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Prussian blue nanoparticles: a simple and fast optical sensor for colorimetric detection of hydralazine in pharmaceutical samples

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A simple, inexpensive and fast colorimetric method was developed for the detection of hydralazine, which is an antihypertensive drug. The method is based on the reaction of HY with ferric ions (as oxidizing agent) in the presence of ferricyanide ion and formation of prussian blue nanoparticles ($KFe^{III}[Fe^{II}(CN)_6]$). A UV-vis spectrophotometer was used to monitor the changes of the absorption intensity of the prussian blue nanoparticles. These nanoparticles exhibited a strong UV-vis extinction band at 700 nm. Change in color of the solution, which is directly related to the HY concentration, could be easily observed with the naked eye in the presence of a sub-ppm level of HY. The effect of several reaction variables on the rate of the PBNP formation was studied and optimized. A linear relationship between absorbance intensity of PBNPs and the concentration of HY over a range of 0.4 μg mL^{-1} to 2.0 μg mL^{-1} with correlation coefficient (R^2) of 0.9967 was observed; moreover, the detection limit was found to be 0.33 μg mL^{-1}. The proposed method showed a good detection limit, and compared to other methods it is very fast, simple and inexpensive. Furthermore, the proposed method was successfully applied for the determination of HY concentration in pharmaceutical samples with satisfactory results.

1. Introduction

The development of sensitive and selective colorimetric sensors has come into wide demand due to their simplicity, rapidity, precision and use of common laboratory equipment.[1–3] Nanoscale metal particles are attracting considerable attention from researchers due to their intriguing properties and potential applications. These nanoparticle materials often exhibit very interesting magnetic, electrical, optical, and chemical properties that cannot be achieved by their bulky counterparts.[2–5] Metallic nanoparticles such as silver,[1,6,7] gold[8,9] and copper[10] nanoparticles with well-controlled size have recently been of great interest because of the color changes associated with the surface plasmon absorption band and fluorescence properties. Recently, prussian blue nanoparticles as a new colorimetric nanoprobe have been developed for detection of chemical species.[11–13]

Prussian blue-type metal complexes, which are called metal hexacyanoferrates, have been extensively investigated for their practical applications. Prussian blue belongs to a group of excellent electron transfer mediators that have attracted great attention.[11,14,15] Prussian blue nanoparticles (PBNPs) have an intense absorption band near 700 nm due to a transition, during which an electron is transferred from a ground state $Fe_A(III)Fe_B(II)$ to an excited state $Fe_A(II)Fe_B(III)$ form. The molar absorption coefficient of the soluble form is $3.0 \times 10^4\ M^{-1}\ cm^{-1}$ at 700 nm.[5,12,16]

Hydralazine (1-hydrazinophthalazine, HY) is an anti-hypertensive drug, and its chemical structure is shown in Fig. 1. HY has been among the drugs of choice for the treatment of hypertension during pregnancy for many years. It is also used to cure hypertension by reducing the blood pressure to help avoid heart attacks. It is usually prescribed with a dosage of 50 to 200 mg daily to control high blood pressure; however, the excessive uptake of HY can cause harmful symptoms such as headache, joint or muscle pain and swollen ankles.[17,18] Several analytical methods have been developed for the assay of HY in pharmaceutical formulations. These methods include UV-vis spectrophotometry,[19,20] flow injection chemiluminescence,[21] chromatography (both HPLC and gas chromatography [GC])[22,23] and electrochemistry.[24,25] Although each method has certain advantages, some defects exist in each method. The operation of some methods, like HPLC, GC and electroanalytical methods, is complex, and these methods require expensive apparatus and costly maintenance; however, in comparison, spectroscopic analysis is simple and sensitive. Furthermore, electroanalytical and chromatographic methods require specially trained persons to perform the methods. In contrast, colorimetric methods are generally inexpensive, safe, easy to use and need only simple pretreatment of analytes.

In this study, a new simple and fast method for the determination of HY concentration is proposed. This method is based on the reaction of HY with an oxidizing agent (ferric ion)

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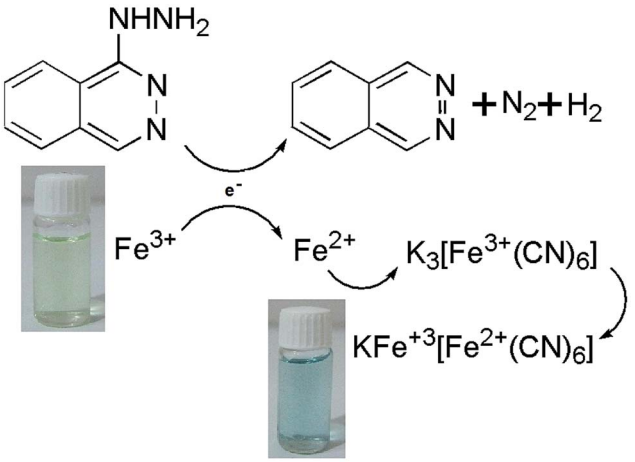

Fig. 1 Schematic mechanism for colorimetric detection of HY.

in the presence of ferricyanide while preparing PBNPs in a slightly acidic medium. The intensity of absorption of PBNPs was monitored spectrophotometrically at a maximum wavelength of 700 nm *vs.* time. With the increase of HY concentration, the absorption intensity of the PBNPs formed increased, and the enhanced intensity was linearly proportional to the HY concentration. The change in color of the solution, which is directly related to the HY concentration, can be easily observed with the naked eye in the presence of sub-ppm levels of HY in tablet samples. This colorimetric method has been successfully applied to determine HY concentration in tablets with satisfactory results.

2. Experimental

2.1. Apparatus

UV-vis absorbance spectra were recorded by a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia) and 1.0 cm plastic cells. pH measurements were performed with a Denver Instrument Model 270 pH meter equipped with a Metrohm glass electrode. Images of nanoparticles were obtained by a transmission electron microscope (TEM) model Zeiss EM 10C (Carl Zeiss Inc., Oberkochen, Germany) operated at 80 kV.

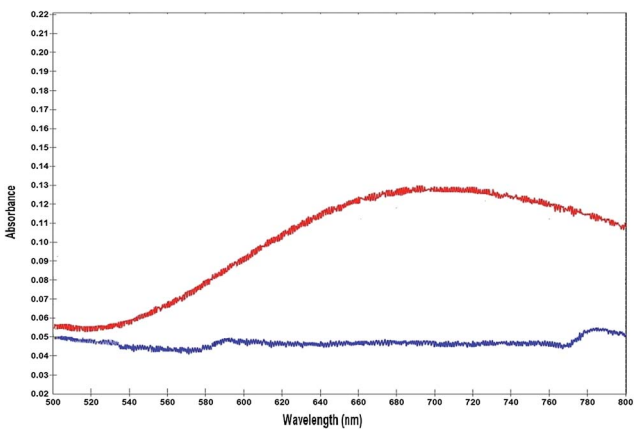

Fig. 2 UV-vis absorption spectrum of PBNPs obtained at 1.0 μg mL^{-1} concentration of HY.

2.2. Reagents

All chemicals were of analytical reagent grade purity. Hydralazine (99.9%) was purchased from Sigma, whereas potassium hexacyanoferrate(III), NaOH, HCl, ferric chloride and acetic acid were purchased from Merck (Darmstadt, Germany) and used without further purification. Phosphoric acid (84%–85%) was purchased from Fluka (Fluka, Buchs, Switzerland). All solutions were prepared in distilled water. Acetic acid solution (0.1 M) was prepared by dissolving the appropriate amount of acetic acid in water and adjusting to the desired pH by NaOH solution (0.1 M). All experiments were performed at ambient temperature (25 ± 2 °C).

2.3. Sample treatment

Prior to analysis, three tablets of HY (25 mg HY per tablet, each tablet 2.0 g) and HY (50 mg HY per tablet, each tablet 2.0 g) were ground separately. The sample powder (5.0 mg) was accurately weighed using an analytical balance, and then dissolved in distilled water. The solution was filtered and the filtrate was transferred to a 100 mL volumetric flask. Subsequently, the solution was diluted to the mark, mixed well and maintained at 4 °C.

2.4. Colorimetric detection of hydralazine

1.0 mL of 0.01 mol L^{-1} acetic acid buffer (pH ~ 3) and an appropriate volume of 10 μg mL^{-1} HY solution were added in a 10 mL calibrated flask. Subsequently, 1.0 mL of 100 μg mL^{-1} $K_3[Fe(CN)_6]$ solution and 1.5 mL of 100 μg mL^{-1} Fe^{3+} solution were added in succession. The mixture was then diluted to the mark with distilled water and mixed. Then, within 9–10 min, a portion of the mixture was transferred into a 1 cm spectrophotometric plastic cell to record absorbance. The absorbance of solution was measured at 700 nm against a blank prepared with same reagent concentrations, except for the HY. It should be noted that the order of addition of reagents is very important, even critical. The UV-vis spectrum obtained by changes in color of the mixture in the presence of HY is shown in Fig. 2.

3. Results and discussion

3.1. Mechanism of detection of hydralazine

The mechanism of the formation of PBNPs is shown in Fig. 1. It should be noted that the absorption of PBNPs is not observed in the presence of other reagents without HY in the region of 500–800 nm. By the addition of HY as a reducing agent, an absorption peak appeared at about 700 nm, indicating the formation of PBNPs. Fig. 2 shows the absorption peaks of PBNPs with different concentrations of HY. The mechanism[26] of the synthesis of the PBNPs is suggested in the following equations:

$$Fe^{3+} + HY \leftrightarrow Fe^{2+} + HY_{(OX)} + 2H^{+} \quad (1)$$

$$K_3[Fe^{3+}(CN)_6] + Fe^{2+} \leftrightarrow K_3Fe^{3+}[Fe^{2+}(CN)_6] \quad (2)$$

where $HY_{(OX)}$ is oxidized form of hydralazine. The order of addition of the reagents as stated in section 2.4. is very important to obtain PBNPs in the solution.

3.2. Effect of reaction time

Fig. 3 shows the changes of absorbance at 700 nm *versus* time. In the first few minutes from initiation of the reaction, the color of the solution changes to blue-green and the absorbance changes slowly, and then the absorbance reaches a maximum after about 9–10 min and remains nearly constant afterwards; therefore, all the absorbance measurements were performed within 9–10 min from addition of the Fe^{3+} solution.

3.3. Characterization studies

Transmission electron microscopy (TEM) was used to obtain images of as-prepared PBNPs. Fig. 4 shows the TEM image of the PBNPs and the size distribution of nanoparticles, which had an average size of about 11–13 nm.

3.4. Effect of pH of solution

The effect of the acidity of the solution on the absorbance intensity of the reaction system was investigated in different reaction mediums such as phosphate, acetic acid and hydrochloric acid solutions. This parameter has a critical effect on the formation of PBNPs. Generally, when the pH was higher than 3, Fe^{3+} ions begin to hydrolyze and precipitate. The experimental results showed that the absorbance intensity of the PBNPs in hydrochloric acid solution and acetic acid was the highest. It is well known that HY is a hydrazine derivative having a reducing ability and that the reaction between HY and Fe^{3+} is a redox reaction. Therefore, HY can reduce Fe^{3+} ion at room temperature in solution. Since H^+ was produced from the reaction between HY and Fe^{3+} ions, consumption of H^+ can accelerate Fe^{3+} ion reduction, and low pH media (pH < 2.0) are not suitable for the reaction. Moreover, a pH media more than 4 is not suitable for the reaction because of ferric hydroxide formation.

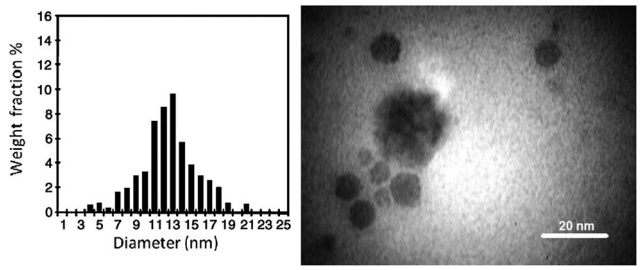

Fig. 4 Transmission electron microscopy image of PBNPs and the size histogram of the PBNPs.

Furthermore, PBNPs are unstable at higher pH values, as they then transform to $Fe(OH)_3$;[11,26] therefore, pH = 3 was selected for further analysis. The pH dependence of the reduction process was studied in the range 2.0–6.0. Fig. 5 shows the effect of the acidity of the solution on the absorbance intensity. Note that acetic acid was selected to produce the acidic condition. It has two roles: (a) to provide acidic conditions (pH = 3) and (b) to fix the pH of solution (*i.e.*, it works as a buffer). Therefore, different concentrations of the acetic acid solution were investigated and the optimum concentration was determined (Fig. 6), and the highest absorbance intensity was obtained at 0.01 mol L^{-1} acetic acid.

3.5. Effect of stabilizer

Generally, nanoparticles formed by colloidal methods have a high free energy state; therefore, they tend to aggregate due to van der Waals forces, which lowers their energies. Agglomeration and flocculation can be prevented by increasing repulsive contribution to the potential energy.[27,28] To prevent PBNPs from agglomerating, a protective agent or stabilizer is very important. Surfactants and polymers are common stabilizers that have been used as stabilizers to prevent nanoparticle agglomeration because they provide steric.[27] In this study triton X-100 was selected as stabilizer to prevent PBNPS agglomeration. It has been reported that triton X-100 is a

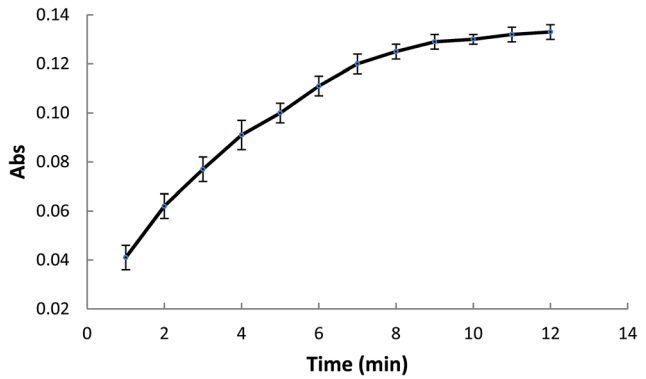

Fig. 3 Effect of reaction time from addition of Fe^{3+} solution on the absorbance [composition of 10 mL solution: 1 μg mL^{-1} HY; 0.01 mol L^{-1} HCl; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}; $[Fe^{3+}]$: 15 μg mL^{-1}, each data point is the average of 5 determinations].

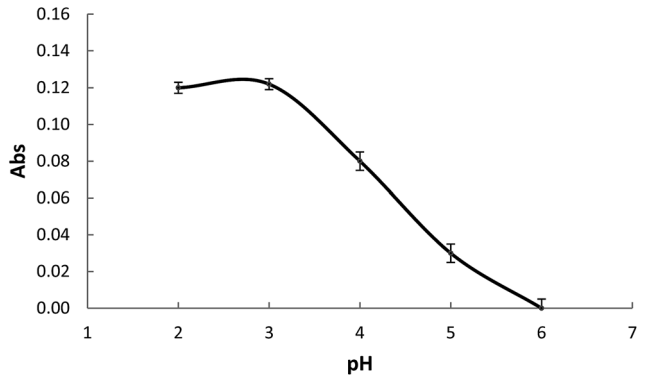

Fig. 5 Effect of pH variation on the intensity absorbance [composition of 10 mL solution: 1 μg mL^{-1} HY; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}; $[Fe^{3+}]$: 15 μg mL^{-1}, each data point is the average of 5 determinations].

suitable surfactant for use as a stabilizer for different nanoparticles.[29–31] The stock solution of stabilizer was obtained by dilution of Triton X-100 in deionized water with a 1 : 100 ratio (1% W/V); moreover, different amounts of surfactant stock solution (1% (w/v)) were added to the reaction mixture. The results obtained (not shown) revealed that the addition of more than 0.5 mL of the surfactant solution has no significant effect on absorption intensity; thus, 0.5 mL of 1% solution of surfactant was chosen as optimum value.

3.6. Effect of Fe^{3+} concentration

The effect of Fe^{3+} concentration on the absorption intensity of the reaction was investigated, and the results are shown in Fig. 7. As can be seen, when the Fe^{3+} concentration was in the range of 5.0–20.0 μg mL^{-1} in the presence of 1 μg mL^{-1} of HY, the absorption intensity of the system reached the maximum value. Therefore, the Fe^{3+} concentration of 15.0 μg mL^{-1} was chosen and used in the further study. However, when the Fe^{3+} concentration was low, the absorption intensity decreased due to an incomplete reaction.

3.7. Evaluation of the performance of the method

Our method showed good linearity over the calibration range of 0.4–2.0 μg mL^{-1}, and the linear regression equation was $y = 0.1224x - 0.0297$ with a correlation coefficient (R^2) of 0.996 ($n = 8$). The curve is shown in Fig. 8. The limit of detection ($3S_b$) was calculated as 0.33 μg mL^{-1}. The relative standard deviation (R.S.D.) for determination of 0.5 μg mL^{-1} and 1.0 μg mL^{-1} of hydrazine was 2.64% and 2.3% ($n = 5$), respectively. A comparison between the proposed method and other methods for the determination of hydralazine are presented in Table 1. The proposed method has shown better or comparable limit of detection values compared with a variety of methods reported in the literature for the determination of HY.

3.8. Interferences studies

In order to study the effect of various species on the determination of HY concentration, a fixed amount of HY (1 μg mL^{-1}) was taken with different amounts of foreign species and the recommended procedure was followed. The influence of some possible coexisting foreign substances, including inorganic ions (K^+, Ca^{2+}, Na^+, F^-, NO_3^-, HCO_3^-, Cl^-) and organic compounds (ascorbic acid, starch, glucose and sucrose), was tested for the analysis of real samples. A relative error of 5% was considered tolerable. The results showed that vitamin C and glucose interfered with the determination even with an equal amount of HY; however, species that are usually found in HY tablets do not have severe effects on the determination. In contrast, other species, including K^+, Ca^{2+}, Na^+, F^-, NO_3^-, HCO_3^-, Cl^-, sucrose and starch, even at a 50-fold higher concentration than that of HY (1 μg mL^{-1}), did not show any interference. The results are shown in Table 2.

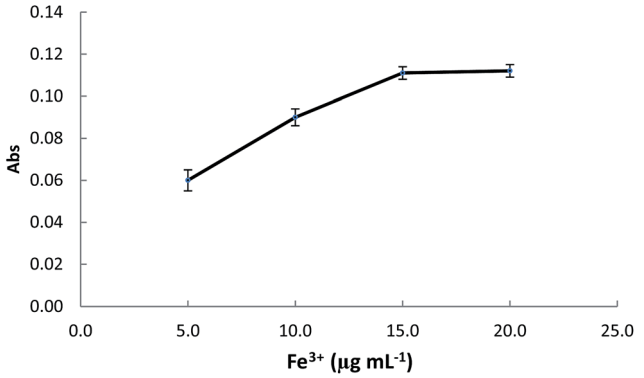

Fig. 7 Influence of amount of Fe^{3+} [condition of 10 mL solution: 1 μg mL^{-1} HY; 0.01 mol L^{-1} CH_3COOH; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}, each data point is the average of 5 determinations].

3.9. Determination of hydralazine concentration in real sample

The proposed method was successfully applied to the determination of HY concentration in tablet samples (25 mg per

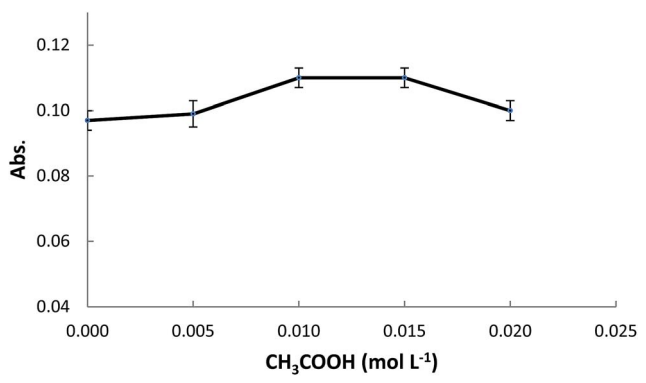

Fig. 6 Influence of different amounts of acetic acid: [composition of 10 mL solution: 1 μg mL^{-1} HY; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}; [Fe^{3+}]: 15 μg mL^{-1}, each data point is the average of 5 determinations].

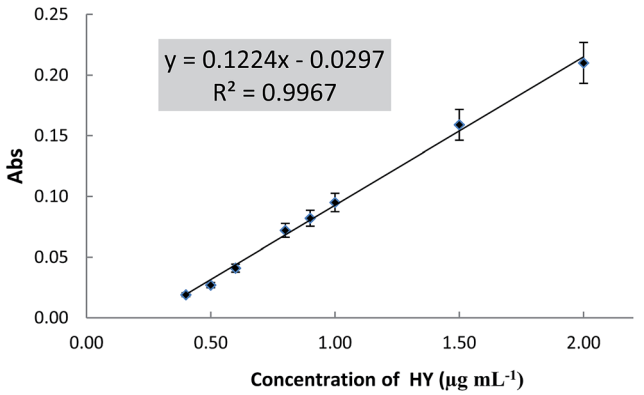

Fig. 8 The linear relationship between the absorbance and concentrations of HY. [Composition of 10 mL solution: 0.4, 0.5, 0.6, 0.8, 0.9, 1.0, 1.5, 2.0 μg mL^{-1} HY ($n = 8$); 0.01 mol L^{-1} CH_3COOH; Triton X-100, 0.05% V/W; $K_3[Fe(CN)_6]$, 10 μg mL^{-1}; [Fe^{3+}], 15 μg mL^{-1}; each data point is the average of 3 determinations].

Table 1 Comparison of the purposed method with some methods reported in literature for determination of HY concentration

Analytical technique	Sample matrix	LDR[a] (μg mL^{-1})	LOD[b] (μg mL^{-1})	Ref.
Spectrophotometric method	Tablet	0.4–2	0.33	This work
Spectrophotometric method	Tablet, capsule	0.1–12	DNA[c]	19
Spectrophotometric method	Tablet	2–10	0.50	20
Derivative spectroscopy method	Tablet	0.5–4.0	DNA[c]	32
Chemiluminescence method (time-resolved)	Tablet	0.2–5	0.2	33
Kinetic potentiometric method	Tablet	80–1600	16.0	34
Electrochemical method (ion-selective electrode)	Tablet	64–16 010	1.25	24
Electrochemical method (screen printed electrode)	Tablet	0.01–4.7	0.003	25

[a] Linear dynamic range (LDR). [b] Limit of detection (LOD). [c] Data is not available (DNA).

Table 2 Determination of HY concentration in the presence of various species. [Composition of 10 mL solution: 1 μg mL^{-1} HY; 0.01 mol L^{-1} CH_3COOH; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}; [Fe^{3+}]: 15 μg mL^{-1}]

Interfering species[a]	Tolerated ratio $[S_{species}]/[C_{HY}]$
K^+, Na^+, Cl^-, NO_3^- starch	100
Ca^{2+}, F^-, HCO_3^-, sucrose	50
Glucose, ascorbic acid	1

[a] All cations were prepared from nitrate and chloride salts, and anions were prepared from sodium and/or potassium salts.

tablet and 50 mg per tablet) using a standard addition method. Three tablets (25 mg and 50 mg of HY per tablet, purchased from a local pharmacy) were finely powdered and mixed with 2.0 g of powder (equal to the weight of one tablet), and the mixture was accurately weighed and dissolved in 100 ml distilled water. The mixture was stirred for few minutes and filtered through a filter paper. The filtered solution (the prepared drug solution) was analyzed using standard addition and the proposed method. In order to validate the methodology developed in this study, a recovery test was also carried out. The recovery of each measurement was calculated by comparing the results obtained before and after the addition of the HY standard solutions (Table 3).

Table 3 Results of determination of HY concentration in tablet samples by a standard addition method [composition of 10 mL solution: 0.01 mol L^{-1} CH_3COOH; Triton X-100: 0.05% V/W; $K_3[Fe(CN)_6]$: 10 μg mL^{-1}; [Fe^{3+}]: 15 μg mL^{-1}]

Sample	Added (μg mL^{-1})	Expected (μg mL^{-1})	Identified[c] (μg mL^{-1})	Recovery (%)
Tablet 1[a]	0	0.5	0.48 ± 0.04	95.50
	0.3	0.8	0.81 ± 0.01	100.7
	0.6	1.1	1.10 ± 0.01	100.0
Tablet 2[b]	0	0.5	0.52 ± 0.03	104.0
	0.3	0.8	0.72 ± 0.02	96.30
	0.6	1.1	1.13 ± 0.01	102.7

[a] Tablet (50 mg HY per tablet). [b] Tablet (25 mg HY per tablet). [c] Average of three determinations.

4. Conclusion

In this study, a new and simple optical assay is proposed for the determination of HY concentration. The assay is based on the formation of PBNPs induced by the analyte itself. As a consequence, there was an increase in the absorbance with increase in the HY concentration, allowing for analyte quantification based on the absorption at a single wavelength. Comparison between the method developed here and some other previously reported analytical methods for the determination of HY concentration is summarized in Table 1. We believe that the proposed method is very simple, inexpensive and shows an excellent detection limit in comparison to most other methods. Furthermore, HY could be detected at a sub-ppm concentration level (without any pre-concentration step) by the naked eye alone. Moreover, this method provides good sensitivity for detecting HY without resorting to advanced or complex readout equipment.

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