



Derivatized silver nanoparticles as sensor for ultra-trace nitrate determination based on light scattering phenomenon

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ABSTRACT

New silver nanoparticles coated with EDTA (EDTA-AgNPs) have been synthesized by citrate reduction method and characterized by UV–vis spectroscopy, molecular fluorescence and scanning electron microscopy (SEM). The derivatized nanoparticles show fluorescent emission and second order scattering (SOS) signals which in presence of nitrate are both attenuated. The SOS decreasing is greater than its fluorescent quenching; considering this fact, a new ultra sensitive methodology using the derivatized silver nanoparticles as sensor for nitrate determination has been developed. Under optimal established conditions, a linear response has been obtained within the range of 6.4×10^{-4} to $3.0 \mu\text{g mL}^{-1}$ nitrate concentrations, with a detection limit of $1.8 \times 10^{-4} \mu\text{g mL}^{-1}$. This novel technique provides a sensitive and selective methodology for nitrate determination and has been satisfactorily applied to its quantification in parenteral solutions.

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1. Introduction

Nitrate is an important anion in environmental and biological analysis [1]. Because it has direct impact on health after chemical transformations, excessive amount of the nitrate anion in water supplies typically indicates pollution from sewage on agricultural effluents. The over exposure of infants to nitrates can lead to methemoglobinemia, commonly known as blue baby syndrome [2].

Nitrate analysis is commonly based on indirect determination after reduction from nitrate to nitrite, either by reducing metals such as zinc [3] or by enzymatic reaction of nitrate reductase [4,5]. Several instrumental techniques for its determination include chromatography [6,7], potentiometry [8], polarography [9], Raman spectroscopy [10], spectrophotometry [11], chemiluminescence [12,13] and spectrofluorimetry [14,15]. From these previously mentioned methods, spectrofluorimetry is the most sensitive for trace analysis, which is based on the diazotation reactions of nitrite with different reagents [16–19]. However, it has disadvantages such as the toxicity of used reagents, time-consuming extraction processes and the presence of serious interferences [20].

Since in parenteral solutions the bioavailability of pharmaceuticals is greatest, their contents have rapid and direct influence on health. The development of sensitive methods for nitrate determination in liquid pharmaceutical formulations acquires main importance and constitutes a challenge for actual researcher.

Nanoparticles in liquid phase have long fascinated scientists because of their novel chemical and physical properties [21–26]. Particularly, silver nanoparticles have attracted the attention for their unique optical properties; particles size may influence all physical properties of such nanoparticles. One of the simplest syntheses consists is the chemical hot reduction of silver salt by the action of sodium citrate. Experimental conditions as reagent concentrations, time and temperature of heating, cleanliness of glassware must be carefully controlled to achieve stable and reproducible colloids. The obtained products tend to form agglomerates and/or change the size or shape during the storage. As silver nanoparticles are fairly unstable in solution [27], the derivatization step is necessary to obtain monodispersed nanoparticles.

For analytical chemistry, any signal, if its intensities have simple functional relationship with analyte concentration, can be applied with analytical purposes. The light scattering signals and fluorescence signals are twins in fluorospectroscopy and the light scattering signals are frequently sources of interferences in spectrofluorimetry [28]. In recent years, the light scattering technique has been increasingly applied to analytical chemistry; the most

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common method used is resonance light scattering. The strong scattering of light at double incident wavelength ($\lambda_{em} = 2\lambda_{ex}$) is named as second order scattering (SOS) [29]. In fluorimetric analytical methodology, scattering signals can appear as potential spectral interference and the instrumental conditions are selected to minimize this harmful phenomenon [30].

Since Liu et al. first studied SOS as an analytical technique and applied in the determination of metal ions in 1995 [31,32], it has been used as a new analytical technique with application prospects to ultra-trace determinations [33–36].

Till date no research has been reported on the quenching effect of nitrate on fluorescence signal of silver nanoparticles or SOS decrease phenomenon. Based on this approach, a novel methodology for nitrate ultra-traces determination employing Ag-EDTA NPs as luminescent sensor is presented. The novel nanomaterial has been characterized by UV-vis spectroscopy, molecular fluorescence and SEM images.

2. Experimental

2.1. Apparatus

The SOS spectra and fluorescent intensities were measured on a RF-5301PC spectrofluorimeter (Shimadzu Corporation, Analytical Instrument Division, Kyoto Japan) equipped with a Xenon discharge lamp and 1 cm × 1 cm quartz cell.

A pHmeter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 with combined glass electrode was used for monitoring pH adjustment.

A Hewlett-Packard spectrophotometer with 10 mm optical path cells was used to record UV-vis absorption spectra.

The microphotographies were taken from a screening electron microscopy model LEO 450 VP (Carl Zeiss).

2.2. Reagents

All reagents and solvents were of analytical grade (Each origin is specified in the text); ultra-pure water was provided from MiliQ system.

2.3. Synthesis and derivatization of silver nanoparticles

Silver nanoparticles were prepared by citrate reduction of silver nitrate as described in literature [37]. 17.0 mg of AgNO₃ (Sigma-Aldrich) was dissolved in 100 mL ultra pure water in a 250 mL tri-neck flask. The solution was heated to boiling with a hemisphere heating mantle under vigorous magnetic stirring. After boiling for 2 min, a 10 mL aqueous solution of sodium citrate (3×10^{-3} mol L⁻¹, Sigma-Aldrich) was rapidly added to the flask. The solution gradually turned yellow within a few minutes, indicating the formation of Ag nanoparticles. The solution was kept boiling for an additional 6 min. After cooled, the solution containing the silver nanoparticles was transferred to a 250 mL flask. 1.0 mL of EDTA (0.10 mol L⁻¹, Merck) and 0.5 mL of NaOH (3.0 mol L⁻¹) were added and the vigorous magnetic stirring was maintained for 30 min till complete reaction.

Immediately after adding the derivatizing reagent, the color of reaction system turned to violet and after few minutes the homogeneous colloidal solution suffered a flocculation process forming flaks which were separated from the aqueous medium by centrifugation to remove the excess of reagents. The derivatized nanoparticles deposited on the bottom of centrifugal tube were removed with chloroform and collected in flask crystallizers. 100 mL of ultra pure water were added to each system. The

magnetic stirring at 333 K was applied to contribute with the complete removal of chloroform, obtaining a transparent solution of derivatized nanoparticles.

2.4. General procedure

0.50 mL Ag-EDTA NPs, 1.0 mL buffer Tris (0.10 mol L⁻¹) and nitrate standard solution or 1.0 mL of sample solution were added to graduated volumetric flasks and then diluted to 10 mL with ultra pure water.

The synthesized Ag-EDTA NPs presented an excitation and emission maximum at 225 and 295 nm, respectively.

In order to choose the optimal SOS peak, different exciting wavelengths, from 220 to 350 nm, were used; the SOS signals were recorded from 440 to 700 nm ($\lambda_{SOS} = 2\lambda_{ex}$). 225 nm was chosen as excitation wavelength and 450 nm as measurement wavelength, both with slit width of 5 nm. All SOS intensities were measured against the blank which was prepared in the same way.

2.5. Pharmaceutical samples

The samples A and B were NaCl physiological solution (NaCl 0.90 mol L⁻¹) and dextrose isotonic solution (glucose 5%) respectively for intravenous use, both purchased from Lab. Roux-Ocefa (Buenos Aires, Argentina).

3. Results and discussion

3.1. Formation of nanosized Ag particles

The use of EDTA allowed the stability of these nanoparticles to be monodispersed in aqueous medium.

During the silver nanoparticles synthesis by conventional heating it was observed that after citrate was added, the color of reaction solution changed from colorless to yellow, making evident the formation of colloidal silver. SEM images (Fig. 1A) show that in this instance the particles which were nearly spherical were not well separated and stuck together to form many small groups. This typical behavior has been reported by other researchers [38,39]. The introduction of derivatization step resulted necessary to stabilize the silver nanoparticles as monodispersed material in aqueous medium.

The chelating reagent EDTA has been used as derivatizing agent for obtaining stable nanoparticles [40]. This coater suffers a chemisorption process onto the surface of AgNP through carboxylate groups. The two oxygen atoms of the carboxylate groups are coordinated symmetrically to the Ag atoms. The surface of AgNP remains negatively charged and, in presence of counter ions, acquires an electrostatic double layer. This double layer provides a repulsive force enabling to silver colloid to be stable in aqueous solution [41–43].

Attending that the possibility of using EDTA-AgNPs with analytical purposes depends on obtaining nanomaterial of high pure grade, it was necessary to add a purification step to eliminate all excess of reactant. With this aim, concentrated NaOH aqueous solution was added to EDTA-AgNPs solution and, after 15 min of reacting time, the flocculation process took place [38]. It was observed that the solution color changed immediately from yellow to violet. The dramatical diminution of their Z potential led to form the big flaks of nanoparticles, which facilitated the phases separation by flocculation. This phenomenon was reversible once removing the hydroxide by subsequently washing steps, obtaining a transparent solution of monodispersed nanoparticles with average size of 40 nm (Fig. 1B).

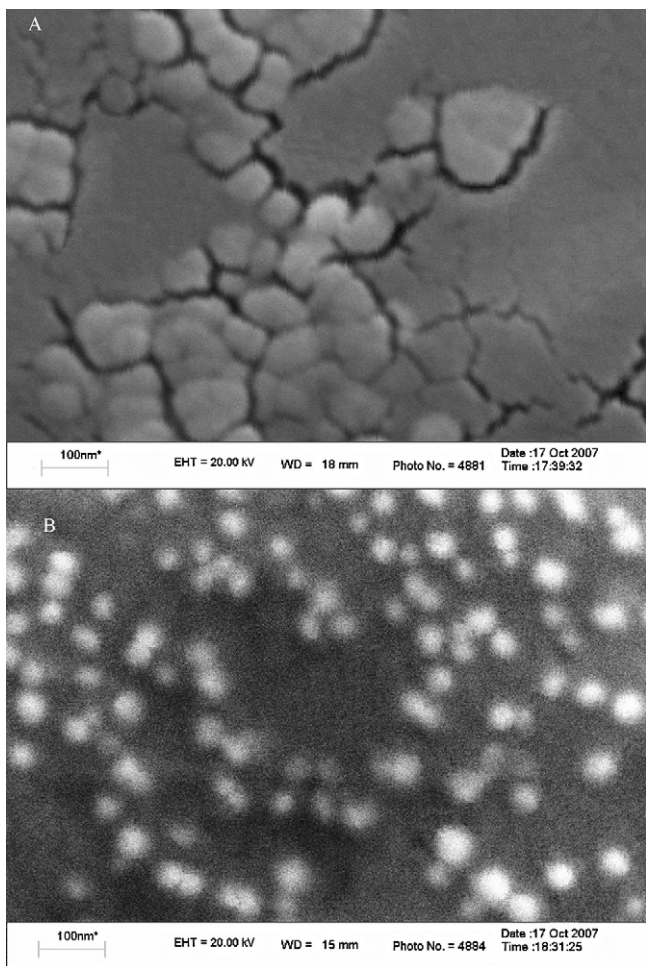


Fig. 1. SEM micrographics of synthesized AgNPs before and after of EDTA derivatization. (A) AgNPs and (B) AgNPs-EDTA.

3.2. Spectral characteristics of EDTA-AgNPs

UV–vis absorption spectra have proved to be quite sensitive to the presence of silver colloids because these nanoparticles exhibit an intense absorption peak due to the surface plasmon excitation [44]. The absorption band in visible light region (350–550 nm) is

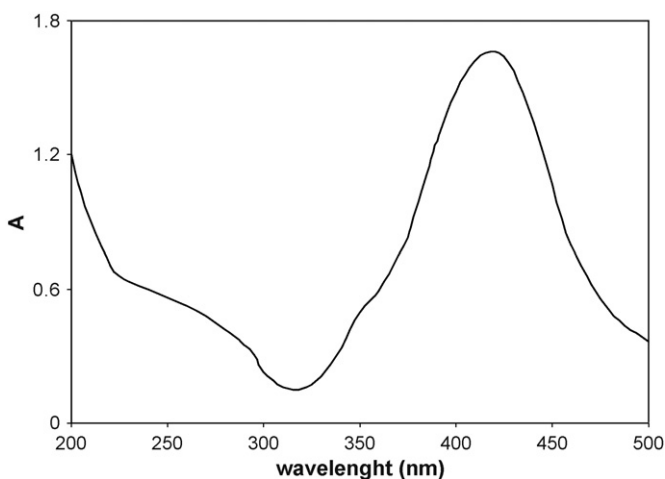


Fig. 2. Absorption spectrum of synthesized AgNPs-EDTA ($\lambda_{\max} = 415$ nm).

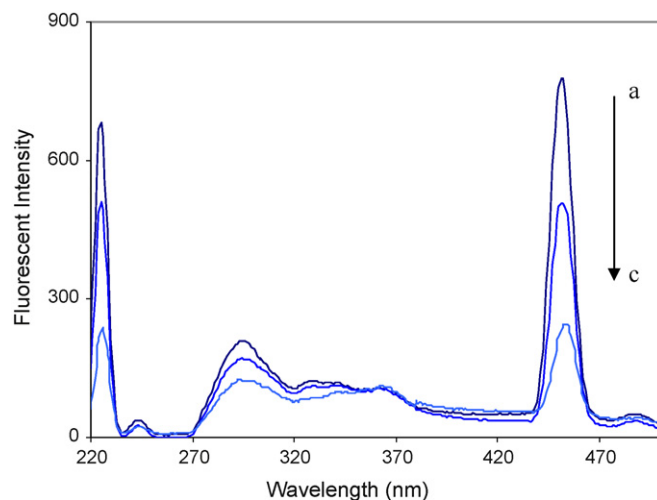


Fig. 3. Fluorescence spectra and SOS spectra of AgNPs-EDTA in absence and presence of NO_3^- . (a) Blank of the AgNPs-EDTA system (prepared as described in general procedure); (b) $1.25 \mu\text{g mL}^{-1}$ of NO_3^- ; (c) $2.5 \mu\text{g mL}^{-1}$ of NO_3^- . Instrumental conditions: $\lambda_{\text{ex}} = 225$ nm; slits of excitation and emission, both 5 nm.

typical for silver nanoparticles. With increasing particles size, the plasmon absorption shifts toward red.

The EDTA-AgNPs obtained showed an UV–vis absorption spectrum with a maximum at 415 nm [27,35,45] (Fig. 2). Proceeding with the spectral studies the synthesized nanomaterial was explored by fluorescent spectroscopy. These nanosized colloids presented an excitation and emission maximum at 225 and 295 nm, respectively (Fig. 3).

In presence of nitrate, the fluorescent emission decreased significantly; simultaneously to the fluorescence quenching, the SOS peak also decreased but in a more pronounced way (see Section 4.3). This observation led to the development of an ultra sensitive methodology using the derivatized silver nanoparticles as luminescent sensor for nitrate determination. Fig. 4 shows the SOS spectra beginning at excitation wavelength of 220 nm in step of 5 nm, in presence and absence of nitrates; the maximum ΔI is located at 225/450 nm for $\lambda_{\text{ex}}/\lambda_{\text{em}}$, respectively.

3.3. Quenching proposed mechanism

There exist a wide variety of substances which act as quenchers of fluorescence as well as different types of quenching process. Nitrate is considered an electron scavenger. This kind of quencher probably involves donation of electrons from the surface of nanoparticles to the quencher, deactivating the excited state

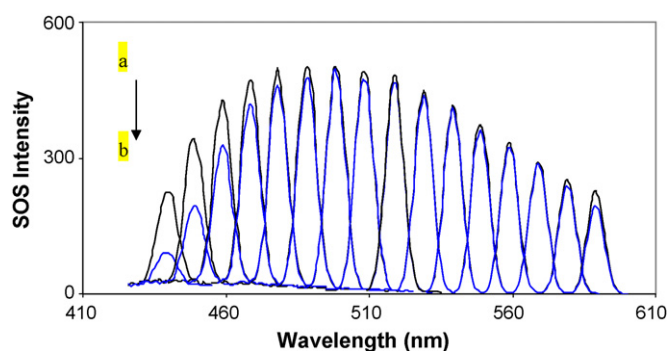


Fig. 4. SOS spectra of AgNPs-EDTA in presence and absence of NO_3^- . (a) AgNPs-EDTA system (prepared as described in general procedure); (b) system "a" with $[\text{NO}_3^-] = 1.75 \mu\text{g mL}^{-1}$. Instrumental condition: slit of excitation, 3 nm; slit of emission, 5 nm.

Table 1
 K_{SV} values^a for different experimental temperatures

Temperature (K)	K_{SV} value ($\mu\text{g mL}^{-1}$)
293	0.736
303	0.991
313	1.213
323	1.456

^a EDTA–AgNPs systems prepared and measured as described in general procedure; $[\text{NO}_3^-]$: 0.00, 0.30, 0.60, 0.90, 1.20 $\mu\text{g mL}^{-1}$.

responsible of fluorescence [46]. It is well known that fluorescent emission and SOS are associated phenomena; consequently the fluorescence quenching of EDTA–AgNPs by nitrates affects directly to its SOS signals.

In order to determine the quenching type, a study of the K_{SV} (Stern–Volmer constant) from the modified Stern–Volmer equation (Eqs. (1) and (2)) was carried out at different experimental temperature conditions submerging the systems in thermostatic bath.

$$\frac{F_0}{F} = 1 + K_{SV}C_q \quad (1)$$

Stern–Volmer equation for fluorescent quenching, where F_0 and F are fluorescent emissions of the fluorofore in absence and presence of the quencher respectively; K_{SV} is the Stern–Volmer constant; and C_q is the concentration of the quencher.

Replace the term F_0/F by I_0/I :

$$\frac{I_0}{I} = 1 + K_{SV}C_q \quad (2)$$

modified Stern–Volmer equation for SOS decrease; where I_0 and I are SOS intensities of EDTA–AgNPs in absence and presence of nitrates, respectively.

The obtained K_{SV} values for each studied temperature are listed in Table 1. The linearity of the Stern–Volmer plot, as the value of K_{SV} which enhanced with increasing temperature (Fig. 5), indicated that the quenching mechanism of Ag–EDTA NPs by presence of nitrate is a single dynamic quenching [46].

The experimental results of decreasing SOS signals by nitrates showed a good fit to Stern–Volmer plots, giving linear relationship with quencher concentration. Additionally, the SOS signals present better sensitivity than the fluorescent emission; thus, the SOS signals were chosen for nitrate determination.

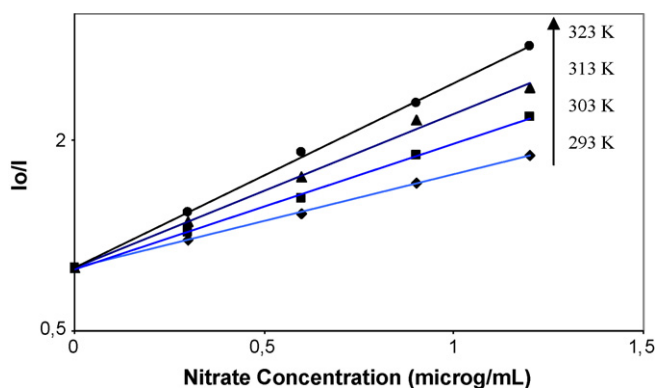


Fig. 5. Influence of temperature on AgNPs–EDTA SOS signals in presence of nitrate. $[\text{NO}_3^-]$: 0.00; 0.30; 0.60; 0.90; 1.20 $\mu\text{g mL}^{-1}$. Instrument conditions: $\lambda_{\text{ex}} = 225 \text{ nm}$; $\lambda_{\text{em}} = 450$.

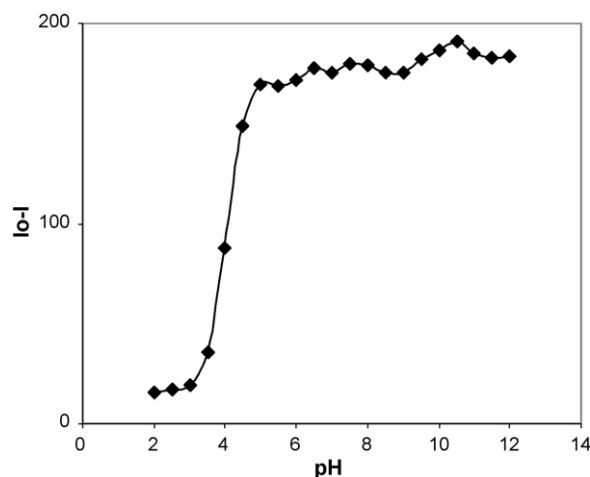


Fig. 6. Influence of pH on ΔI_{SOS} of AgNPs–EDTA in presence of 1.25 $\mu\text{g mL}^{-1}$ NO_3^- ; buffer: Tris ($1 \times 10^{-2} \text{ mol L}^{-1}$) adjusted with NaOH (d) or HCl (d).

4. Optimization of analytical parameters

4.1. Influence of pH

In order to study the influence of pH on the SOS signal, different buffers (TRIS, borax, phosphoric acid/phosphate, and acetic acid/acetate) were tested over pH range of 2.0–12.0 (Fig. 6). The SOS decrease value (ΔI_{SOS}) enhanced with increasing pH. At pH 10.5, ΔI_{SOS} reached a maximum value. Below pH 5.0, the ΔI_{SOS} decreased greatly and the EDTA–AgNPs solution color turn to red, regardless the assayed buffer nature. This change in color accompanied with bathochromic shift of plasmon absorbance, indicated the growth on the particles size [47]. The results showed that TRIS buffer provokes the most intensive luminescence and consequently, the best ΔI_{SOS} . Additionally, in this experimental condition, the stability of the system was optimal. Thus, 0.10 mol L^{-1} TRIS buffer was used for further experiments.

4.2. Effects of size and concentration of EDTA–AgNPs

When the time of AgNPs synthesis process is extended, a larger size of nanoparticles is obtained and in the fluorescence spectrum, the huge dispersion of the light produces an increase of the noise. After derivatization, the noise of fluorescent spectrum was

Table 2
 Tolerance of potentially interfering substances^a

Foreign substance	Tolerance ($\mu\text{g/mL}$)	Relative error (%)
Na^+	4600	–1.5
K^+	310	–2.2
Ca^{2+}	100	+2.1
Cu^{2+}	3.10	–3.7
Cd^{2+}	5.60	+2.3
Mg^{2+}	30	+1.2
Zn^{2+}	0.91	+4.5
Al^{3+}	16	+1.5
Fe^{3+}	6.70	–1.2
Pb^{2+}	0.20	+3.6
CH_3COO^-	630	–2.3
SO_4^{2-}	1900	+1.6
ClO_4^-	1000	–2.6
PO_4^{3-}	550	+3.1
Br^-	650	–4.5
Glucose	9000	+3.6

^a Conditions: EDTA–AgNPs systems prepared and measured as described in general procedure, with coexisting concentration of NO_3^- of 0.1 $\mu\text{g mL}^{-1}$.

Table 3
Nitrate determination in parenteral solutions (recovery of the method^a)

Samples	Base value	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	Recovery ^b \pm R.S.D. ^c (%)
A	–	0.000	0.006	–
	0.006	0.250	0.252	98.43 \pm 1.89
	0.006	0.500	0.503	99.40 \pm 1.77
	0.006	0.750	0.768	101.50 \pm 2.21
B	–	0.000	0.009	–
	0.009	0.250	0.263	101.54 \pm 1.45
	0.009	0.500	0.507	99.60 \pm 2.10
	0.009	0.750	0.749	98.68 \pm 1.87

^a AgNPs-EDTA systems prepared and measured as described in general procedure.

^b Recovery = $100 \times [(found - base)/added]$.

^c $n = 6$.

minimized; nevertheless, the decreasing of SOS and fluorescence quenching for these nanoparticles in presence of nitrate was not efficient. This phenomenon maybe due to the superficial activities diminution produced by the increase of the particles size and simultaneously, the reduced capability of nitrate to produce the deactivation process of the excited state.

The effect of EDTA-AgNPs concentration was studied for $1.25 \mu\text{g mL}^{-1}$ of nitrate varying the volume of EDTA-AgNPs within the range of 0.25–3.0 mL. The SOS signals in absence and presence of nitrates (I_0 and I) were both enhanced with the increase of EDTA-AgNPs concentration, remaining ΔI practically constant. Therefore, the concentration of EDTA-AgNPs chosen is given by the maximal intrinsic intensity obtained (blank signal) with constant excitation and emission slit widths. A volume of 1 mL EDTA-AgNPs was chosen as optimal.

4.3. Interference of foreign ions

The effects of the coexisting ions were tested according to the standard procedure and the results are listed in Table 2. The ions were considered no interference if the variation of the intensity was $\leq \pm 5\%$. The results indicated that the most of assayed ions could coexist at high concentration with nitrite, and for substances present in tested real samples like NaCl and glucose, the developed methodology could tolerate higher level of concentration than labeled values.

4.4. Analytical performance

Under the optimal experimental conditions, calibration curves for the determination of nitrate by SOS and fluorescence were obtained. By SOS decrease, the results showed a good linear relationship over the range 6.4×10^{-4} to $3.0 \mu\text{g mL}^{-1}$. The linear regression equation was $\Delta I_{\text{SOS}} = 228.50 C (\mu\text{g mL}^{-1}) + 0.84$ with regression coefficient $r = 0.997$. The limit of detection (LOD) and quantification (LOQ) were calculated in accordance to the official compendia methods by $k(S_b)/m$, where $k = 3$ for LOD and $k = 10$ for LOQ, S_b is the standard deviation from 10 replicate blank measurements ($S_b = 0.0146$) and m is the slope of the calibration curve. The LOD estimated was $1.8 \times 10^{-4} \mu\text{g mL}^{-1}$; while for quenching of fluorescence emission the equation of calibration curve was $\Delta F = 34.40 C (\mu\text{g mL}^{-1}) + 1$, value means lost of sensitivity compared with SOS technique.

4.5. Nitrate determination in parenteral solutions

The proposed method was applied to nitrate present in 1.0 mL commercial parenteral samples solutions giving values of 6 ppb of nitrate in sample A and 9 ppb in sample B. In order to validate the developed methodology, a recovery test was carried out

giving satisfactory results and presented in Table 3. Compared to other methodologies for nitrate determination [8,48,49] the present work has lower detection limit with the additional advantage of direct analysis of sample without pretreatment.

5. Conclusions

In this paper, a new modified silver nanoparticles (EDTA-AgNPs) have been synthesized and characterized (SEM, UV-vis and fluorescence spectroscopy). Through SEM images we could confirm that these EDTA-AgNPs were monodispersed in aqueous medium in contrast to before be derivatized. The fluorescent quenching and SOS decrease of these nanoparticles by presence of nitrate was studied. Quenching mechanism was proposed for SOS phenomenon. An innovative methodology was developed for ultra-trace nitrates quantification and successfully applied for its determination in commercial parenteral solutions. The main advantage of the proposed method is the possibility of direct nitrates determination with very good accuracy, sensitivity and tolerance, without the need of previous reduction to nitrite, neither any previous treatment for samples used. The obtained results showed that the EDTA-AgNPs can be applied as sensor for nitrate determination in real pharmaceutical samples.

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