated metal nanoparticle is lower than the redox standard potential of the bulk metal depending on the radius and the surface energy of the nanoparticle[15]. Surface interactions between the electrode material and the nanoparticle affect the oxidation potential shifting its value according to the surface Gibbs free energy. If this value is positive, the metal does not interact with the electrode material and the oxidation potential shift with decreasing radius towards lower values than the bulk oxidation potential of the nanoparticle[16] metal. Theoretical studies have been developed to explain the experimental data through mathematical models that consider these factors whose purpose is to describe the electrochemical and surface energy properties of the nanoparticles[13,14].

Surface coverage is another factor that should be accounted for to explain the oxidation voltammograms of metal nanoparticles. The diffusion of the oxidation products away from the nanoparticle should be considered since it affects the peak potential at the reversible limit. If particles are too close then the diffusion layers of the neighbour nanoparticles overlap and this affects the position of the corresponding oxidation peak which shifts towards more positive values. In the irreversible limit the peak potential is independent of the surface coverage[12,17].

Glassy carbon electrode has been used in most of the experiments but the working electrode of a screen printed set has been successfully used to study the processes taking place at the electrode surface. Here we propose the use of screen printed electrodes instead the traditional bulk experiment in a three electrode cell. To achieve this goal a more stable and reproducible reference electrode is needed. Over the years many different methods to produce stable all solid reference electrodes have been proposed[18-20] and nowadays they can be bought from some purveryors. The simplest procedure consists on developing a layer of AgCl on the Ag pattern of the pseudoreference electrode and then it is covered with a polymer layer that contains chloride and a protective external layer to prevent chloride from diffusing away[21]. A simple but efficient proposal was offered by Nolan et al.[22]. They covered a Ag/AgCl wire with Nafion containing chloride and obtained an all solid state reference electrode stable enough to be used for the voltammetric determination of Hg in natural waters at ppb level.

All things considered, electroanalytical techniques are a unique tool for the study, detection and characterization of nanoparticles in all kind of samples. Voltammetry of immobilized particles (VIP) and APC have been successfully applied to the detection, identification and sizing of silver nanoparticles in a colloidal silver spray available in the market[23]. The detection of AgNP in environmental samples has been successfully attained using a chemically modified glassy carbon electrode with cysteine that is able to bind AgNP and concentrate them on its surface[24] that opens a door to the design of sensors for field analysis.

The authors present here a methodology to detect and identify silver nanoparticles in real samples providing information about their concentration and size using VIP with GC and SPE for the first time. The use of disposable mass produced devices simplifies the procedures and enables the use for field analysis since the SPE instrumental design is small enough to make it portable and the adequate selection of the voltammetric technique allows the user to attain lower and lower limits of detection to cope with environmental analysis requirements and convenient selectivity.

Experimental

Reagents and instrumentation

Al reagents were of analytical grade. Suspensions of 20 ± 5, 40 ± 5, 60 ± 5 and 80 ± 7 nm silver nanoparticles were purchased from BB International (Cardiff, UK), the suspension of 10 nm was provided by PlasmaChem GmbH and the 100 nm suspension by Sigma. Diluted suspensions of silver nanoparticles were prepared from commercially available suspensions after 1 minute sonication. All of them were prepared with ultrapure water (Milli Q Advantage), stored in the dark at 5ºC. They were sonicated for just 1 min before their use, care should be taken not to heat the nanoparticles to avoid oxidation. Standards were periodically checked using cathodic voltammetry for Ag(I) detection as it is described in 3.1. They were discarded when Ag(I) was detected.

Three different samples purchased in health care specialized shops were studied. These samples were kept in a dark place at room temperature. Dilution with ultrapure water was performed when necessary after one minute sonication. Diluted samples were kept in the dark at 5ºC and sonicated for 1 min prior use. Sonication periods longer than 1 min are not recommended due to the heating of the sample. The power of ultrasonic bath used for all these experiments was 50W.

To determine the diameter of the samples Transmision Electron Microscopy (TEM) was used with a JEOL-2000 FXII. 10 μL of the sample were deposited on a 400 mesh grid and allowed to dry.

The silver concentration of the samples was determined by ICP mass spectrometer (ICP-MS) using a Perkin-Elmer Sciex model ELAN DRC-e.

Voltammetric measurements were carried out with a computer controlled AutoLab PGSTAT-12 potentiostat (Utrecht, The Netherlands) connected to three electrode screen-printed carbon electrodes (SPCEs) or to a 10 mL voltammetric cell with a Ag/AgCl/ 3 M NaCl reference electrode from BAS, Pt auxiliary electrode and glassy carbon (GC) electrode, 3 mm diameter. The diameter of the working electrode in SPCEs was 4 mm. Working and auxiliary electrodes were printed from a carbon-based ink (Gwent, C2091208D1) and the pseudo reference electrode with a silver-based ink.

Procedure

The silver contents of commercial suspensions were determined by acid digestion followed by ICP-MS determination. Aliquots of each suspension (1g) were placed into PTFE beakers, 1mL of concentrated HNO_3 was added and the mixture heated in a sand bath to almost dryness. The digested sample was diluted up to 200 mL with 1% (v/v) HNO_3. Analysis was performed in duplicate.

To perform the voltammetric studies 3 μL of a suspension were drop cast on the working electrode. The drop was placed just on the graphite disk. It has to wet just the graphite surface and should no reach the polymeric substrate or electrodes. Then the drop was dried under nitrogen flow avoiding its displacement or a fast drying that should result in loss of material and aggregation.

The Electrochemical cell was filled with 10 mL of $KClO_4$ 0.1 M as supporting electrolyte to obtain the voltammograms with GC electrode.

Whenever SPE were used, 70 μL of $KClO_4$ 0.1 M were deposited to fully cover the three electrodes and the voltammogram was recorded. If the SPE was to be reused, it was carefully rinsed with MilliQ water and allowed to dry at room temperature.

Linear sweep voltammetry was used in all instances, scan speed 20 mV/s.

All the electrochemical measurements were performed five times, analysis were performed in duplicate.

Results and discussion

Screen printed electrode modification

To relate peak potential to diameter of the nanoparticles it is necessary a stable and reproducible potential measurement. Reference electrode of our screen printed electrodes (SPE) are made form a silver ink and they are not stable enough to achieve a reliable and reproducible peak potential measurement only dependent on surface coverage and particle diameter. A modification of the screen printed electrodes is necessary. This modification should be simple enough to need just a few minutes and if possible to require just one or two steps. Two options were tested, deposition of an agar electrolyte layer or a Nafion film on a chemically or electrochemically deposited layer of AgCl.

We found the chemical way a simpler solution for the deposition of a AgCl layer, whose thickness was controlled by exposure time and concentration of the reagent, 1 M $FeCl_3$ in our case.

A 3 μL drop of 1M $FeCl_3$ was deposited on the pseudoreference electrode for 1 min to develop a AgCl layer and them thoroughly rinsed with Milli Q water to remove the excess of reagent and allowed to dry under a nitrogen current[19]. On this layer two different chloride containing layers were tested, agar and Nafion.

A 3 μL drop of KCl saturated agar was deposited on the Ag/AgCl and allowed to dry at room temperature. The resulting device was tested with a 10 nm solution of AgNP but it was discarded straight away because the agar layer peeled off after the first measurement. A third layer of a polymer should be necessary to keep it in its place. For the sake of simplicity, this option was disregarded and the Nafion layer option[22] was investigated.

A 3μL drop of 5% Nafion in ethanol saturated with KCl was placed on top of the Ag/AgCl layer and allowed to dry at room temperature. The screen printed device was tested through 12 voltammograms and the polymeric layer kept in place. To check the reapeatability of the modified device, 10 SPE were modified and tested using 3 μL of 1 g mL^{-1} AgNP (60nm). Twelve measurements were performed with each electrode. The peak potential was 0.055 ±0.006 V.

The comparison between the three types of SPE is shown in table 1. We concluded that the Nafion modified SPE offered repeatability and stability of the peak potential measurement so, it was selected for the study of the samples.

Since the geometric area of the screen printed working electrode was similar to the glassy carbon, the same considerations about surface coverage were followed.

Table1: stability and reproducibility of peak potential measurements. Each screen was used for 12 measurements but the one sporting the agar modification that stood only for one experiment. 3 μL of 1 g mL^{-1} AgNP of 10nm were deposited on the working electrode for each measurement. Results as mean ±standard deviation.

Device	**Without modification (V)**	**Nafion modification (V)**	**Agar modification (V)**
Screen 1	0.023±0.009	0.020±0.006	0.074
Screen 2	0.063±0.008	0.021±0.006	

AgNP and Ag(I) detection

The presence of AgNP in the samples was determined by anodic voltammetry of a 3 μl drop of the undiluted sample cast on the glassy carbon electrode and allowed to dry under a N_2 current to avoid oxidation from atmospheric oxygen. Then a voltammogram is obtained from 0.0 V to 0.8V at 20mV/s scan rate in 0.1 M $KClO_4$. All the samples showed a characteristic anodic voltammogram of AgNP.

The same procedure was used to detect the presence of Ag(I) but a cathodic scan was performed instead. Ag(I) standards of decreasing concentration were prepared to determine the minimum concentration that resulted in a peak. The minimum detectable concentration was 5 μM. The cathodic voltammograms of all the samples did not show any peak and they were coincident with a blank voltammogram.

No influence of Ag(I) on reference electrode potential was expected when using the modified SPE.

Size characterization

TEM images were used to determine the size and shape of the nanoparticles in the samples. As it can be seen in figure 1 the silver nanoparticles exhibit a rounded shape. It can be observed that the nanoparticles of these samples are covered with a non-metallic layer. The diameter of nanoparticles in sample AP10 is between 10nm and 50 nm, in sample AP25 between 10 nm and 30 nm and in SN30 between 20 nm and 30 nm.

For a determined electrode material, the peak potential depends on the size of the nanoparticle and the surface coverage of the electrode if the electrode process is reversible. If the coverage is kept constant and as low as possible in order to get particles diffusionally independent from each other with a radial mass transport form the NP, the peak potential can be used to estimate the diameter of the attached nanoparticles (di). In this case, there is a linear relationship between the peak potential and lndi with a slope of 2RT/nF, with n=1 in our case.

The dependence of peak potential with radii of the nanoparticles was studied using glassy carbon electrode as a reference procedure and screen printed electrode. The calculated diameters were compared with those obtained using TEM.

First of all, a suitable concentration of AgNP in the diluted suspension was selected to obtain peaks whose peak potential depends only on particle diameter. 3 μL of suspensions of different concentrations of the standards were cast on the electrode surface and allowed to dry under a nitrogen flow. The peak potential was measured and its relationship with the oxidation charge of the particles deposited on its surface was studied. As the particle coverage is decreasing, the particle size becomes the main factor that affects peak potential. When a suitable value is reached the peak potential is governed by the size of the nanoparticles. It was found that whenever the concentration was lower than 2 g mL^{-1} of Ag, the peak potential was independent of the surface coverage, see figure 2.

To choose the dilutions of the samples, dilutions with milliQ water were performed till constant potential was attained. It happened when the natural logarithm of the peak charge, lnQ, was lower than -14. Dilution also helped to diminish the effect of the sample matrix, lowering the baseline and minimizing agglomeration especially when SPE were used.

The diameter calibration was performed using a 0.5 g mL^{-1} dilution of the standards. Five measurements were performed for each standard. The calibration was performed in duplicate. The slope values obtained using glassy carbon electrode are 0.054 and 0.066, according to an experiment performed at quite high particle coverage (0.5ppm=2.10^{-6}mol m^{-2}), small particles (10 to 60 nm) and low scan rates (20 mV/s)[12,25]. The screen printed electrode experiment was performed in duplicate. Linearity was observed from 20 nm to 100 nm. The slopes were different from the GC ones, 0.100 and 0.092 that are consistent with a model of partially overlapping diffusion layers of the deposited NP's. The regression coefficient was in all instances greater than 0.99. Diameter calibration plots and voltammograms obtained with GC and SPE are shown in figure 3.

We consider that the differences between the GC and SPE slopes are due to aggregation of the nanoparticles on the electrode surface during the drying period, this caused the broadening of the peaks and shifting towards more positive potentials, sometimes two peaks could be appreciated clearly[17,26] due to the oxidative dissolution of the AgNP aggregates of different size . This problem was minimized by using a convenient dilution and using freshly prepared dilutions every time it was detected. We also noticed that SPE is prone to this phenomenon, especially with nanoparticles of smaller diameter, probably due to a stronger interaction between the electrode material (because of its chemical composition and surface roughness) and the sample. An example of multiple peaks for two different nanoparticle diameters are shown in figure 4.

Polydispersity not only affects the width of the voltammograms that are broader for SPE than form GC, it also accounts for the lower values of peak intensity obtained with SPE with the same conditions[26].

As it can be seen in table 2, the diammeters of the nanoparticles obtained with GC and TEM are similar, but there are some differences when SPE are used. As a general rule the SPE values are greater than the GC ones, due to the nanoparticle agglomeration on the surface of the SP working electrode.

Table 2: AgNP diameter (nm) and peak potential (V) of the particles in silver colloidal products available in the market for health care use. Each value is the mean of two different experiments. Five measurements were performed for each experiment. Results as mean ±standard deviation.

Electr.	**AP10**		**AP25**		**SN30**	
	nm	**V**	**nm**	**V**	**nm**	**V**
SPE	52±1	0.056±0.003	26±1	0.028±0.003	28±2	0.029±0.004
GC	45±15	0.240±0.025	14±2	0.250±0.010	20±2	0.260±0.005
TEM (nm)	10-50		10-30		20-30	

Concentration of AgNP in the colloidal products commercially available

Quantitative analysis was performed studying the relationship between the area under the peak and the concentration of AgNP in the suspension.

It was found that the slope of the calibration depends on the diameter of the nanoparticles, especially for the screen printed electrode experiments, so it was necessary to use a calibration with nanoparticle standards close to the diameter of the nanoparticles of the sample. Linear response was obtained from 0.5 g mL^{-1} to 6 g mL^{-1}. Several voltammograms were obtained to be sure that all the nanoparticles were stripped before depositing a second drop of standard or sample. It was observed that all of them were oxidized in the first voltammogram. In all instances the regression coefficient was greater than 0.99.

AP10 and AP25 were diluted with Milli Q water five times and SN30 ten times. 3 μL of the diluted sample were placed on the working electrode, then at least two voltammograms are obtained to be sure that the nanoparticles are totally stripped. Recovery test were also performed with the glassy carbon electrode and addition of 0.5 g mL^{-1} of the AgNP standard to each sample. The recovery values are 99% for AP10, 95% for AP25 and 110% for SN30. The standard deviation of the recovery values was less than 10%. The quantitative results are listed in table 3, as it can be seen there is good agreement between experiments. Voltammograms of the samples obtained with the GC and the SPE are shown in figure 5.

Table 3. AgNP determination in silver colloidal products. Analysis were performed in duplicate. AgNP Diameter of the calibration standards AP10; AP25 40 nm and SN30 20 nm. Results as mean ±standard deviation.

Electrode	**AP10 (ppm)**	**AP25 (ppm)**	**SN30 (ppm)**
SPE	9.65±1.77	5.9±1.37	26.3±2.51
GC	13.2±0.4	4.1±0.2	32.3±0.01
ICP	11.36±0.26	5.34±0.23	23.8±0.80

Conclusions

All the samples contained silver nanoparticles mainly in the form of Ag(0). Ag(I) can be detected using CSV down to 5 μM.

In all the samples tested Ag(I) concentration was lower than 5 μM. Consequently no influence of Ag(I) concentration on the performance of the reference electrode was considered.

The diameter of the silver nanoparticles can be estimated from the peak potential if the surface coverage is kept constant. If aggregation takes place, two peaks can be observed. Aggregation effect can be minimized by adjusting dilution or preparing a fresh solution for each measurement. 0.5 g mL^{-1} was found to be an adequate concentration for these experiments with AgNP. It was also noticed that SPE were prone to cause aggregation of the nanoparticles, that could explain why the diameter values obtained with them are bigger than the ones obtained with GC, but anyway they are within the diameter range observed by TEM.

The concentration of AgNP in the sample can be determined by anodic stripping voltammetry from a solid deposit of a 3μL drop of the sample adequately diluted so the lnQ is lower than -14. In this case the results obtained with both SPE and GC electrodes and ICP-MS procedures are in good agreement.

It can be concluded that voltammetry of the immobilized particles on the electrode surface can be used to obtain information about the redox forms present in a commercially available sample of AgNP as well as the concentration and diameter of the NP. The procedure is quite simple and takes a few minutes. It is of relevance the fact that SPE are an alternative to the three electrode voltammetric cell since they can offer the same information, opening the door to the development of field sensors for the accurate detection and characterization of nanoparticles, AgNP in this case.

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Figure captions

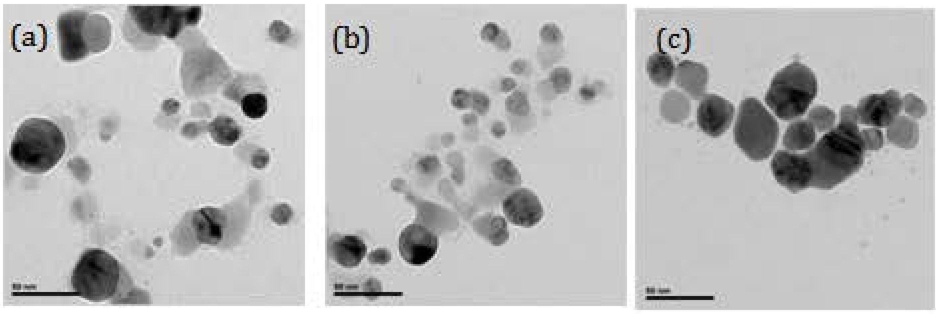
Figure 1: TEM images obtained from (a) AP10, (b) AP25 and (c) SN30

Figure 2: influence of the surface coverage on the peak potential. 3 μL of suspensions of different concentrations were deposited on the GC electrode. Three measurements were performed for each concentration.

Figure 3: Diameter calibration plots for GC (A) and SPE(C). Each point is the media of five values. Voltammograms of nanoparticles of different diameter 10 nm (1), 20 nm (2), 40 nm(3), 60 nm (4) and 100 nm (5) for GC(B) and SPE(D).

Figure 4: SPE Voltammograms of 5 g mL^{-1} AgNP (10nm and 100 nm) showing multiple peaks due to aggregation. 3 μL were deposited on the electrode. Supporting electrolyte $KClO_4$ 0.1 M, 70μL

Figure 5: A Voltammograms obtained with the GC. 3 μL of the diluted sample deposited on the electrode. B SPE Voltammograms. . 3 μL of the diluted sample cast on the electrode. SN30 (a), AP25 (b) AP10 (c).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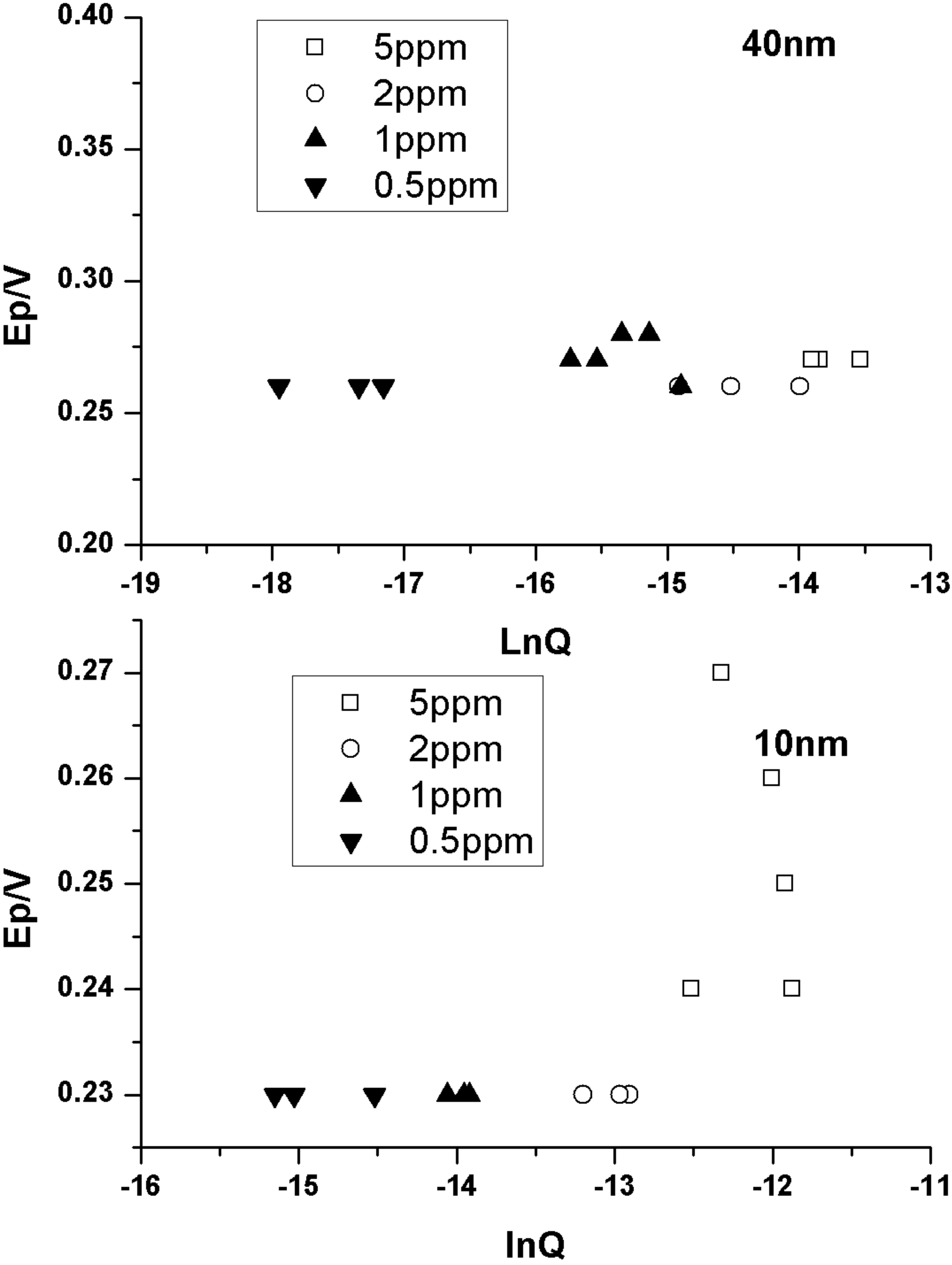
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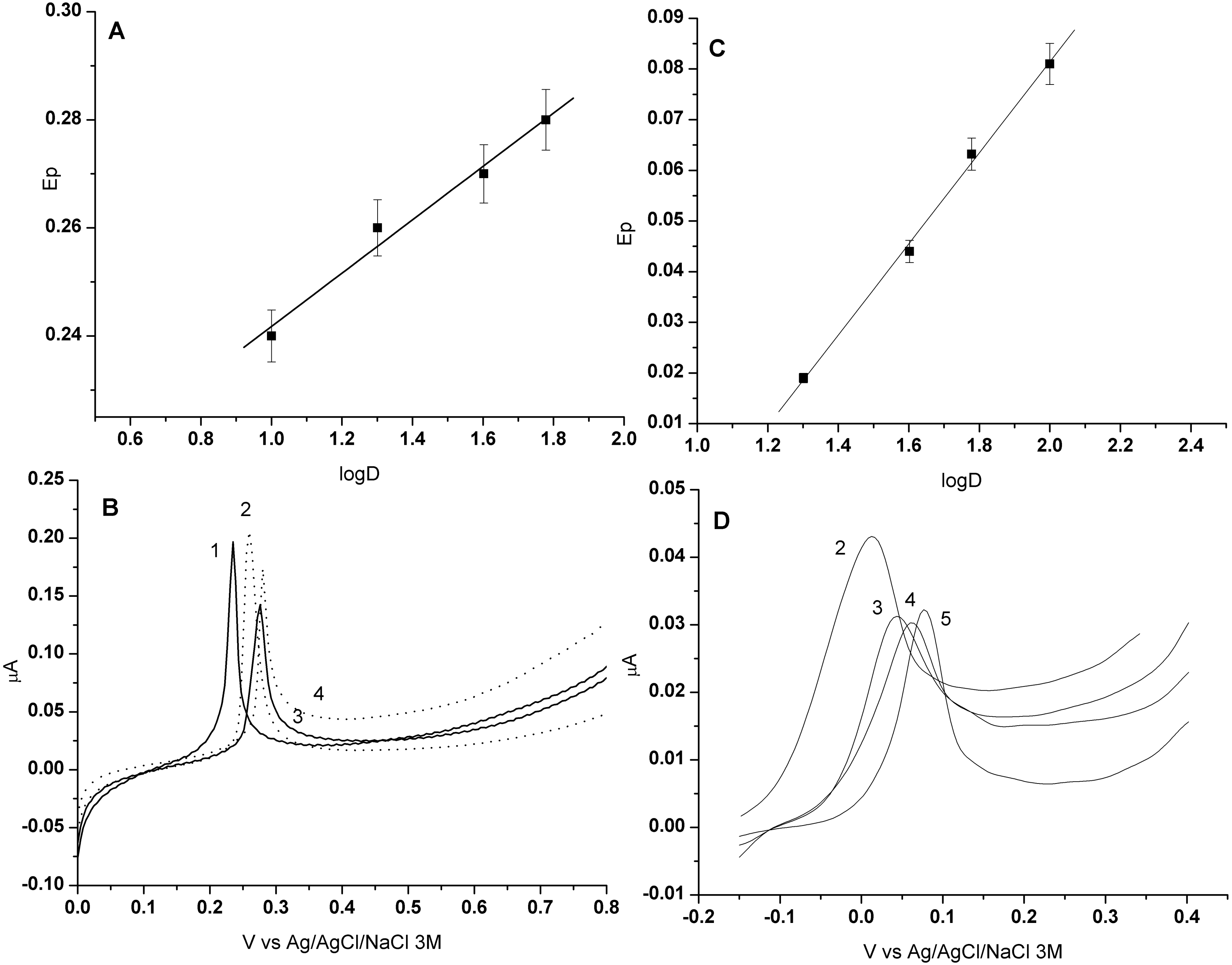
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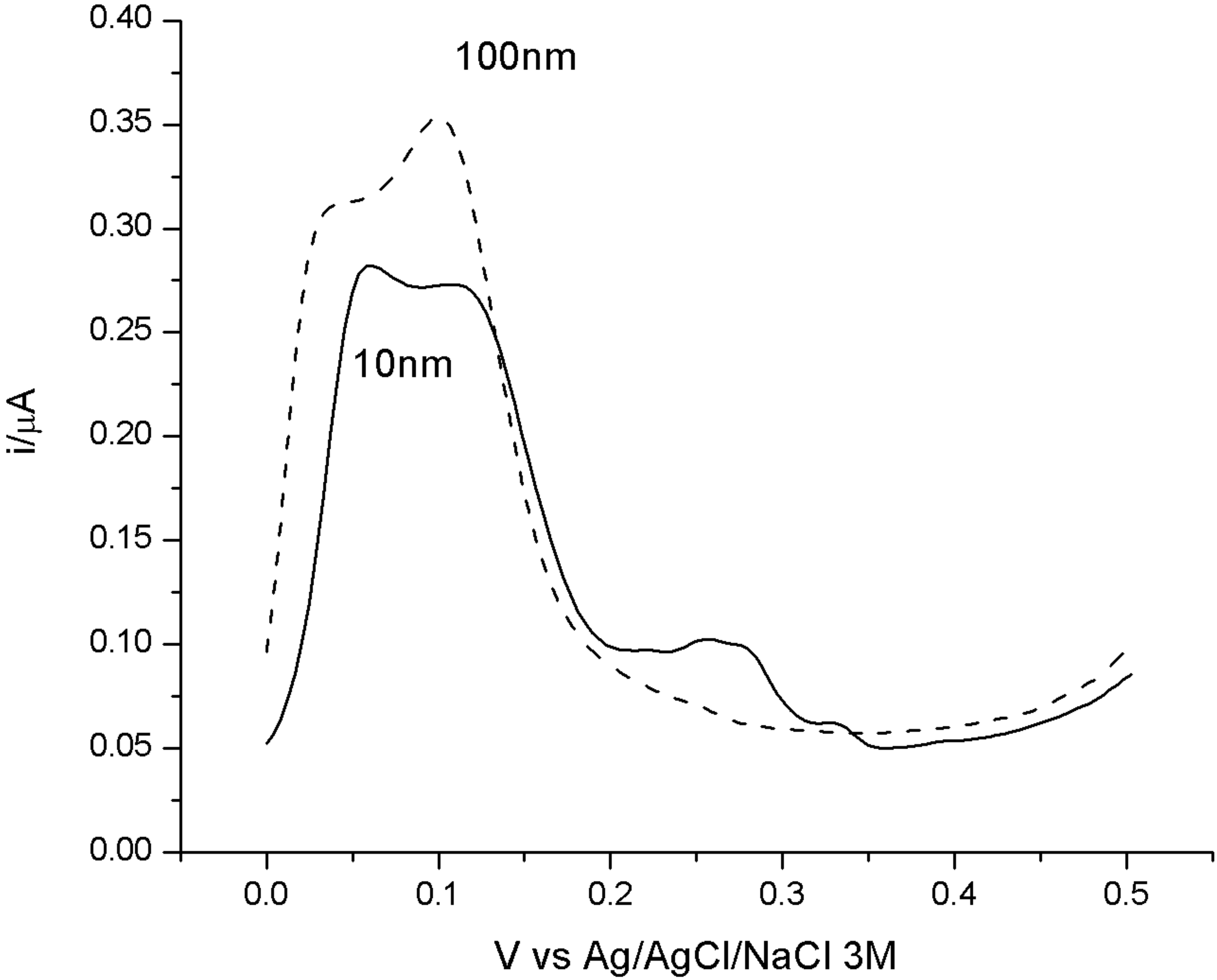
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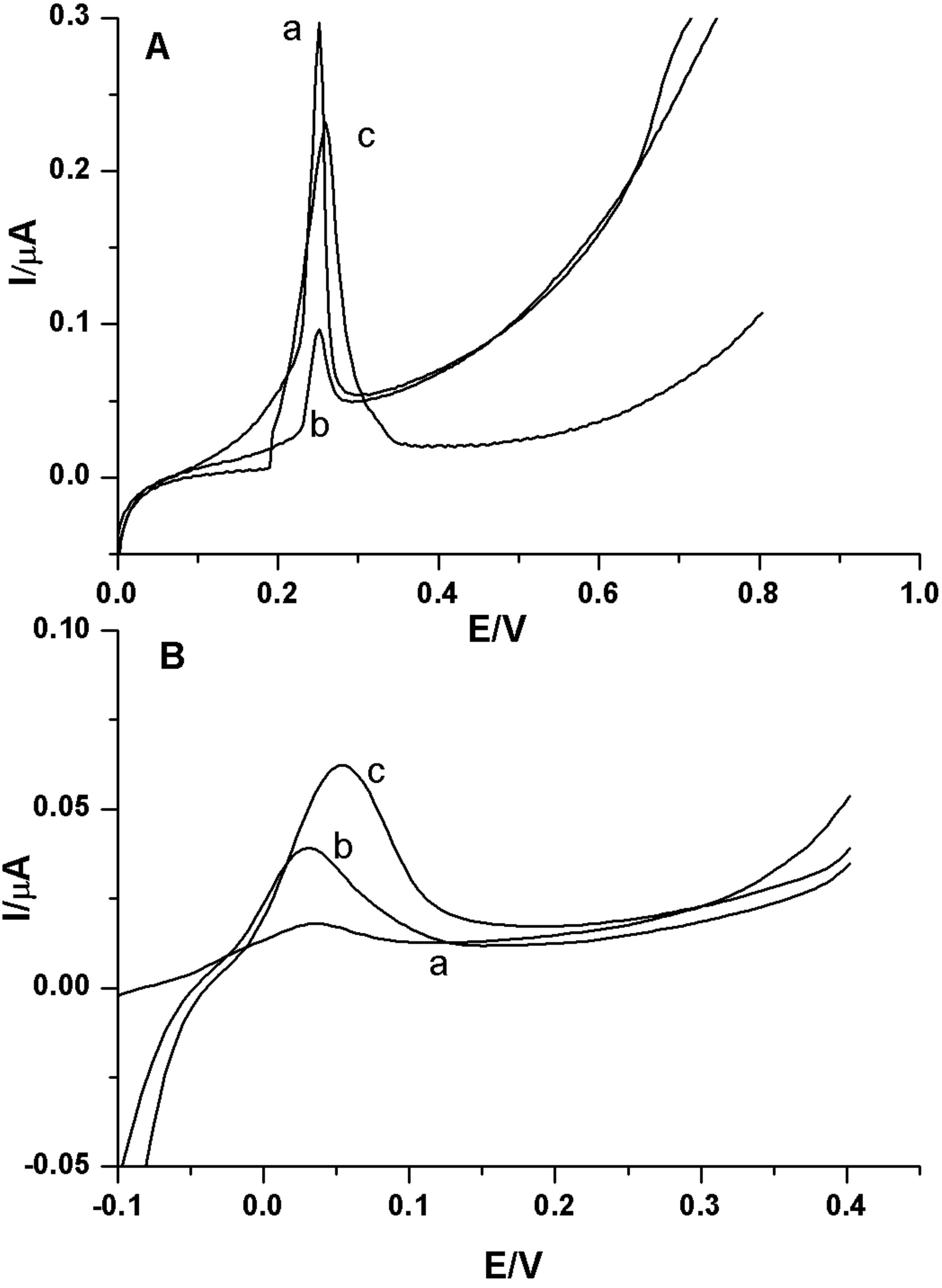
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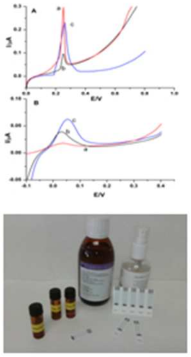
B
c
b
a
I/μA
0.10
0.05
0.00
-0.05
E/V
-0.1
0.0
0.1
0.2
0.3
0.4



Screen Printed Electrodes are used to characterize silver nanoparticles in real samples through an inexpensive and time saving procedure
190x254mm (96 x 96 DPI)