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Simple Characterization of Green-Synthesized Silver Nanoparticles by Capillary Electrophoresis

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Abstract The development of methodologies for the characterization of silver nanoparticles (AgNPs) synthesized using natural products has received increasing attention, especially to monitoring its stability and size for further application. In this paper, a capillary electrophoretic (CE) method is presented for characterization of AgNPs synthesized using honey or glucose as reducing agents. A simple electrolyte solution composed of 20 mM sodium borate and 20 mM sodium dodecylsulfate (SDS) at pH 8.5 was used for separation of AgNPs within a short analysis time (<12 min). The obtained results were compared with the traditional characterization techniques, such as transmission electron microscopy (TEM) and dynamic light scattering (DLS), showing satisfactory correlation in terms of size distribution. In addition, valuable information about electrophoretic mobility and zeta potential values of AgNPs was obtained by applying the CE-UV/Vis method. Thus, the proposed methodology represents a straightforward tool for the fast and cost-effective characterization of AgNPs within a single analysis, employing minimal amounts of reagents and samples.

Keywords Capillary electrophoresis · Electrophoretic mobility · Silver nanoparticles · Size characterization · Green synthesis

Introduction

Silver nanoparticles (AgNPs) have gained great interest in recent years because of the unique optical and electronic properties directly related to their small size and specific surface structures. Therefore, the application of these nanomaterials becomes significant in the manufacture of electrodes and optical sensors, as well as in water treatment, pretreatment of complex samples and as antimicrobial agents, among others [1–5]. Conventional methods used for these nanoparticles synthesis can include expensive and harmful reagents, such as sodium borohydride, followed by time-consuming reactions which increase the cost of the process [6]. For this reason, new alternative ways of synthesis involving natural and eco-friendly reagents are sought, commonly known as "green synthesis". Some of these methods include the use of starch [7], glucose with bamboo hemicelluloses [8], leaf aqueous extract of *Ocimum basilicum* (L.) [9], and so forth. Nevertheless, the AgNPs derived by the conventional and these new "green" methods require a proper characterization to validate the effectiveness of these syntheses. Several parameters such as size distribution, shape, colloidal stability, zeta potential, and excess of reagents and impurities, which can cause agglomeration and image artifacts during transmission electron microscopy (TEM) analysis, must be analyzed for the whole characterization of the synthesized material.

The traditional techniques used for the characterization of AgNPs are TEM and scanning electron microscopy (SEM) [6, 10]. Although these techniques are very useful

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to observe the size and morphology of nanoparticles, poor accuracy on size determination can occur. This is due to the limited examined regions and the lacking of representativeness of samples. In addition, artifacts can be generated during the sample preparation (e.g., drying process) [11]. Moreover, dynamic light scattering (DLS) is commonly used for determining the hydrodynamic diameter of particles in suspension. Although this technique is simple and rapid, size overestimation may occur due to results are obtained using specific data treatment software (e.g., CONTIN algorithm) which cannot be suitable to describe correctly bi- or trimodal dispersions [10]. On the other hand, the mentioned techniques do not involve any size separation process, which leads to a disadvantage, since physical and chemical properties of AgNPs depend on their size distribution.

Capillary electrophoresis (CE) has emerged as a suitable technique for nanoparticles characterization, because it is possible to separate them from further constituents of the samples and allows their separation according to size and/or surface charge density. In addition, CE has several advantages, including small volumes of samples and reagents, short analysis time, ease of operation, and miniaturization [12]. At the present time, there are some researches available in the literature where CE is proposed to characterize nanoparticles in different media. Liu et al. [13] studied the separation of citrate capped silver nanoparticles obtained by microwave irradiation, employing a combination of CE and diode array detection (DAD). In addition, other authors combined ICP-MS detection to capillary electrokinetic method for size distribution and characterization of AgNPs [14] and also for speciation and quantification of AgNPs and Ag^+ present in commercially available dietary supplements [15]. Recently, a mixture of latex nanoparticles was characterized by the in-line hyphenation of CE to Taylor dispersion analysis (TDA), which is based on the diffusion coefficients of each sample zone for separation of particles with radius between 56 and 70 nm [16]. Other authors proposed a CE-evaporative light scattering (ELSD) customized coupling to separate citrate capped gold nanoparticles by droplet formation and evaporative process aiming to obtain suspended particles for appropriate detection [17]. In the same way, a CE-ELSD coupling was employed to identify and separate silica nanoparticles of 20, 50, and 100 nm diameters in aqueous solution [18]. On the other hand, silver and gold nanoparticles were characterized and quantified using micellar electrokinetic chromatography (MEKC) combined to inductively coupled plasma-mass spectrometry (ICP-MS) [19]. Although these methods have been demonstrated to be useful for separation and characterization of different nanoparticles, their main limitation is the commercial availability of equipment and/or the fabrication and handling of customized interfaces, which are required for the effective hyphenation. Then, the widespread development and implementation of low cost and rapid CE methods is highly useful for the routine characterization of nano-sized particles.

In this work, a CE-UV/Vis method has been developed to obtain simultaneous information about the size distribution, zeta potential, and colloidal stability of AgNPs synthesized at pH 5.0 and 10.0 using honey or glucose as reducing agents. Furthermore, the proposed method requires small volume of sample and the analysis is performed within a short time (<12 min). To the best of our knowledge, this is the first time that a simple CE method is applied to the characterization of AgNPs synthesized in a greener way.

Materials and Methods

Reagents and Solutions

All reagents were of analytical grade. Ultra pure water (18 MΩ cm^{-1}) was used for preparation of solutions. Sodium tetraborate (Baker, Griesheim, Germany), sodium dodecylsulfate (SDS), and hydrochloric acid (Cicarelli, Buenos Aires, Argentina) were used to prepare the electrolyte solution (BGE) for CE separation. $AgNO_3$ (purity, 99.9%; Merck, Argentina), honey harvested in the region of Buenos Aires (Argentina), glucose (Sigma-Aldrich), and sodium hydroxide (Cicarelli) were employed to the synthesis of AgNPs.

Instrumentation

A Beckman Coulter capillary electrophoresis instrument P/ACE™ MDQ equipped with a diode array detector was used (Sciex, Redwood, CA, USA). The capillaries were also from Beckman Coulter. Control and data processing was carried out with the 32 Karat™ software.

The electrophoretic mobility and hydrodynamic diameter of AgNPs were measured with a Zetasizer Nano S90 instrument (Malvern Instruments Ltd.) at 25 °C, and the zeta potential was calculated using the Smoluchowski equation [20]. TEM studies were performed with a TEM-JEOL-100 CX II instrument equipped with an acceleration voltage of 100 kV. AgNP samples were prepared by deposition of small droplets of freshly prepared solutions onto the standard TEM grid and drying slowly in air naturally.

Surface plasmon resonance bands (SPR) of AgNPs were recorded on an Agilent Carry 60 UV–Vis spectrometer from 300 to 700 nm using a quartz cuvette of 1 cm of optical path. Sample concentration was made with Thermo Scientific Savant Spd 111v speedvac concentrator (Thermo Scientific, Waltham, MA USA).

AgNP Colloidal Dispersions

AgNPs were synthesized separately using silver nitrate solution as precursor and reducing agents such as honey solution or glucose [8]. Stock solution of honey was prepared by weighing 25.0 g of this reducing and stabilizing agent and dissolving with ultrapure water to 100.0 mL. On the other hand, a stock solution of glucose was prepared by dissolving 7.82 g of this carbohydrate with ultrapure water to 100.0 mL. Different volumes were taken from these solutions to prepare the colloidal dispersions (CD) of AgNPs. In all cases, sodium hydroxide solution (0.1 M) was employed to set the pH to 5.0 or 10.0 and ultrapure water was added to a final volume of 10.00 mL [21]. In this way, five CD of AgNPs were synthesized. On one hand, CD1 and CD2 were obtained by mixing 0.10 g% (w/v) honey and 3.12×10^{-4} M silver nitrate solutions at pH 5.0 and 10.0, respectively. In addition, CD3 and CD4 were prepared at pH 10.0 by mixing 4.75×10^{-3} M silver nitrate solution with two honey solutions at low (0.038 g% w/v) and high (0.46 g% w/v) concentrations, respectively. Finally, CD5 was synthesized with 0.069 g% (w/v) of glucose and 3.12×10^{-4} M of silver nitrate at pH 10.0. Then, each mixture was stirred for 1 min in a vortex until the dispersion of AgNPs was obtained and a yellow color appeared. All samples were dried using vacuum centrifugation until reach half of its volume.

AgNP dispersions were diluted in BGE (1:6 ratio) before DLS analysis aiming to avoid possible multiple scattering due to the high concentration and/or turbidity of the samples [22]. The AgNP dispersions were sonicated during 10 min and filtered through a 0.45 µm pore size syringe filter before analysis.

CE Analysis

The separation was carried out in a fused-silica capillary (62 cm total length, 51 cm effective length, 50 µm i.d, and 375 µm o.d) with a separation voltage of 20 kV at 20 °C. A mixture of 20 mM sodium borate, 20 mM SDS at pH 8.5 was used as BGE. The capillary was daily conditioned by flushing 0.1 M NaOH (3 min), ultrapure water (2 min), and BGE (5 min). All solutions were filtered through a 0.45 µm pore size syringe filter. AgNP dispersions were sonicated for 10 min and injected in the CE system without dilution by applying 55 mbar for 10 s.

Results and Discussion

Characterization of Synthesized AgNPs by TEM and UV–Vis

From the UV–Vis spectra, it can be seen the characteristic SPR around 411 nm of AgNPs synthesized with honey at both pH values (Fig. 1). The symmetric narrow shape of SPR bands in samples CD1 and CD2 correlates with a monodisperse nanoparticle suspension of mainly spherical shape which is in good agreement with the obtained TEM images [23, 24]. Hence, highly monodisperse nanoparticles with an average size of 18 nm were observed for CD1. Nevertheless, a slightly narrower SPR band was obtained

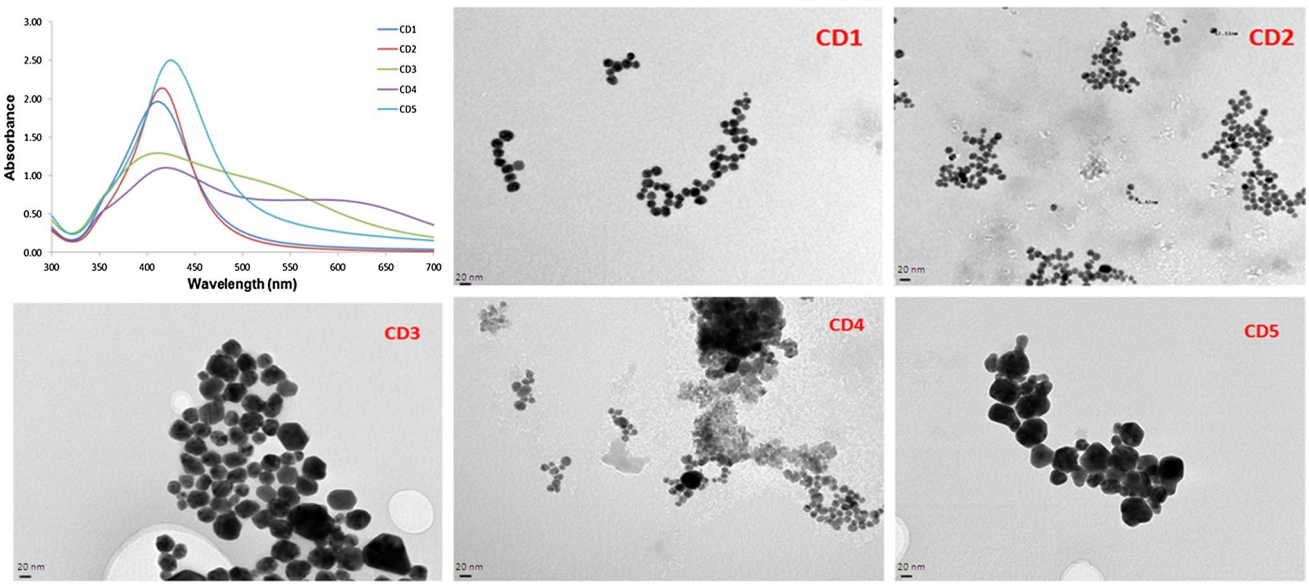

Fig. 1 SPR of AgNPs obtained with different concentrations of honey, glucose, and silver nitrate at pH 5.0 and 10.0 and the associated TEM images of the bio-synthesized AgNPs

in CD2 dispersion, which was confirmed by TEM analysis showing AgNPs with an average size of 12 nm. In the case of CD3 and CD4, the SPR bands suggest a polydisperse suspension of AgNPs with two absorption maxima and larger peak width. In addition, an evident shoulder can be observed around 350 nm in both samples. Figure 1 also shows SPR of AgNPs obtained with glucose at pH 10.0 (CD5). It can be seen a considerable red shift from 411 to 426 nm in the plasmon band with a broad bandwidth in accordance with the increased size and polydispersity of the nanoparticles [25]. Moreover, a shoulder around 350 nm was also observed, probably due to the presence of nanoprisms [24, 26]. These characteristic shapes and the nanoparticles size are observed in TEM images, where the presence of nanoprisms and polydispersion was confirmed for CD3, CD4, and CD5 (Fig. 1). The nanoparticles size varies between 20 and 50 nm for CD3, while CD4 shows nanoparticles size between 10 and 20 nm. Concerning CD5, the size distribution varied between 23 and 50 nm (additional details in Fig. S1).

Optimization of the CE Method

Characterization of the electrophoretic mobility, zeta potential, and size of AgNPs by CE requires the use of a BGE that can ensure the appropriate electric conductivity and ionic strength aiming to reduce the peak broadening and distortion due to electrophoretic dispersion. In the same way, wall adsorption of AgNPs must be controlled during separation. Taking this into account, a BGE solution composed by sodium borate and SDS was selected [13]. The pH of this solution was evaluated between 7.5 and 10.0. Under these conditions, two aspects are covered: (1) AgNPs are stabilized by the anionic surfactant avoiding possible agglomeration and growth during the separation process and (2) the inner walls of the fused-silica capillary are negatively charged, preventing the AgNP-wall adsorptive interaction. The ionic strength was maintained using 20 mM sodium borate as electrolyte solution and SDS concentration was varied between 0 and 20 mM. From the experimental results, well-defined peaks for AgNP suspensions were obtained when 20 mM sodium borate—20 mM SDS at pH 8.5 was chosen as BGE. It was observed that the inclusion of SDS allows the stabilization of the AgNPs in the separation media. Although there is no experimental evidence about the type of layer formed on nanoparticles (e.g., double layer or monolayer), several authors have previously demonstrated the long-term stabilization of AgNPs by double SDS layers [27]. According to Franze & Engelhard [19], the number of SDS molecules adsorbed on the AgNPs can be considered proportional to the surface area of spherical particles which also modifies the net charge of the nanoparticles. Hence, a 20 mM sodium borate—20 mM SDS-based BGE (pH 8.5) was used for AgNPs analysis taking into account the area and shape of electrophoretic peaks and also their electrophoretic mobility.

Pressure and time were evaluated for hydrodynamic injection of the studied AgNP dispersions in a range between 34 and 69 mbar and 5 and 10 s, respectively. Taking into account the peak shape and sensitivity, all samples were injected during 10 s by applying 55 mbar. The separation voltage was also changed between 10 and 25 kV to achieve satisfactory separations within a short analysis time (Fig. S2). Thus, a voltage of 20 kV was selected according to the optimal electrophoretic separation and current intensity. The precision for the migration time (tm) was evaluated considering that it can vary due to the characteristics of the surface covering of nanoparticles, also taking into consideration that the particles were not subjected to any purification process prior to CE analysis. Satisfactory RSD values were obtained for the analyzed AgNP dispersions, ranged from 0.9 to 2.6% ($n = 3$), which resulted comparable with reported values in the literature when metallic nanoparticles are analyzed by CE [12, 28].

Under optimized CE conditions, well-defined peaks were obtained for all AgNP dispersions within a short analysis time and no extra peaks from constituents of the matrix samples (e.g., honey components) were observed at 411 nm (Fig. 2).

Performance of the Developed CE Method for Characterization of AgNPs

Electrophoretic Mobility and Zeta Potential

During CE separation, AgNPs are considered as spherical particles (with radius r) surrounded by electric double layers of thickness $1/\kappa$, where the Debye–Hückel parameter κ (nm^{-1}) is directly proportional to the square root of ionic strength of separation medium. When dimensionless quantity κr is larger (limiting case, $\kappa r \gg 1$) Smoluchowski formula can be used to estimate the electrophoretic mobility as [29]

$$\mu = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta}, \quad (1)$$

where ε_r and ε_0 are the relative and vacuum permittivity, respectively, ζ is the zeta potential, and η is the dynamic viscosity of the electrolyte solution (25 °C). Nevertheless, several authors have demonstrated that if $\zeta > 25$ mV, the electrophoretic mobilities of nanoparticles can be affected by the relaxation effects due to the distortion of the ionic surrounding under an external field applied which becomes a function of the κr quantity [30–32]. In addition, Ohshima et al. [33] derived an analytical expression from the Henry's

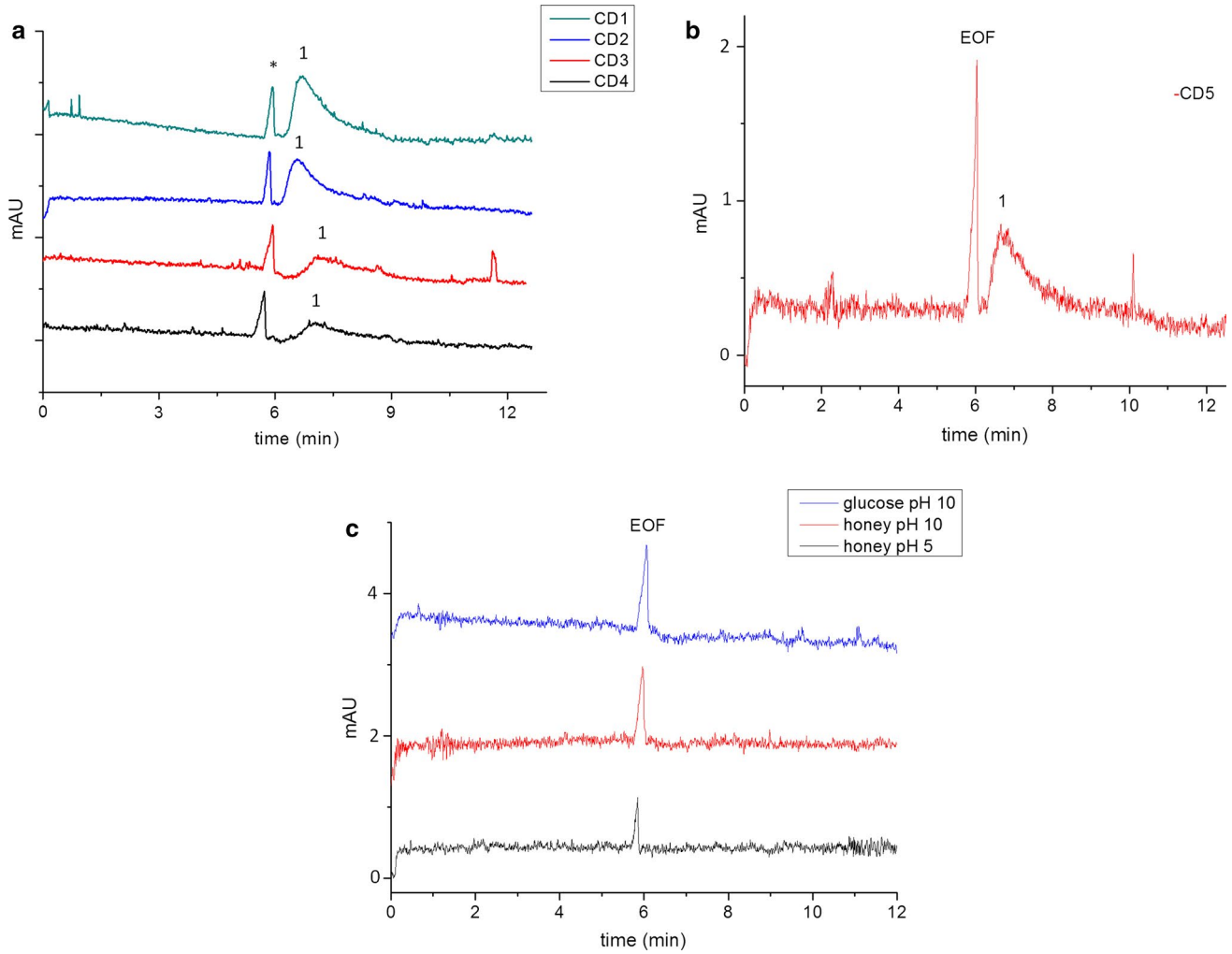

Fig. 2 Electropherograms of AgNPs obtained under optimized CE conditions. **a** AgNPs synthesized using honey as a reducing agent. **b** AgNPs synthesized using glucose as a reducing agent. **c** Blank samples obtained with both reducing agents. *Asterisk* Electroosmotic flow (EOF). Peak (1) corresponds to the main distribution of AgNPs. BGE: 20 mM sodium borate—20 mM SDS, pH 8.5; separation voltage: 20 kV; injection: 10 s (55 mbar)

function to estimate the electrophoretic mobility that has no restrictions concerning the applicable κr range (Eq. 2):

$$\mu = \frac{2}{3}\frac{\varepsilon_r \varepsilon_0 \zeta}{\eta}\left[f_1(\kappa r) - \left(\frac{ze\zeta}{kT}\right)^2 \left\{f_3(\kappa r) + \frac{(m_+ + m_-)}{2} f_4(\kappa r)\right\}\right], \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, z is the charge number of the electrolyte ions, and m are the ionic drag coefficients. The functions f_i are widely extended in the aforementioned work [33]. Thus, Eq. 2 was applied to estimate the zeta potential values from electrophoretic mobility of synthesized AgNPs (additional details in Supporting Material).

Table 1 shows the electrophoretic mobility (μ_{ep}) and zeta potential (ζ) for selected AgNP dispersions (CD1, CD2, and CD5) analyzed by the proposed CE method and compared to those results obtained from DLS analysis. As mentioned before, CD1, CD2, and CD5 were synthesized under the same Ag+/reducing agent ratio thus obtaining nanoparticles with comparable size and shape (Fig. 1), which resulted convenient for this analysis. As can be seen, electrophoretic mobility values obtained by CE are correlated with the DLS analysis for the three analyzed samples ($t_{cal} = 1.60 < t_{tab} = 4.30$, 95% confidence level) [34]. On the other hand, the Ohshima's equation provides a good approximation of ζ values for these samples.

Table 1 Calculated zeta potential and measured electrophoretic mobility values obtained by the proposed CE method (mean value) and the comparison to DLS analysis

AgNP dispersion	CE			DLS
	Zeta potential (mV)		Electrophoretic mobility ($\times 10^{-4}$ cm^2 V^{-1} s^{-1})	Electrophoretic mobility ($\times 10^{-4}$ cm^2 V^{-1} s^{-1})
	(1)	(2)		
CD1	−48	−61	3.85 ± 0.02	3.82 ± 0.10
CD2	−48	−60	3.81 ± 0.02	4.24 ± 0.04
CD5	−48	−59	3.80 ± 0.03	4.04 ± 0.13

(1) Smoluchowski's equation

(2) Ohshima's equation

AgNPs Size

It is well known that the apparent mobility (μ_{app}) can be defined by the general expression:

$$\mu_{app} = \mu_{eo} + \mu_{ep}, \quad (3)$$

where μ_{eo} is the electroosmotic mobility and μ_{ep} is the electrophoretic mobility of AgNPs [13]. It has to be noted that in this work, AgNPs are negatively charged and migrate counter the EOF direction ($-\mu_{ep}$).

In a principle, the size distribution of unknown AgNPs could be analyzed due to the relationship between electrophoretic mobility and particle size. To this purpose, AgNP dispersions synthesized at pH 5.0 and 10.0, and previously characterized by TEM were analyzed by the proposed CE method. Experimentally, good correlation was obtained between μ_{app} (or observed mobility) and particle size in the studied size range (Fig. S3). Because a linear correlation exists ($R^2 > 0.90$), electrophoretic mobility (μ_{ep}) of AgNPs can be considered proportional to the nanoparticles size, as represented in Eq. 4:

$$\mu_{ep} = Kr + C, \quad (4)$$

where K is the slope and C is the intercept of the linear regression ($y = 4.00 \times 10^{-6}x + 1.00 \times 10^{-5}$, $R^2 = 0.942$). The satisfactory relationship between the electrophoretic mobility and the size of these negatively charged nanoparticles is in agreement with the literature [13, 35]. Since these kinds of AgNPs are not commercially available, the obtained sizes for all analyzed samples were only compared to data collected by TEM and DLS analysis (intensity-based distribution data). As can be seen in Table 2, good agreement between values obtained by CE and those from TEM and DLS is obtained for CD1, CD2, and CD5. In the case of CD3 and CD4, more accurate approximation of AgNP size distribution is obtained by CE data and TEM regarding DLS. The hydrodynamic diameters obtained from DLS are biased from the other values which can be associated with possible aggregation of nanoparticles in the solution leading to an overestimation of the mean values. Taking this into account, a paired t test was applied to compare the results obtained from CE and TEM for samples CD1 to CD5. The t_{cal} value (2.24) resulted lower than the t_{tab} value (2.57) at 95% of confidence level, showing no evidence of statistically significant differences between CE and TEM for the analysis of these AgNPs. In addition, it is clearly observed that CE allows identifying possible aggregation of AgNPs and estimates size distribution of each subpopulation for CD3 if compared to TEM and DLS.

Table 2 AgNP size distribution obtained using DLS, TEM and CE

AgNPs	Particle size (nm)		
	CE[a]	TEM[b]	DLS[a]
CD1	16.8 ± 0.6	18.4	9.1 ± 2.2
CD2	15.6 ± 0.4	12.3	10.5 ± 4.2
CD3	27.9 ± 3.3 47.2 ± 2.5	36.8	82 ± 0.7
CD4	15.4 ± 1.5	11.3	98.5 ± 2.9
CD5	16.0 ± 0.5	23.2	11.2 ± 1.2
	–	52.6	58.2 ± 6.2

[a] Mean of three measurements ($n = 3$) ± standard deviation

[b] Mean size reported with a 7% of error

Evaluating the Stability of AgNP Suspensions

To evaluate the capability of the proposed CE method to monitor the colloidal stability of AgNP dispersions and follow possible particles aggregation, CD2 and CD4 samples were chosen and subjected to analysis after time storage (20 days) and sonication process. These samples were selected considering the experimental conditions for their synthesis and the differences initially observed in the SPR bands. In the first case, CD2 was injected in the CE system before and after sonication for 40 min. As can be seen in Fig. 3, an enhancement of the intensity of electrophoretic peak (t = 9.5 min) is observed after sonication, while no extra peaks are found between 7 and 9 min if compared with the same sample before sonication process, which can be associated with the aggregation of AgNPs during sonication process (Fig. S4). Moreover, CD4 was subjected to the same treatment aiming to follow the changes on peak areas and size distribution by

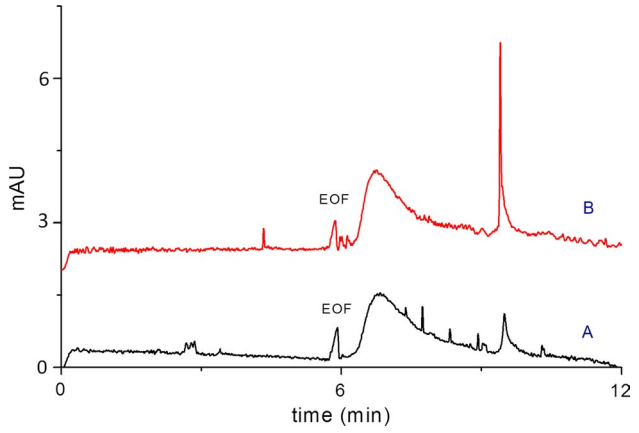

Fig. 3 Study of AgNP stability in CD2 sample after 20 days. *a* Before sonication, *b* after sonication [see Supporting Material for additional details (Fig. S3)]. Separation conditions: BGE, 20 mM sodium borate—20 mM SDS, pH 8.5; separation voltage, 20 kV; injection, 10 s (55 mbar). Detection: 411 nm

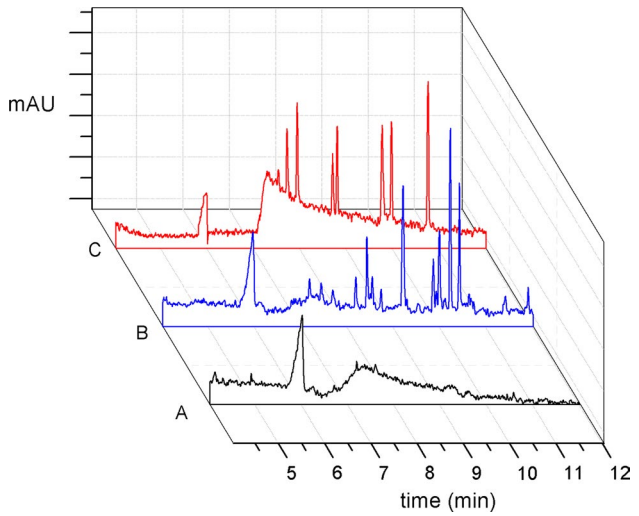

Fig. 4 Comparative electropherograms of sample CD4. *a* Freshly prepared, *b* before sonication, and *c* after sonication. CE conditions: BGE, 20 mM sodium borate—20 mM SDS, pH 8.5; separation voltage, 20 kV; injection, 10 s (55 mbar). Detection: 411 nm

CE. As can be observed from Fig. 4, CD4 tends to aggregate after storage for 20 days, evidenced by the electrophoretic peaks in the electropherogram between 7.5 and 11 min (trace B), which can be attributed to the honey/Ag^+ ratio in this sample if compared to CD2 sample. Size distribution is slightly affected during sonication process due to apparent debundling of aggregated AgNPs (Fig. 4, trace C).

These findings demonstrate the satisfactory performance of the proposed CE method to evaluate the colloidal stability and size distribution of AgNPs even when aggregates of nanoparticles are observed.

Conclusion

In this work, a straightforward CE method was proposed for the analysis of silver nanoparticles synthesized in a green way using honey or glucose as reducing agents. Under optimized CE conditions, it was possible the analysis of silver nano-sized particles within a short analysis time (<12 min) and without any purification process involved. In addition, minimal volumes of AgNPs dispersion and reagents were required which involves low costs and reduced amounts of residues generated per analysis. By applying the proposed CE method, valuable information about size, zeta potential, and colloidal stability of silver nanoparticles was obtained from a single CE run. Hence, the collected data were successfully compared with the traditional characterization techniques, such as TEM and DLS. From the obtained results, it can be concluded that the proposed CE method represents a useful tool for the screening and characterization of silver nanoparticles dispersions, also giving multi-purpose information if compared with the existing characterization methods.

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Compliance with Ethical Standards

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Conflict of interest AGonzález Fá declares that he has no conflict of interest. I. Cerutti declares that she has no conflict of interest. V. Springer declares that she has no conflict of interest. S. Girotti declares that he has no conflict of interest. M. E. Centurión declares that she has no conflict of interest. M. S. Di Nezio declares that she has no conflict of interest. M. F. Pistonesi declares that he has no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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