Spectrofluorometric Determination of Acetylsalicylic Acid Based on the Plasmonic Interaction between Its Fluorescent Europium Complexes and Silver Nanoparticles

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***Abstract*— A simple and highly sensitive spectrofluorometric method has been developed for the determination of Acetylsalicylic Acid (ASA) based on Europium (Eu^{3+}) sensitized fluorescence (FL) that is plasmonically increased by silver nanoparticles (Ag NPs). The increment of FL intensity of Eu^{3+}-ASA complex by Ag NPs was found as the excited-state fluorophores interact with the surface plasmon electron on the metal nano surface and so the resonance energy was transferred to the fluorophores. The FL intensity of Eu^{3+} was enhanced by ASA at 614 nm after being excited at 373 nm, which corresponds to the $^5D_0$-$^7F_2$ transitions of Eu^{3+} ion. At the optimum experimental conditions, the FL intensity increases linearly with the concentration of ASA in the range of 3.1×10^{-11}-1.2×10^{-9} g mL^{-1} with correlation coefficient of 0.9996. The limit of detection of ASA was found to be 1.3×10^{-12} g mL^{-1}. The relative standard deviations (RSD) for 5 determinations of 4.2×10^{-9} g mL^{-1} ASA are 1.21. The proposed method was successfully implicated to determine ASA in pharmaceutical samples.**

Keywords*— Acetylsalicylic acid; Europium (III); Silver nanoparticles; Fluorescence; Plasmonic interaction.

I. INTRODUCTION

Europium complexes have been paid much attention to use as spectroscopic probes due to their large Stocks shift, narrow emission bandwidths, and long emission lifetimes [1-3]. These characteristics make europium complexes suitable candidates to apply for various fields including fluoroimmunoassay [4], energy producing devices [5], optical signal intensification [6] etc. The use of europium complexes in fluoroimmunoassay faces the quenching problem due to a coupling with vibrational modes of solvent molecules. In order to overcome the quenching problem, different types of chelating agents like metal nanoparticles, macrocyclic ligands are used. In the recent years, the metal nanoparticles are extensively used for many applications including signaling, sensing, imaging and the modulation of fluorescence properties by forming novel donor-acceptor systems with fluorophores [1, 7-9]. Furthermore, nanostructured metallic surfaces can consequence in the fluorescence increment attributed to enhance the local electromagnetic field caused by plasmons resonance known as surface-enhanced fluorescence (SEF) whereby the spectral properties of fluorophores can be modified [10-13]. Europium complexes among the plasmon-enhanced lanthanides luminescence, were paid much attention owing to their highly efficient luminescence center and the complexes tend to assemble on noble-metal nanostructured surface [14-17]. Therefore, the nanostructured particles are widely used in various analytical methods by enhancing the fluorescence of lanthanide ions forming strong complexes with lanthanide ions through covalent bond.

Acetylsalicylic Acid (ASA) is a prototypical analgesic used for the treatment of mild to moderate pain, which has anti-inflammatory and antipyretic properties. ASA acts as an inhibitor of the biosynthesis of prostaglandins through the inhibition of cyclooxygenase. It can also inhibit platelet aggregation. Because of the availability and inexpensive property, ASA has been most widely used among all of the NSAIDs [18]. A variety of methods have already been reported to determine ASA in biological samples and pharmaceutical preparations including fluorescence spectroscopy [19-21], spectrophotometry [22-24], electrochemistry [25-28], chromatography [29-31], chemiluminescence [32] and FT-Raman spectroscopy [33]. Among the reported methods to determine ASA, spectrofluorimetric method provides high sensitivity and selectivity with simple instrumentation and has been widely used to estimate ASA quantitatively in pharmaceutical preparations and biological fluids. a

In this study, an interaction between silver nanoparticles and europium- acetylsalicylic acid complexes for the increment of fluorescence intensity (FL) has been examined based on the catalytic activity

of silver nanoparticles (Ag-NPs). Eu^{3+} formed complex with ASA in a buffer solution, and enhanced the FL intensity. Under the optimum conditions, the representative fluorescence of Eu^{3+}-ASA complex was obtained at 591 and 614 nm when excited at 373 nm corresponding to the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transitions of Eu^{3+} ion, respectively. The FL intensity of the Eu^{3+}-ASA complex was increased markedly in the presence of Ag NPs by transferring the fluorescence resonance energy from the Eu^{3+}-ASA complex to the Ag NPs. Based on the above phenomenon, a simple and sensitive spectrofluorimetric method has been proposed for the determination of acetylsalicylic acid in pharmaceutical preparations.

II. Materials and Methods

A. Reagents

All reagents used were of analytical reagent grade without further purification. Distilled deionised (DI) water (Millpore, MilliQ Water System, USA) was used throughout. Acetylsalicylic acid, silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were obtained from Sigma-Aldrich (St. Louis, USA). A stock solution of ASA (1.0×10^{-3} mol L^{-1}) was prepared by dissolving appropriate amount of ASA in DI water and stored at 4 ℃. The possible decomposition of ASA to salicylic acid was prevented by using freshly prepared solutions prior to the experiments. Stock standard solution of Eu^{3+} (1.0×10^{-3} mol L^{-1}) was prepared by dissolving Eu_2O_3 (purity, 99.99%) in 1:1 HCl and evaporating the solution to almost dryness before diluting to 100 mL with DI water. $AgNO_3$ (1.0×10^{-3} mol L^{-1}) and $NaBH_4$ (2.0×10^{-3} mol L^{-1}) solutions were prepared by dissolving in DI water. Desired concentrations of the working solutions were achieved by adding DI water every time before use. Other chemicals were also of analytical grade.

B. Apparatus

A spectrofluorimeter (Model F-4500, Hitachi, Japan) equipped with a xenon lamp (150 W) and photomultiplier tube (Model R 928, Hamamatsu, Japan) was used to measure all the luminescence. The excitation and emission slits for all the luminescence spectra were of 10 nm. A pH meter (Model Orion, 520A, USA) was used to adjust the pH. Every UV-visible spectrum was measured in UV-1800 (Shimadzu, Japan). Transmission electron microscopic (TEM) image of Ag NPs was obtained using TEM (Hitachi-7100, Japan) with an accelerating voltage of 100 kV. All the experiments were carried out at room temperature.

C. Preparation of Ag NPs

Chemical reduction method was utilized to prepare silver nanoparticles as per described in literature [34]. Silver nitrate was reduced in presence of sodium tetrahydridoborate as a reducing agent in aqueous solution. Briefly, 25 mL aqueous solution of $AgNO_3$ (1×10^{-3} mol L^{-1}) was added drop-wise to 75 mL freshly prepared aqueous solution of $NaBH_4$ (2×10^{-3} mol L^{-1}) with vigorous stirring. The completion of the reduction of silver ions in the solution was indicated by the change of the color of the solution as it turned into bright yellow. 5 mL aqueous solution of sodium citrate (1% w/w) was added to the final solution after 10 min to stabilize the Ag NPs. The colloidal solution of Ag NPs was stirred for another 20 min and stored at 4º C for 2 days before use.

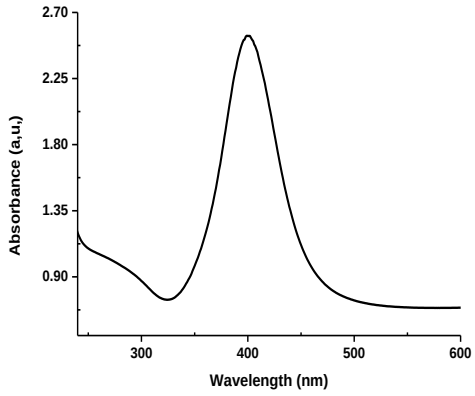
D. Analytical Procedure

To measure the fluorescence spectra the following procedure is maintained in this study. 1 mL of Eu^{3+} solution, 1.0 mL of buffer (pH=7.2), appropriate volume of ASA solutions were taken into a 10 mL volumetric flask. The mixture was then diluted with 5 mL DI water and allowed to stand for several minutes for complex formation. 1 mL of Ag NPs (colloidal solution) was added to the complex. The luminescence spectra of Eu^{3+}, Eu^{3+}–ASA complex and Eu^{3+}–ASA–Ag NPs were measured in a 1 cm quartz cell with the excitation and emission wavelengths of 373 and 614 nm respectively. The high voltage for the photomultiplier tube was set to 950 V.

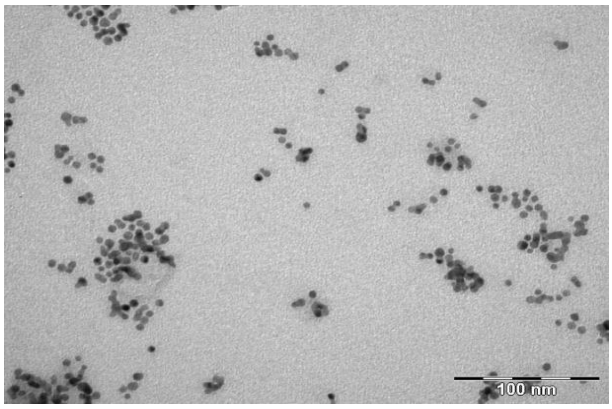
III. Results and Discussion

A. Fluorescence spectral characteristics with Ag NPs

The prepared Ag NPs were characterized using UV-visible spectrum and TEM image observation. Colloidal solution of Ag NPs shows a broad absorption peak at 400 nm (Fig 1a) attributed to the characteristic surface plasmonic band of Ag NPs [35]. TEM image (Fig 1b) of Ag NPs shows the morphology and the average diameter of the particle, approximately 15±2 nm. The fluorescence spectra of Eu^{3+}, ASA, Eu^{3+}-ASA and Eu^{3+}-ASA-Ag NPs were recorded and shown in Fig. 2. Eu^{3+} solution produced very weak peak due to the weak absorption of metal ion itself (Fig. 2, curve 1). Eu^{3+} ions can act as an energy acceptor from the lowest triplet state of organic ligand which have strong absorption in the UV region and could interact to increase the FL intensity of Eu^{3+}. When ASA solution was added to Eu^{3+} solution, the characteristic FL peaks were observed at 591 and 614 nm (Fig. 1a, curve 3) exited at about 373 nm corresponding to the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transition of Eu^{3+}, respectively. The most intense peak was obtained at 614 nm, which was chosen for the measurement of fluorescence in the whole experiment. According to the observed results, it is assumed that ASA can absorb energy and transfer it to Eu^{3+} through intermolecular energy transfer.



(a)



(b)

Figure 1. (a) UV-visible spectrum of Ag NPs; (b) TEM image of Ag NPs

Therefore, a binary complex between ASA and Eu^{3+} can be formed and emit the characteristic enhanced FL peak of Eu^{3+} at 614 nm. Several folds observed a significant increment of the FL intensity of Eu^{3+}-ASA complex when Ag NPs were added to the Eu^{3+}-ASA complex solution (Fig. 2, curve 4). The fluorescence enhancement of the complex by Ag NPs is due to the interaction between the luminescent materials and the surface plasmon of metallic nanostructure leads to two effects such as increase of fluorescence decay rates and enhancement of excitation fields, which may induce the fluorescence enhancement. In the first case, the quantum yield of the luminescence materials increases due to increment of the fluorescence decay rate of the excited states fluorophores [1]. In the second case, the incident lights are concentrated by the metallic surfaces, which enhance the excitation near the metal particles [1]. Therefore, Ag NPs leading to a strong coupling between the surface plasmon resonance of the Ag NPs and the excited fluorescence centers enhance the fluorescence intensity of the Eu^{3+}-ASA complex significantly.

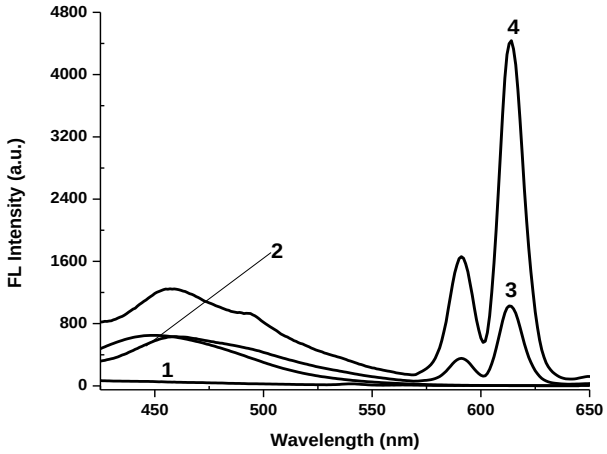


Figure 2. FL emission spectra of (1) Eu^{3+}; (2) ASA; (3) Eu^{3+}-ASA; (4) Eu^{3+}-ASA-Ag NPs. Conditions: [ASA], 2.5×10^{-8} g mL^{-1}; [Eu^{3+}], 6.0×10^{-5} mol L^{-1}; [Ag NPs], 7.0×10^{-4} mol L^{-1}; Tris-HCl (0.1 mol L^{-1}); pH, 7.2, λex/λem=373/614 nm

B. Possible Mechanism

In order to understand the complex formation between Eu^{3+} and ASA and the interaction of the complex with Ag NPs, the UV-visible spectra of Eu^{3+}, ASA, Eu^{3+}-ASA, Eu^{3+}-ASA-Ag NPs were recorded as shown in Fig. 3. In Fig. 3 (curve 2) ASA showed a characteristic maximum absorbance spectra at about 268 nm. When ASA was added to the Eu^{3+} solution, intensified maximum absorption of ASA was found to be red shifted from 268 nm to 298 nm (Fig. 3, curve 3, red shift) which indicated the formation of the Eu^{3+}-ASA complex and the FL intensity has been increased. This is because Eu^{3+} is a high efficient luminescence center and the complex of Eu^{3+} with strong light-absorbing ligand transfer energy from the ligand to the lanthanide ion. Ag NPs showed a notable absorption peak at about 399 nm (Fig. 1a). When Ag NPs were added to the Eu^{3+}-ASA complex, the absorption peak of the complex was increased with red shift from 399 nm to about 425 nm (Fig. 3, curve 4), representing that more energy had been transferred to Eu^{3+}. Therefore, Ag NPs can interact with the Eu^{3+}-ASA complex and enhanced the fluorescence intensity of the complex markedly (Fig. 2).

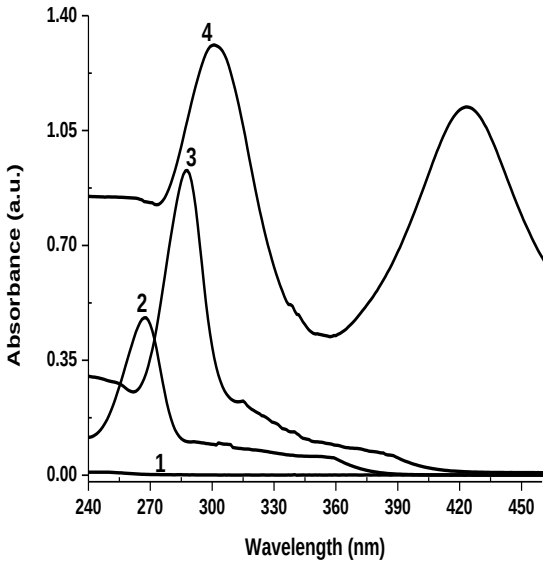


Figure 3. Absorbance spectra of (1) Eu^{3+}; (2) ASA; (3) Eu^{3+}-ASA; (4) Eu^{3+}-ASA-Ag NPs. Conditions: [ASA], 3.0×10^{-7} g mL^{-1}; [Eu^{3+}], 1.5×10^{-5} mol L^{-1}; [Ag NPs], 7.0×10^{-4} mol L^{-1}; Tris-HCl (0.1 mol L^{-1}); pH, 7.2

C. Effect of pHand buffer solution

pH plays an important role to boost up the luminescence intensity of the system. Thus, pH was investigated over the range of 5-8 and the maximum intensity was obtained at pH of 7.2 (Fig. 4). Therefore, pH value of 7.2 was chosen as optimum pH. Buffer solutions also have influence on the luminescence intensity. The effect of the following buffers was investigated to obtain highest intensity; KH_2PO_4-Na_2HPO_4, borax-HCl, $(HOCH_2)_3CH_2N$-HCl, $Na_3C_6H_5O_7$-HCl, KH_2PO_4–NaOH, and tris-HCl. It was observed that tris-HCl buffer provided the highest intensity. Thus tris-HCl buffer concentrated to 0.01 mol L^{-1} was selected for this experiment.

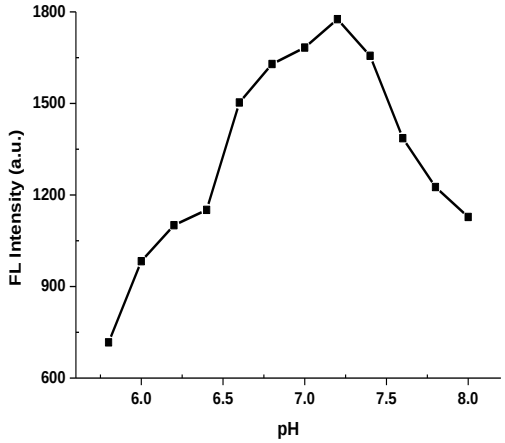


Figure 4. Effect of pH on the FL intensity of Eu^{3+}-ASA-Ag NPs system. Conditions: : [ASA], 2.5×10^{-8} g mL^{-1}; [Eu^{3+}], 6.0×10^{-5} mol L^{-1}; [Ag NPs], 7.0×10^{-4} mol L^{-1}; Tris-HCl (0.1 mol L^{-1})

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D. Effect of Eu^{3+} concentration

The effect of europium (Eu^{3+}) concentration on the analytical signal for Eu^{3+}-ASA-Ag NPs system was investigated in the range of 1.0×10^{-5}-1.2×10^{-4} mol L^{-1}. The maximum FL intensity is observed at a europium concentration of 6.0×10^{-5} mol L^{-1} (Fig. 5). Hence europium concentration of 6.0×10^{-5} mol L^{-1} was selected for the experiment. The increased intensity with the increase in Eu^{3+} concentration can be attributed to the fact that excess of Eu^{3+} makes the coordination equilibrium shift to the formation of the complex and the efficiency of the energy transfer is enhanced when the ASA molecules are involved in the coordination.

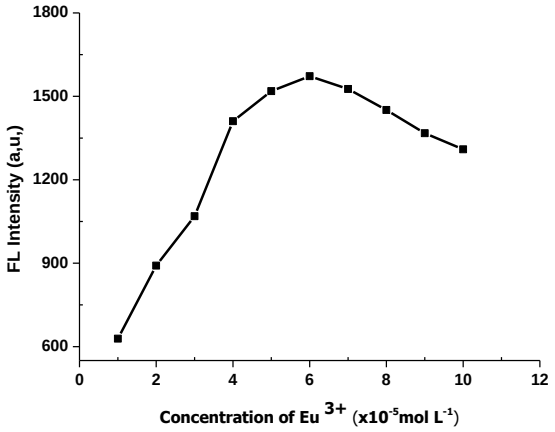

Figure 5. Effect of Eu^{3+} concentration on the FL intensity of Eu^{3+}-ASA-Ag NPs system. Conditions: [ASA], 2.5×10^{-8} g mL^{-1}; [Ag NPs], 7.0×10^{-4} mol L^{-1}; Tris-HCl (0.1 mol L^{-1}); pH, 7.2.

E. Effect of colloidal Ag NPs concentration

The concentration of colloidal Ag NPs greatly influenced the FL intensity of the present system. The effect of Ag NPs concentration was examined in the range of 2.0×10^{-4}-2.5×10^{-3} mol L^{-1} and 7.0×10^{-4} mol L^{-1} of Ag NPs produced the highest intensity (Fig. 6). When the colloidal solution of Ag NPs was added to the Eu^{3+}-ASA complex, the local refractive index around the complex might be changed which amended the electric dipole transition rate. Therefore, the colloidal Ag NPs solution above 7.0×10^{-4} mol L^{-1} may cause the distortion of local field arising from the self-interaction of plasmonic electron of Ag NPs, which might be, quenched the luminescence intensity. Considering the sensitivity and linearity to determine ASA, 7.0×10^{-4} mol L^{-1} was considered as the optimum concentration of colloidal Ag NPs.

F. Effect of reagent addition order and flourecence stability

The effect of the reagent addition order on the FL intensity was also investigated. The results showed that an addition order of Eu^{3+}, tris-HCl, ASA and Ag NPs colloidal solution offered the maximum intensity that was chosen for this study. It was found that the luminescence intensity of the system reached its apex

in 20 min after all the reagents had been added and remained stable for 2 h. Therefore, 20 min was set as the optimum time for all intensity measurements.

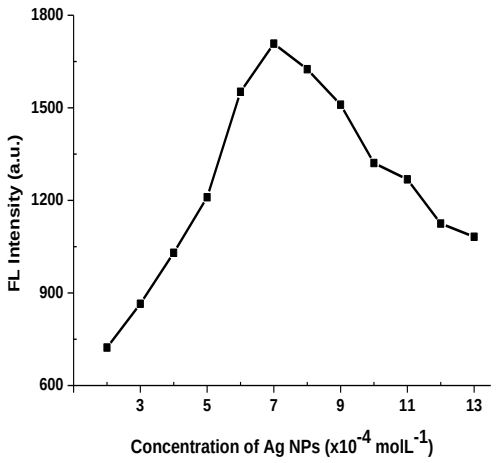

Figure 6. Effect of colloidal Ag NPs solution concentration on the FL intensity of Eu3+-ASA-Ag NPs system. Conditions: [ASA], 2.5×10^{-8} g mL^{-1}; [Eu^{3+}], 6.0×10^{-5} mol L^{-1}; Tris-HCl (0.1 mol L^{-1}); pH, 7.2

G. *Analytical Characteristics*

Analytical characteristics of the method was evaluated by plotting calibration curves of ASA concentrations versus FL intensities. To get the calibration curve a series of standard solutions were prepared. Under the obtained optimum conditions, the enhancement of the FL intensity was found to be linear with the concentrations of ASA and the dynamic range for ASA was found from 3.1×10^{-11} to 1.2×10^{-9} g mL^{-1} with regression equations of $Y=6.2\times10^{11}C_{ASA}+538$ ($r=0.9996$) where C_{ASA} indicate the concentration of ASA. The limits of detection (LOD) as defined by IUPAC, C_{LOD} = 3Sb/m (where Sb is the standard deviation of the blank signals and m is the slope of the calibration graph) were found to be 1.3×10^{-12} g mL^{-1} for ASA. The relative standard deviations (RSD) for 5 determinations of 4.2×10^{-9} g mL^{-1} ASA are 1.21. Therefore, the present method offered lower limit of detection that can be successfully applied for the determination of ASA.

H. *Interference Study*

To examine the selectivity of this method a systematic study with various interfering species was carried out which may increase or decrease the luminescence intensity of the Eu^{3+}-ASA-Ag NPs system. All investigations were carried out by comparing the intensities obtained with and without the addition of potentially interfering substances. If any species can produce an error greater than ±5% then it is considered as an interfering species in the determination of ASA. The results are listed in Table 1. These results signify that most of ionic interfering substances did not interfere in the determination of ASA. Thus, the proposed method can be applied to determine ASA without any pretreatment.

Interfering substances	Tolerable Concentration (mol L^{-1})	Change in fluorescence intensity (%)
Na^{+}, K^{+}	1.5×10^{-5}	-1.15
Fe^{3+}, Fe^{2+}, Cu^{2+}, Ca^{2+}	2.2×10^{-5}	+0.41
Zn^{2+}, Al^{3+}	1.4×10^{-5}	+2.01
Starch, fructose, glucose, ascorbic acid	1.2×10^{-5}	-2.1
Paracetamol	2.2×10^{-4}	-0.85

Table 1 Effect of interfering substances on the Eu^{3+}-ASA-Ag NPs system

I. *Application of the method*

The method was applied to determine ASA in commercially available pharmaceutical preparations to evaluate the validity of the proposed method using standard addition method. 5 tablets (each contains 400 mg ASA) collected from local drug store were weighed, grounded in to fine powder and dissolved in DI water in a beaker. After complete dissolution of a tablet, a known amount of ASA was added to the solution and used to determine recovery. The results obtained are summarized in Table 2. The results showed that there were no significant differences between the labeled contents and those obtained by the proposed method. Recoveries were observed in the range of 98.9-104.0% for ASA.

Sample	Amount (mg)		Added ($\times10^{-8}$ mol L^{-1})	Found ($\times10^{-8}$ mol L^{-1}) ±RSD [a]	Recovery (%)
	Labled (mg)	Found by the proposed method±RSD[a]			
Tablet	400 mg of CIP	401.6±0.50	2.0	2.06±1.02	103.0
			4.0	3.98±1.15	99.5
			6.0	5.89±1.05	98.2
			8.0	8.11±1.55	101.4
			10.0	10.09±1.45	100.9

[a]Relative standard deviation for five replicate measurements

IV. CONCLUSION

A simple and highly sensitive spectrofluorometric method has been described for the determination of ASA based on the plasmonic interaction of europium (Eu^{3+}) ion complex with Ag NPs. The fluorescence intensity was increased significantly by incorporating Ag NPs to the Eu^{3+}-ASA complex allowing the

determination of trace amount of ASA. The enhanced intensity was in proportion to the concentration of ASA over the range of 3.1×10^{-11}-1.2×10^{-9} g mL^{-1}. The limit of detection was found to be 1.3×10^{-12} g mL^{-1} with good reproducibility. The presented method has been applied to the determination of ASA in pharmaceutical preparations and the recovery test was performed under standard addition method with satisfactory results.

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