New Silver Nanosensor for Nickel Traces: Synthesis, Characterization and Analytical Parameters

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"In memoriam" of Dr. Adriana Masi, prominent researcher, dear colleague and friend, who passed away prematurely, as a consequence of public insecurity, killed by a shot in the head at the door of her house.

Abstract: A new fluorescence silver nanosensor assisted by surfactant has been synthesized and applied to ultra trace nickel determination. Operational variables which influence nanomaterial synthesis have been studied and optimized. Synthesis was very fast and simple using non polluting solvents; silver chemical reduction was carried out at room temperature. Spectroscopic studies were carried out in order to assure the uniformed of nanomaterial obtained. Fluorescent signal of silver nanoparticles resulted enhanced in presence of Ni(II). At optimal experimental conditions, a detection limit of 0.036 pg·L^{-1} and quantification limit 0.12 pg·L^{-1} were obtained. The calibration sensitivity was 2×10^{14} L·pg^{-1}·cm^{-1} for the new methodology, with a range of linearity of six orders of magnitude between 0.12 and 2.93×10^5 pg·L^{-1}. The tolerance levels for potential interferent ions were studied with good results. The proposed methodology represents a promising approach for Ni(II) traces quantification due to its low operation cost, simplicity of instrumentation, high sampling speed and non-polluting solvents.

Key words: Fluorescence nanosensor, micellar silver nanoparticles, nickel traces.

1. Introduction

Silver nanoparticles (AgNPs) have acquired importance due to their unusual optical, electronic and chemical properties [1-3]. The spectral characteristics of silver nanoparticles are strongly dependent on their size, shape, interparticle spacing and environment [4]; therefore, the geometry of noble metal nanoparticles may provide important control on optical properties [5-7]. The characteristics of nanomaterials depend on the method employed in the synthesis [8-10]. A common difficulty of nanomaterials is related to the aggregation of colloids, which causes modifications in their optical properties [11]. Many efforts have been done to stabilize nanoparticles in solution and improve the reproducibility and performance of the synthesis step. The most common strategy for the formation of stable nanoparticles is the use of a protective agent, which prevents their aggregation through functionalization reactions [12]. In this respect, surfactants have been used with success [13-16].

It has been observed that the size distribution and stability of nanoparticles depend critically on the properties of the surfactant employed [17]. Sodium dodecyl sulphate (SDS), an anionic surfactant, has been shown to be a very appropriate capping agent [18].

In this work, a fluorescence sensitive nanosensor is presented as an advantageous alternative to traditional instrumental methods. AgNPs are synthezised in SDS medium (SDS-AgNPs) and the obtained nanomaterials are applied to trace nickel quantification.

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2. Experimental

2.1 Reagents

Ni(II) stock solutions 1×10^{-9} mol·L^{-1} were prepared by dilution of 1,000 μg·mL^{-1} standard solution plasma-pure (Leeman Labs, Inc.). Tris (Mallinckrodt Chemical Works, NY, USA) solution 1×10^{-2} mol·L^{-1} was prepared by weighting and subsequent dilution with ultrapure water and adjusted to the desired pH, with aqueous HClO$_4$ (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works, NY, USA). AgNO$_3$ (Sigma-Aldrich, St. Louis, USA) 1×10^{-3} mol·L^{-1} was prepared by dilution of 17 mg in 100 mL ultrapure water. Citric acid (Hopkin and Williams, England), hexadecyltrimethylammonium bromide (J.T. Baker, Mallinckrodt Baker, Inc., NJ, USA) and sodium dodecylsulfate (J.T. Baker, Mallinckrodt Baker, Inc., NJ, USA) were used without further purification. All used reagents were of analytical grade.

2.2 Apparatus

Fluorescence measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. A combined glass electrode and a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 were used for pH adjustments. A centrifuge was used in AgNPs purification. All used glass materials were previously washed with a 10% v/v HNO$_3$ water solution and then with ultrapure water.

2.3 Micellar AgNPs Synthesis and Purification

0.5 g SDS were dissolved in 4 mL AgNO$_3$ 1×10^{-3} mol·L^{-1}. Immediately, 0.5 g citric acid was added. The reacting mixture was vigorously stirred for 1 min at room temperature and then put into 15 mL centrifuge tube and centrifuged for 10 min at approximately 1,000 g. The rinsing step was repeated three times to remove excess of reagents. Sediments containing SDS-AgNPs were redissolved in 5 mL absolute ethanol.

2.4 Proposed Methodology

Appropriate aliquots of standard solution Ni(II) (1.2×10^{-4}-2.93×10^{2} ng·L^{-1}), 100 μL buffer Tris solution 1×10^{-2} mol·L^{-1} (pH = 6.3) and 500 μL of synthesized SDS-AgNPs, were placed in a 10 mL graduated centrifuge tube. The whole mixture was diluted to 3 mL with ultrapure water. Fluorescent emission was measured at $\lambda_{em} = 348$ nm using $\lambda_{exc} = 240$ nm.

2.5 Interferences Study

Different amounts of common ions were added to the test solution containing 5.81 ng·L^{-1} of Ni(II) and the proposed methodology was applied.

3. Results and Discussion

3.1 Spectral Study of Synthesized Micellar Ni(II) Nanosensor

Optical absorption spectrum of silver nanoparticles is a good indicator of their size and shape. The plasmon absorption of synthesized nanoparticles in the visible region presented an absorption maximum in the 440 nm region (Fig. 1), in agreement with other studies [19-21]. Spectral studies of the synthesized nanomaterial were performed by fluorescent spectroscopy. The nanosized colloids presented an excitation and emission maximum at 240 and 348 nm, respectively (Figs. 2a and 2b). In presence of nickel traces, the AgNPs fluorescent signal showed a notable increase (Figs. 2c-2e), which was validated scanning blank solutions (SDS solution; citric acid solution; Ni(II) + SDS solution; Ni(II) + citric acid solution). For consigned systems, there were no fluorescent signals.

This spectral behavior could be justified by the postulation of an association between the SDS-AgNPs (negatively charged) and nickel ions by electrostatic interaction. The association thus formed presents a more rigid configuration, minimizing the nonradiative deactivation phenomena and promoting the fluorescent emission.
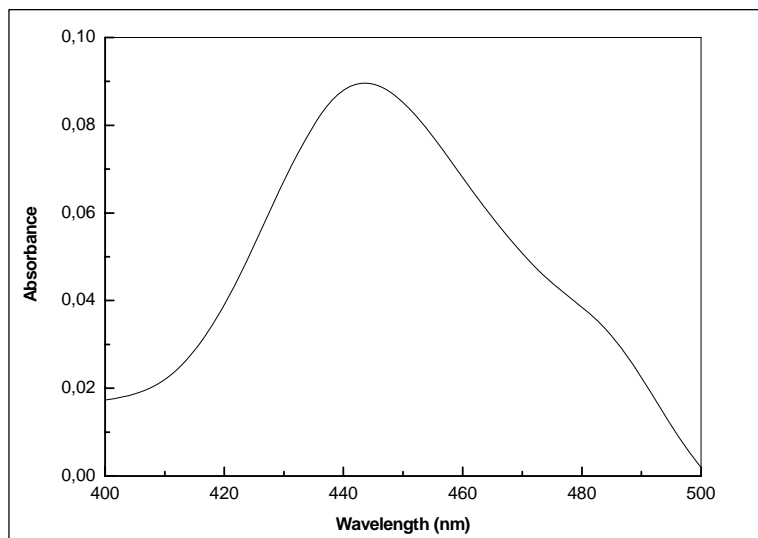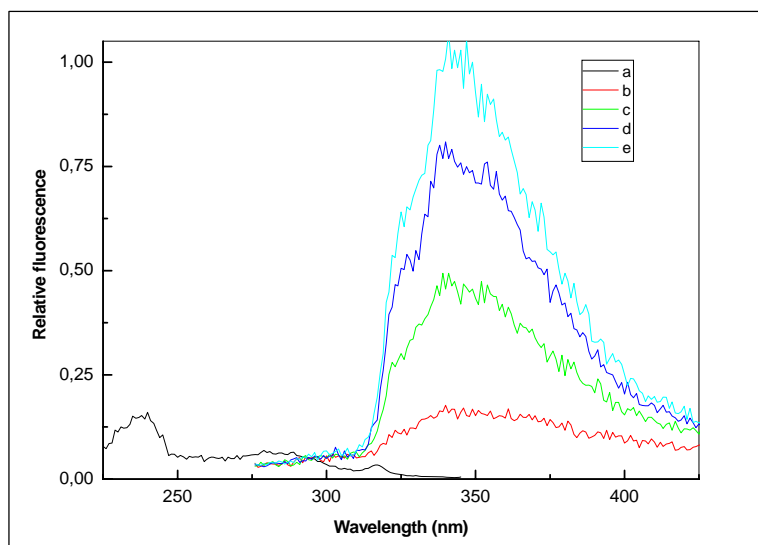
Fig. 1   Absorption spectrum of synthesized SDS-AgNPs.

Fig. 2   Excitation and fluorescent emission spectra of SDS-AgNPs and Ni(II)-SDS-AgNPs systems.
a: Excitation spectrum of SDS-AgNPs (λ_{em} = 348 nm); b: Emission spectrum of SDS-AgNPs (λ_{exc} = 240 nm); c: Idem b with Ni(II) 2.60 ng·L^{-1} (λ_{exc} = 240 nm); d: Idem b with Ni(II) 4.73 ng·L^{-1} (λ_{exc} = 240 nm); e: Idem b with Ni(II) 5.81 ng·L^{-1} (λ_{exc} = 240 nm).

In order to find the optimum experimental conditions for trace nickel determination, parameters affecting the synthesis and association reaction between Ni(II) and AgNPs were investigated.

3.2 AgNPs Synthesis Optimization and Its Luminescent Response in Presence of Ni(II)

Table 1 shows fluorescent intensity of synthesized AgNPs in presence of SDS (anionic surfactant) and CTAB (cationic surfactant), at three different reaction times. The results indicated that the fluorescent characteristics of AgNPs were not influenced by this parameter. However, there were well marked differences between the fluorescence intensities of the AgNPs assisted by different surfactants, being the highest that obtained in presence of SDS.

In order to optimize the fluorescent signal of obtained AgNPs, synthesis reactions were carried out

Table 1 Surfactant assisted AgNPs, time of reaction and fluorescent response without and with Ni(II).

Parameter	Fluorescence intensity	
	SDS	CTAB
Reaction time (min)		
1.0	47.21	22.01
2.5	47.52	20.10
5.0	48.01	21.80
Surfactant concentration		
250 CMC	20.74	12.77
500 CMC	47.65	18.55
1,000 CMC	18.85	11.68
With Ni(II)		
250 CMC + 77 ng·L^{-1}	20.56	13.21
250 CMC + 102 ng·L^{-1}	21.44	12.04
500 CMC + 77 ng·L^{-1}	190.33	15.44
500 CMC + 102 ng·L^{-1}	236.84	18.95
1,000 CMC + 77 ng·L^{-1}	20.9	12.03
1,000 CMC + 102 ng·L^{-1}	17.65	10.57

at different surfactant concentration levels. Best results were obtained when using 500 × critical micellar concentration (CMC) for surfactant SDS, in agreement with previous reports [18].

The AgNPs resulting from synthesis in the different surfactant media were explored in presence of increasing Ni(II) concentrations. Luminescent responses indicated that SDS-AgNPs are adequate for trace Ni(II) detection.

In order to establish the adequate SDS-AgNPs volume for Ni(II) determination, experiments were carried out keeping other variables constant. Results are shown in Fig. 3. A volume of SDS-AgNPs of 500 µL was chosen for the following assays.

3.3 Influence of pH on Ni(II) Nanosensor Fluorescent Response

Taking into account that pH plays a important role on the formation of metallic associations, the luminescent response of the Ni(II)-SDS-AgNPs system was evaluated at different pH values (Fig. 4). A plateau was obtained at pH between 6.0 and 7.0. Due to this behavior, pH 6.3 was selected as the working value for the following experiments.

In acidic medium, protons compete effectively with Ni(II) for bonding sites of SDS-AgNPs. On the other hand, in alkaline medium, the interaction between Ni(II) and SDS-AgNPs is hindered by the presence of hydroxile ions.

3.4 Order of Reagents Addition

The best order of reagent addition proved to be SDS-AgNPs, buffer Tris and Ni(II). The complex was stable for at least 12 h.

3.5 Influence of Nature and Concentration of Buffer

Effects of different buffers on the fluorescent Ni(II)-SDS-AgNPs system were tested. The most enhanced fluorescent emission was obtained for buffer Tris. The system was studied within a Tris concentration range from 5×10^{-3} to 4×10^{-2} mol·L^{-1}. Best stability and sensitivity were achieved for a Tris concentration of 1.1×10^{-2} mol·L^{-1}.

3.6 Interferences Study

The effect of foreign ions on Ni(II) determination was tested. An ion was considered as interferent when it caused a variation in the fluorescent signal of the analyte greater than ± 5%. At optimal conditions, Na^{+}, K^{+} can be present at 1,000:1 excess to Ni(II) without interfering; Fig. 5 and Table 2 show the obtained tolerance results for a group of regular ions. Considering these results, it can be concluded that the proposed methodology exhibits an adequate tolerance.

Table 2 Study of anions interferences.

Anion	Tolerated interferent/Ni(II) ratio	Fluorescent emission	% RE[a]
CO$_3$$^{2-}$	1,000/1	41.52	0.09
SO$_4$$^{2-}$	1,000/1	41.48	0.01
NO$_3$$^{-}$	1,000/1	42.21	1.76
CH3COO^{-}	1,000/1	41.35	0.30
Cl^{-}	1,000/1	42.03	1.33
Br^{-}	1,000/1	40.59	- 2.15
F^{-}	100/1	43.05	3.77

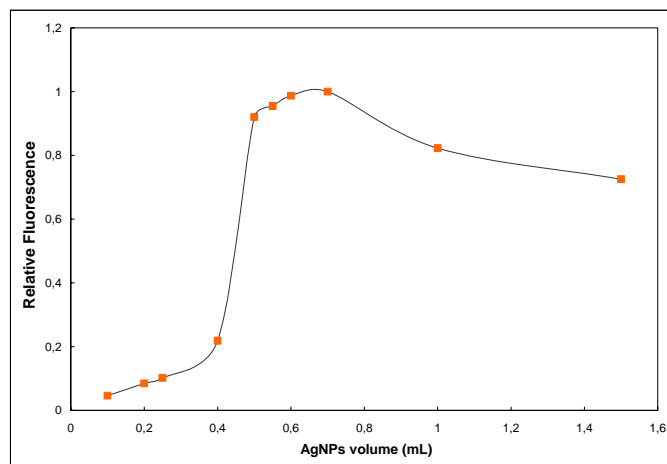[a]: 100 × relative error; Ni (II): 5.81 ng·L^{-1}; other experimental conditions are described in the manuscript.

Fig. 3   Optimization of volume of SDS-AgNPs.

Experimental conditions: Ni (II) 5.81 ng·L^{-1}; pH = 6.3 buffer Tris; λ_{em} = 348 nm and λ_{exc} = 240 nm.

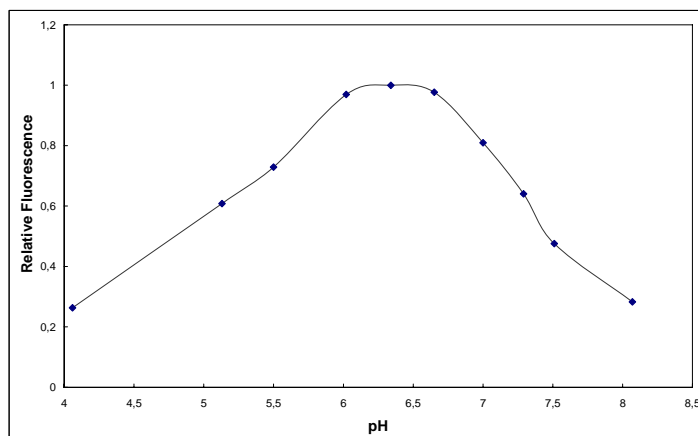**Fig. 4   Influence of pH on fluorescent emission of Ni(II)-SDS-AgNPs.**

Experimental conditions: Ni(II) 5.81 ng·L^{-1}; SDS-AgNPs volume 0.5 mL; λ_{em} = 348 nm and λ_{exc} = 240 nm.
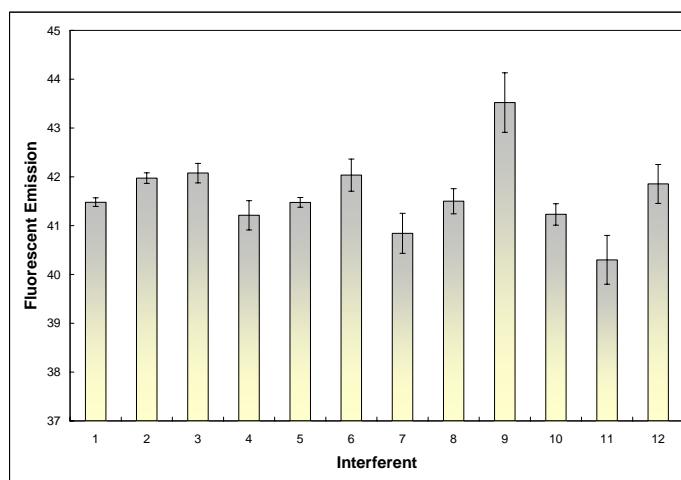

Fig. 5   Tolerances of cations in (interferent/Ni(II)) ratio for Ni(II)-SDS-AgNPs system, for each interferent, %SD has been included.

Fluorescence signal ± SD. 1: Ni(II) 5.81 ng·L^{-1}; 2: Ni(II) in presence of K(I); interferent/Ni(II) ratio 1,000/1; 3: Idem 2 for Na(I); 4: Ni(II) in presence of Cu(II); interferent/Ni(II) ratio 100/1; 5: Idem 4 for Pb(II); 6: Idem 4 for Zn(II); 7: Idem 4 for Mg(II); 8: Idem 4 for Mn(II); 9: Idem 4 for Co(II); 10: Idem 4 for Cd(II); 11: Idem 4 for Ca(II); 12: Idem 4 for Fe(III).

4. Conclusion

In the present work a surfactant assisted fluorescent nanosensor has been synthesized. The enhancement of AgNPs fluorescent signal in presence of Ni (II) has been proposed for ultra trace nickel quantification. The method showed good sensitivity and adequate tolerance to foreign constituents. The proposed methodology may constitute a promising approach in the area of metal monitoring with low operation costs, simplicity of instrumentation, high sampling speed and non-polluting solvents.

Acknowledgments

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