Silver Nanoparticles for a Colorimetric Determination of Putrescine and Cadaverine in Biological Samples

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A convenient and uncomplicated scheme has been projected for the quantitative determination of essential diamines putrescine (PUT) and cadaverine (CAD) via sodium dodecyl sulfate protected silver nanoparticles (SDS-AgNPs). This scheme is based on the chemical interaction of a SDS-AgNPs probe with PUT and CAD, leading to a color change from yellow to red or reddish brown. The interaction was investigated through different techniques such as using a UV-visible spectrophotometer, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), dynamic light scattering spectroscopy (DLS) and the zeta potential. Both amines possess a close resemblance in structure (except for the addition of one more methylene group in CAD), and no any distinguishable color change was noted. However, the maximum absorption band at 580 and 600 nm was demonstrated for PUT and CAD correspondingly. The methodical response was observed at absorption ratios of 580/410 and 600/410 nm, with the linear regression within 4 - 12 and 6 - 14 μg/mL for PUT and CAD. The detection limits calculated for both the diamines PUT and CAD were 0.333 and 1.638 μg/mL. The scheme was successfully applied for determinations in biological samples, including spiked blood plasma and urine. Putrescine exhibited % recovery within 95.717 - 105.200%, while cadaverine was within 95.940 - 105.109%, respectively. The scheme was reproducible and precise with inter-day RSD (n = 5) within 1.126, 0.018% and the intraday RSD (n = 5) was within 0.005, 0.002% for PUT and CAD, respectively.

Keywords Silver nanoparticle sensor, colorimetric determination, putrescine, cadaverine

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Introduction

Biogenic essential diamines putrescine and cadaverine are basically nitrogen-containing, straight-chain organic compounds, produced by plants, animals and microbes through the decarboxylation of amino acids.1,2 They are habitually found in foodstuff of different kinds, such as fresh meat and meat products, fish, fermented vegetables, dairy products and alcoholic beverages.3,4 Various cellular processes of growth and propagation are controlled by the biogenic aliphatic amines i.e. putrescine (PUT) cadaverine (CAD), spermidine (SPD) and spermine (SPN),5 play significant roles in physiological metabolism.6,7

Furthermore, an imperative role in food poisoning has been shown by aliphatic amines, such as putrescine and cadaverine, since they augment the toxicity of histamine.2,13 PUT and CAD occur in reactions with nitrite produce nitrosamines, a carcinogenic compound.13 In addition, elevated levels of biogenic amine designate a low quality of raw materials, contamination with microbes or inappropriate processing, and storage in the food industry.14 Therefore, the development of simple methods for their analysis is of great importance. Numerous methods have been proposed by the authors to combat with the detection of biogenic amines in different types of foodstuffs, under different optimized conditions, through sensitive and selective, but time consuming, sample pretreatments and complex instrumentation are required with a bulk amount of organic solvents.27

A colorimetric scheme is one of the simplest, emerging techniques when coupled with a UV-visible spectrophotometer, providing intuitive results that are both qualitative and quantitative.28,29 Moreover, colorimetric methods demonstrate excellent tolerance to environmental factors under optimized conditions and high selectivity. This has allowed the colorimetric method to distinguish several analytes due to easy sampling, facile efficiency and a visual sensing mechanism. The above-mentioned properties make the colorimetric methods suitably ideal for analysis to obtained abrupt results.30,31 For this reason, noble metal elements (Ag, Au), due to their unique physical and chemical properties have been employed as a colorimetric sensor for the determination of a vast number of entities, such as heavy metal ions as well as ecological and biochemical elements.32

Silver nanoparticles have gained much attraction relative to gold nanoparticles due to its higher extinction coefficient.33 Silver nanoparticles have inimitable physico-chemical properties, such as antimicrobial activity, chemical stability and excellent catalytic activity, and are also superior conductors of heat and electricity.34 AgNPs have thus been examined in a
number of different fields. Burdusel et al.35 overviewed biomedical applications of AgNPs. Porcaro et al.36 examined structural characterizations of AgNPs stabilized with charged thiols for antibacterial applications. Bordoloi et al.37 reviewed the preparation of AgNPs and AuNPs promoted by plants extracts. Carlini et al.38 compared AgNPs and AuNPs stabilized with negatively charged thiols. Proposito et al.39 reported bi-functionalized AgNPs as being a mercury(II) plasmonic sensor in water. Centeno et al.40 reported infra-red platicon sensors of (Ag and Au) nanoparticles. Chen et al.41 reported on the synthesis and characterization of antibacterial AgNPs encapsulated in cellulose film. Proposito et al.42 reviewed AgNPs as being colorimetric sensors for toxic elements as water pollutants. Firdous et al.43 used a paper-based colorimetric device for portable mercury ions sensing with AgNPs and smartphone.

The present scheme illustrates a rapid and uncomplicated colorimetric determination of aliphatic diamines putrescine (PUT) and cadaverine (CAD) via sodium dodecyl sulfate capped silver nanoparticles (SDS-AgNPs). This physical interaction was examined visibly by naked eye, and also on a spectrophotometer with a change in color from yellow to red. The realistic strength of the SDS-AgNPs sensor was verified by sensing PUT and CAD aliphatic diamines in biological samples (blood plasma and urine). The proposed scheme was rigorously scrutinized in terms of selectivity and reproducibility.

Experimental

Reagents and chemicals

Chemicals of analytical-grade reagents were used throughout the research, devoid of further purification. Double-distilled water was used for the preparation of solutions. The glasswares used during the experimental work were sanitized in nitric acid (HNO3) (0.1 N) (E. Merck, Germany), and then rinsed with double-distilled water and desiccated in a preheated oven (110°C). Sodium-tetrahydridoborate and magnesium carbonate were purchased from Fluka Switzerland; silver nitrate, sodium acetate, and sodium chloride from Scharlu, Spain; hydrochloric acid, sodium dodecyl sulfate, sodium bicarbonate, potassium chloride, ammonium chloride, ammonium acetate, l-tirosine, pyrrolol, gallic acid, l-cystein, valine, lucine, arginine, glutamine, guanidine, cadaverine and guanidine were obtained from Merck, Darmstadt, Germany. Besides, putrescine dihydrochloride was purchased from Aladdin China. To maintain sensor application under suitable pH values in the experimental work, buffers ranging from 1 - 10 were prepared.33

Apparatus

The entire ultraviolet-visible spectra of SDS-AgNPs samples were monitored by a 220 Hitachi double-beam spectrophotometer (Hitachi (Pvt) Ltd, Tokyo, Japan), over range of 700 – 400 nm using dual silica cuvettes having a path length of 1 cm. The FTIR spectra were recorded on a Nicolet Atavar 330 (Thermo Nicolet Corporation, USA) with an attenuated total-reflectance accessory (smart partner) within 4000 – 600 cm–1. The pH of the solutions was measured by an Orion 420 A pH meter (Orion Research Inc., Boston USA). The structural and morphological features (SEM and EDX) of the manufactured silver NPs accompanied aliphatic diamines were confirmed on a scanning electron microscope (JEOL, JSM-6490LV) at the center of Pure and Applied Geology, University of Sindh, Jamshoro. In addition, the zeta potential and dynamic light scattering (DLS) size distribution of the sensor in the interaction with PUT and CAD were determined using a Zetasizer Nano-ZS Malvern instrument Inc, London UK at the Department of Metallurgy and Materials Engineering, Mehran University of Engineering and Technology, Jamshoro.

Preparation of sodium dodecyl sulfate capsulated silver nanoparticles (SDS-AgNPs)

Silver nanoparticles encapsulated with sodium dodecyl sulfate were prepared by reported methods.31,32 In short, 50 mL (1 mM) of silver nitrate was decanted to a 50-mL mixture of sodium-tetrahydridoborate together with sodium dodecyl sulfate drop wisely. The process involved the chemical reduction of AgNO3 salt by NaBH4 in the presence of sodium dodecyl sulfate, acting as a capping agent. The solution was stirred for 1 h more. The stock solutions were prepared at the molar ratio (w/w) of NaBH4:AgNO3 (10:1) and SDS:AgNO3 (2:1). As prepared colloidal solution of SDS-AgNPs was then stored at 4.0 ± 2.0°C in a refrigerator for the dark for stability.

General scheme for colorimetric sensing of PUT and CAD by SDS-AgNPs

To scrutinize the sensing capability of the probe, an interaction was made between Ag nanoparticles and aliphatic essential diamines PUT and CAD. For this, 4 mL of silver nanoparticles (0.5 mM) were taken into an individual vial, followed by the addition of 1 mL of buffer pH 8; we then added 1 mL of PUT and CAD (100 μg/mL) separately. Distilled water was used additionally to make the sample volume up to 10 mL. The solution mixture was agitated and mixed well. An abrupt color change was noticed and monitored on a double-beam spectrophotometer in the range between 350 – 700 nm. Images were also captured.

Analytical method for the determination of PUT and CAD

The aliphatic biogenic diamines PUT and CAD were determined quantitatively at 580 and 600 nm or at absorbance ratios of 580/410 and 600/410 nm against the concentration in μg/mL. Aiming this, sample vials were equipped with 4 mL of SDS-AgNPs (0.5 mM), 1 mL of a buffer, pH 8. Subsequent to this PUT and CAD of varied concentrations ranging from 4 – 12 and 6 – 14 μg/mL were added, respectively. The volume of each sample was adjusted to 10 mL with double-distilled water. It was observed that the color gains intensity with a rise in the concentration of aliphatic amine. The samples were then examined on a spectrophotometer.

Analysis of PUT and CAD from biological sample (blood plasma and urine)

From a healthy volunteer, 10 mL of urine was collected; this volume was doubled with methanol. Prior to analysis, a urine sample was deprotonized by centrifuging at 4000 rpm for 30 min. A supernatant was collected in a flask; 1 mL was added in each vial (10 mL) separately containing 4 mL of AgNPs, 1 mL of buffer pH 8 and different concentrations of PUT (8 – 12 μg/mL) and CAD (10 – 14 μg/mL). Distilled water was used to adjust the volume. Quantitation was made from a regression equation of the linearity, and % recoveries were calculated.

Similarly 10 mL of blood was taken from a healthy volunteer at Institute of Advanced Research Studies in Chemical Sciences, University of Sindh, Jamshoro. A blood sample was made to be centrifuged at 4000 rpm for 30 min to separate the red blood cells. Afterwards, the supernatant layer was separated and followed by the addition of a double amount of methanol; this was again centrifuged at 4000 rpm for 30 min. Then, 1 mL of

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the supernatant was transferred to a sample vial (10 mL), to which was added 4 mL of SDS-AgNPs at pH 8 and different concentrations of PUT (8 - 12 μg/mL) and CAD (10 - 14 μg/mL) to a final volume of 10 mL. Quantitation was made from a linear regression equation. The % recoveries were also calculated for three replicate measurements of analytical samples.

Sample preparation for characterization via FTIR, SEM and EDX

For sample characterization via FTIR, SEM and EDX, a dried powdered form of SDS-AgNPs with and without interactions of PUT and CAD was prepared. Initially, 90 mL of a colloidal solution of freshly prepared SDS-AgNPs (0.5 mM) and 10 mL borate buffer (pH 8) was thoroughly mixed. The solution was centrifuged for half an hour at 6000 rpm. The supernatant was released and a solid mass found at the bottom of each tube was washed and centrifuged again, as mentioned above. The solid mass was collected, transferred to a China dish and dried at 70°C. Once dried, it was scrapped and shifted to another vial for analysis. Following the same procedure, SDS-AgNPs interacted with PUT or CAD, which had a concentration 100 μg/mL, and then processed as discussed above. The precipitates in a dried powder form were then analyzed by FTIR. The IR spectra were recorded in the wavelength region of 4000 – 600 cm⁻¹ with 16 scans at a resolution of 4.0 cm⁻¹, and then the peak figures were assigned. A background correction was done by using smart ATR.

For SEM imaging, a small amount of a dried powdered sample, as prepared, was mounted on a double-sided carbon chip on a sample stub. Later, it was transferred to the JEOL JSM-6490 LV for SEM imaging, working at 10.0 – 20.0 kV. Further, elemental analyses were carried out using an energy dispersive x-ray (EDX) detector equipped with a SEM instrument.

Sample preparation for zeta potential and dynamic light scattering (DLS) (size distribution) measurements

The cationic or anionic charge on the surface of nanoparticles is highly explained by the zeta potential, which is related to the electrostatic interaction between particles, and significantly affects the stability of the constituent part in colloidal solutions.33,46 A Malvern ZS-Nano analyser (Malvern instrument Inc., London, UK) was used to study the zeta potential and the size distribution of SDS-AgNPs and SDS-AgNPs interacted with PUT or CAD. The following parameters were maintained to carry out the analysis; a temperature of 25°C, a dispersant refractive index of 1.330, a dispersant dielectric constant of 78.5, a materials refractive index of 0.14, and a material absorption of 3.990; the medium viscosity was kept at 0.887 cps. Dilute solutions of SDS-AgNPs (0.1 mM) and SDS-AgNPs interacted with PUT and CAD (100 μg/mL) was selected; borate buffer was used to maintain pH 8. The aggregates in the sample solution were broken by ultrasonication and agitation for about 15 min.47 Afterwards, 1 – 2 mL of the so-formed dilute solution was transferred to the disposable cell to carry out analysis. An aqueous solvent was used to prepare all working solutions. As a minimum, each experiment was performed three times and their average values were measured.

Obstruction study of different ionic and organic species

To obtain a comprehensible insight into the probe’s selectivity and sensitivity, SDS-AgNPs interacted with PUT and CAD were treated with a diverse number of obstructing species of equal concentration, 10 μg/mL, such as, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Fe³⁺, Cr³⁺, Cl⁻, CO₃²⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻, ACO⁻, leucine, glutamine, valine, arginine and guanidine under analogous operational conditions and maintaining pH 8 with borate buffer. The intended amount of samples was prepared and their spectra were recorded on a double-beam UV-visible spectrophotometer. The tolerance limit calculated was based on the maximum concentration of interferents causing a ±0.339 – 15.567% error in the inspection of aliphatic amines PUT and CAD. In fact, these ionic and organic species could not verily bring any change in color and spectrum, making probe a suitable candidate for the determination of putrescine and cadaverine successfully.

Results and Discussion

Sensing approach

Putrescine (butane-1,4-diamine) and cadaverine (pentane-1,5-diamine), as their chemical formula reveal, are the basic diamino groups containing nitrogenous compounds. They are highly basic, having a lower molecular weight. Their structures (Fig. S1, Supporting Information) demonstrate that positive signs are distributed along the length of a chain. These charges allow them to interact with a variety of negatively charged molecules.38 SDS-AgNPs are negative surfaced particles because negatively-charged sulfate groups of sodium dodecyl sulfate encapsulating AgNPs assist the particles to scatter well in water.49 It is assumed that SDS-AgNPs senses and becomes intermingled with the basic group of aliphatic amines through an electrostatic interaction. A dipole-dipole attraction may also possibly be established due to hydrogen of the amino groups and oxygen of the capping agent, as reported in the literature.50,51 For proposing a better sensing approach, silver nanoparticles were prepared through other various reported methods using gallic acid, l-tyrosine, pyrogallol and l-cystein.52–55 The so-formed sensor was employed for the analysis of aliphatic amines PUT or CAD using double-beam spectrophotometer scanned within 350 – 700 nm (Fig. S2). Nevertheless the results obtained were not as appreciable as obtained from the SDS-AgNPs sensor employed for the determination of PUT and CAD biogenic diamines. Considering, SDS-AgNPs a suitable probe was used for carrying out colorimetric determinations of essential diamines in biological samples.

General depiction

Primarily, a wet chemical reduction method was used for preparing silver nanoparticles using sodium-tetrahydrodiborate, and finally encapsulated with sodium dodecyl sulfate, as reported.33,44 A yellow colloidal solution, so formed, was stable for the maximum duration; λ max at 410 nm (Fig. S3, a) did not change soon with the lapse of time. This stability is due to the negative surfactant encapsulating the AgNPs, as reported previously.33,56 The FTIR, SEM and EDX results of SDS-AgNPs were mentioned previously.13 Briefly, the previous results showed that the FTIR of SDS-AgNPs (Fig. S3, b) indicated its consequent C-H bands of SDS within 2916 – 2849 cm⁻¹, whereas the SO₃ moiety showed its symmetric and antisymmetric stretching bands at the region of 1078 – 989 cm⁻¹ and the S-O-C group of SDS illustrated its bending vibration at 817 cm⁻¹, which supported the SDS adsorption on the outer surface of the AgNPs. A SEM image (Fig. S3, c) showed a spongy porous exterior of the prepared AgNPs due to the dehydration because the sample was analyzed under a vacuum. The EDX spectrum (Fig. S3, d) indicated the presence of silver, sodium, sulfur, oxygen and carbon in elemental composition. Using a double-beam spectrophotometer, the interaction between aliphatic diamines PUT and CAD with Ag nanoparticles...
was studied within the range of 350 - 700 nm (Fig. 1). An abrupt color change from yellow to red or reddish brown was visible to the naked eye. A remarkable change in the characteristic SPR band of SDS-AgNPs demonstrated a red shift from 410 to 580 and 600 nm upon the addition of PUT and CAD, respectively, considering the interaction of the basic N-H group of aliphatic amines with the SDS-AgNPs, leading to aggregation. Also, the SDS-Ag NPs were negatively charged, when PUT or CAD was mixed with SDS–Ag NPs; an electrostatic interaction between the SDS-AgNPs and aliphatic amines was established, causing extremely nearness between the amines and the surfaces of SDS-AgNPs, which reduced the distances among the particles, as reported.50-51

Moreover, the FTIR of SDS-AgNPs intermingled with PUT indicated its characteristic broad N-H absorption band at 3343 cm⁻¹ and another N-H weak band at 1636 cm⁻¹. C-H bands were recorded at 2917 – 2849 cm⁻¹. An absorption band observed at 1338 cm⁻¹ was due to S=O and at 1078 cm⁻¹ was related to the S-O group of SDS the protecting surfactant (Fig. 2a). Similar absorption bands were noted for SDS-AgNPs with cadaverine, which showed its N-H absorption band at 3340 cm⁻¹ and another weak band at 1632 cm⁻¹. C-H corresponding bands were observed at 2917 – 2849 cm⁻¹. The S=O and S-O group of SDS showed their significant absorption peaks at 1338 and 1079 cm⁻¹, respectively, and illustrate the efficient interaction among nanoparticle and aliphatic diamine (Fig. 2b). In addition, a morphological and elemental study was also made by using SEM and EDX to confirm the interaction established between the probe and the analytes. SEM images of SDS-AgNPs intermingled with PUT and CAD showed a porous rough surface intermingle aggregated particles (Figs. 2c and 2d). Further, an elemental study showed the presence of Ag, N, C, O and Na for both the amines interacting with SDS-AgNPs. The presence of N clearly indicates that the amine group of PUT or CAD experienced an efficient interaction with SDS on the surface of the nanoparticle (Figs. 2e and 2f). The nanol etzation Malvern instrument was used to read the zeta potential and size distribution in the nanosuspension of SDS-AgNPs with and without aliphatic amines. Each sample was deliberated at least thrice, and then the average values were considered. The acquired data (Fig. S4, a, b and c) showed a SDS-AgNPs surface having a negative charge of about 34.8 mV with a zeta standard deviation of 12.3 mV. While that of PUT and CAD had a surface charge of -21.1 and -19.6 mV with standard deviations of 5.75 and 6.28 mV (Fig. S6, a, b and c). It has been reported that a zeta potential of ±30 mV is requisite minimally for the physical stability of a nanosolution exclusively stabilized by electrostatic forces; ±20 mV is adequate if there exist both electrostatic and steric stabilization.57-59 Moreover it was perceived that in the presence of putrescine and cadaverine the surface charge of SDS-AgNPs was greatly reduced. This signified that the electrostatic interaction had predominantly contributed to the cross-linking and agglomeration of SDS-AgNPs.

Also, the dynamic light scattering supplied influential support for the proposed scheme. Dynamic light scattering (DLS) is a general technique used for the determination of particle size. It can evaluate and modulate the dispersed light intensity as a function of time based on the light discrete from colloidal solutions when laser light passes through. Consequently the hydrodynamic size of particle’s can be acquired.60,61 The size distribution outcomes (Fig. S5, a, b and c) indicated an average size of 50.91 nm for SDS-AgNPs with a poly dispersive index (Pdi) of 0.548. Whereas the average size obtained for PUT and CAD were 105.3 and 123.7 nm with Pdi values of 0.483 and 0.422, respectively. This enlargement in size is attributed to aggregation due to positively charged aliphatic diamines and negative SDS-AgNPs.

Factor influencing experimental conditions

pH effect. Eventually the colorimetric sensors exceedingly rely on the pH of the solution and time on color development, leading to aggregation.62 Consequently, the experimental conditions in terms of the pH and time were inspected. SDS-AgNPs and SDS-AgNPs/PUT or CAD were subjected to buffers contributing to the cross-linking and agglomeration of SDS-AgNPs induced by both aliphatic amines PUT and CAD mentioned in (Fig. S6, b). Briefly, a convincing plasmon and color change was noticed at pH 8 for SDS-AgNPs (Fig. S6, a). However, the pH response examined for SDS-AgNPs with PUT/CAD demonstrated that the absorption spectra and color of SDS-AgNPs were almost unaffected upon adding PUT and CAD at pH 2 - 7 and 9 - 10. While the pH was at 8, the surface plasmon resonance peak of SDS-AgNPs was bathochromically shifted to 580 and 600 nm for PUT and CAD (10 μg/mL), resulting a color change from yellow to red, which authenticated the aggregation of SDS-AgNPs induced by both aliphatic amines PUT and CAD. The spectrum indicated a suitable time after 45 min to determine the aliphatic amines PUT and CAD quantitatively, because at this duration the error measured was less than 5% (Fig. S7, Table S1). The effects of time were repeated at least thrice (n = 3).

Concentration of nanoparticle. The influence of the nanoparticle concentration was investigated for the efficient interaction and aggregation of SDS-AgNPs with PUT and CAD scanned by UV-visible spectroscopy. For this, keeping the concentration of amine constant at 100 μg/10 mL, five different concentrations of a silver nano probe ranging over 0.1 – 0.3 mmol, were made to interact with the amines. The absorbance of each solution was taken to be from 350 to 700 nm. It was noted that when the concentration of SDS-AgNPs was less than 0.3 mmol, it agglomerated upon interaction with amines to some extent in the working conditions, resulting in an elevated environment for PUT and CAD analysis. However, if it was greater at 0.3 mmol, since SDS-AgNPs might not create the cross-linking, and agglomeration entirely, leading to inferior sensitivity for PUT and CAD. Thus, the optimum concentration of SDS-AgNPs

Fig. 1 UV-visible spectrum of SDS-AgNPs interacted with PUT and CAD.
was found to be 0.2 mmol, because at this concentration level better results were obtained for a nano probe with a better Plasmon (Fig. S8).

Concentration of aliphatic amines. To inspect the influence of the concentration of PUT and CAD on the absorbance, a quantitative determination of aliphatic amine was made using probe SDS-AgNPSs within linear calibration ranges of 4 – 12 and 6 – 14 μg/mL for PUT and CAD essential diamine, using nine calibrators (Fig. 3). A gradual increase in the absorption intensity was observed with increasing concentration of amines at 580 nm or at a ratio of 580/410 A for PUT, whereas at 600 nm or at an absorbance ratio of 600/410 A. The linearity was observed for PUT and CAD with coefficients of determinations ($r^2$) of 0.992 and 0.991, correspondingly. Besides, it was also noted that the color of the colloidal nano probe solution changed from yellow to reddish or reddish brown upon increasing the concentration of amines visible to the naked eye. In addition, using the standard deviation of the slope of the linear regression curve (LOD = 3.3σ and LOQ = 10σ), the detection limits and quantitation limits were calculated. The detection limits obtained for aforesaid amines PUT and CAD were 0.334 and 1.639 μg/mL, and the quantitation limits calculated were 1.011 and 4.966 μg/mL, correspondingly (Table 1).

Intraday and interday. Intraday and interday investigations were made in order to evaluate the precision and reproducibility of the nano probe. Using a concentration of 10 μg/mL, for putrescine and cadaverine, five replicate observations were made under the optimized conditions. The relative standard deviation (RSD) calculated was < 2%, equally for intra-day and inter-day attempts. The results showed that the proposed method is exceedingly repeatable and reproducible (Table S2).

Selectivity. The selectivity and sensitivity of an Ag nano probe was examined in the presence of various ionic moieties and organo compounds such as Na+, K+, Mg2+, Ca2+, Al3+, Fe2+, Cr3+, Cl–, Co2+, SO42–, NO3–, HPO42–, ACO–, leucine, glutamine,

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**Fig. 2** FTIR of (a) PUT (b) CAD, SEM images of (c) PUT (d) CAD, EDX spectrum of (e) PUT (f) CAD functionalized on the surface of SDS-AgNPs.
valine, arginine and guanidine under analogous operational conditions and maintaining pH 8 with a borate buffer. The concentration of each interfering solution used was 10 μg/mL. Nonetheless, the study demonstrated the interference of ionic and organic species with a relative error of ±0.339 – 15.567% (Table 2). The change in the color and SPR was studied within 350 – 700 nm. It was shown that there was no shift in SPR at 580 and 600 nm in the spectrum of aliphatic essential diamines that interacted with SDS-AgNPs. The reddish color of the solutions remained identical even after the addition of interferents. We concluded that neither any of the species, either ionic or organic, mentioned above, could interfere with the determination of PUT and CAD amines. They also did not induce the aggregation of nano the sensor under the optimum experimental conditions (Fig. 4). The proposed scheme showed superior selectivity towards aliphatic amines PUT and CAD over other interfering species.

**Biological sample fluids.** Furthermore, the proposed scheme was applied for the colorimetric determination of PUT/CAD amine in spiked biological fluid samples including human urine and blood serum. The results obtained showed a standard deviation (SD) within 0.0005 – 0.006 and a % relative standard deviation (%RSD) within 0.071 – 2.125% with the % recoveries being within 95.717 – 105.200% (Table 3). The results indicated that the biological sample fluids did not interfere with the determination of PUT/CAD biogenic amines.

**Conclusions**

In summary, SDS encapsulated AgNPs were prepared by a general methodology using a chemical reduction method.

### Table 1 Quantitative detection of PUT/CAD by SDS-AgNPs

| S. No | Analyte | Calibration range/μg mL⁻¹ | CODa | LODb/μg mL⁻¹ | LOQc/μg mL⁻¹ | Linear regression equation |
|-------|---------|---------------------------|------|--------------|--------------|--------------------------|
| 01    | PUT     | 4 - 12                    | 0.992| 0.334        | 1.011        | y = 0.072x – 0.162       |
| 02    | CAD     | 6 - 14                    | 0.991| 1.639        | 4.966        | y = 0.032x – 0.050       |

a. Coefficient of determination.  b. Limit of detection.  c. Limit of quantitation.

![Fig. 3 Effect of different concentration of the analyte.](image)
The so-formed nano sensor, being uncomplicated, fast and cheaper, was exceedingly sensitive to the essential diamine PUT and CAD with detection limits of 0.334 and 1.639 μg/mL, respectively. The % recoveries within 95.717 - 105.200% were calculated for biofluids samples; the colorimetric determinations of PUT and CAD were performed without the application of any complicated instruments. SDS-AgNPs have been successfully employed for the examining the essential biogenic diamines PUT and CAD. Excluding the method could be extensively employed similarly for the determination of other biogenic amines as well such as spermine, spermidine etc. Considering other noble metal nanoparticles, the silver nanoparticles are thought to be the most cost effective and easy for the routine analysis of biogenic amines.

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### Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

### Table 2: Selectivity of nano silver probe for PUT/CAD in presence of ionic and organic interferents

| S. No | Interferent | Tolerance/μg mL⁻¹ | Putrescine Recovery/% | Error/% | Cadaverine Recovery/% | Error/% |
|-------|-------------|------------------|-----------------------|--------|-----------------------|--------|
| 01    | Leucine     | 10               | 96.604                | 3.395  | 98.153                | 1.847  |
| 02    | Glutamine   | 10               | 93.378                | 6.621  | 98.944                | 1.055  |
| 03    | Valine      | 10               | 100.509               | 0.509  | 97.361                | 2.638  |
| 04    | Arginine    | 10               | 98.642                | 1.358  | 97.625                | 2.375  |
| 05    | Guanidine   | 10               | 93.378                | 6.621  | 98.681                | 1.319  |
| 06    | Na⁺         | 10               | 96.604                | 3.395  | 99.472                | 0.528  |
| 07    | K⁺          | 10               | 97.963                | 2.037  | 98.152                | 1.846  |
| 08    | Mg²⁺        | 10               | 98.642                | 1.358  | 94.723                | 5.277  |
| 09    | Ca²⁺        | 10               | 93.378                | 6.621  | 92.876                | 7.124  |
| 10    | Al³⁺        | 10               | 96.604                | 3.395  | 98.153                | 1.847  |
| 11    | Fe²⁺        | 10               | 92.699                | 7.300  | 89.709                | 10.290 |
| 12    | Cr³⁺        | 10               | 95.246                | 4.754  | 87.599                | 12.400 |
| 13    | Cl⁻         | 10               | 96.604                | 3.395  | 99.472                | 0.528  |
| 14    | CO₃²⁻       | 10               | 93.378                | 6.621  | 84.433                | 15.567 |
| 15    | ACO⁻        | 10               | 100.339               | 0.339  | 96.569                | 3.4301 |
| 16    | SO₄²⁻       | 10               | 92.699                | 7.300  | 90.501                | 9.498  |
| 17    | NO₃⁻        | 10               | 95.246                | 4.754  | 92.084                | 7.915  |
| 18    | HPO₄⁻       | 10               | 91.681                | 8.319  | 104.749               | 4.749  |

### Table 3: Quantitative determination of PUT/CAD from spiked biological fluids sample

| S. No | Matrix Added/ Found/μg mL⁻¹ | Recovery/% | Error/% | Standard deviation % |
|-------|----------------------------|------------|---------|----------------------|
| 01    | PUT spiked                              | 8          | 9.416   | 105.200              |
| 02    | PUT spiked                              | 9          | 9.180   | 102.000              |
| 03    | PUT spiked                              | 10         | 10.388  | 103.880              |
| 04    | PUT spiked                              | 11         | 10.875  | 98.864               |
| 05    | PUT spiked                              | 12         | 11.777  | 98.142               |
| 06    | CAD spiked                              | 8          | 8.319   | 103.987              |
| 07    | CAD spiked                              | 9          | 9.361   | 104.011              |
| 08    | CAD spiked                              | 10         | 10.028  | 100.280              |
| 09    | CAD spiked                              | 11         | 10.594  | 95.940               |
| 10    | CAD spiked                              | 12         | 11.037  | 99.627               |
| 11    | CAD spiked                              | 13         | 11.687  | 97.392               |
| 12    | CAD spiked                              | 14         | 12.156  | 101.300              |
| 13    | CAD spiked                              | 15         | 13.156  | 101.200              |
| 14    | CAD spiked                              | 16         | 14.375  | 102.678              |

**Fig. 4:** Selectivity and sensitivity of a nano sensor in the presence of different ionic and organic species.
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