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Flow-injection chemiluminescence determination of tryptophan through its peroxidation and epoxidation by peroxynitrous acid

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Abstract

A flow-injection chemiluminescence method for the determination of tryptophan was proposed, which was based on an intense chemiluminescence of tryptophan in hydrogen peroxide–nitrite–sulfuric acid medium. The chemiluminescence reaction was attributed to peroxidation and epoxidation of tryptophan by peroxynitrous acid, and subsequent decomposition of the formed dioxetane. The chemiluminescence intensity was linear with tryptophan in the range of 6.0×10^{-7} to 3.0×10^{-5} mol l^{-1} and the limit of detection (S/N = 3) was 1.8×10^{-7} mol l^{-1}. The proposed method was applied to the analysis of tryptophan in pharmaceutical preparations and human serum.

Keywords: Chemiluminescence; Peroxynitrous acid; Flow-injection; Tryptophan

1. Introduction

Tryptophan was an important amino acid that occurred in natural proteins. It was the precursor of the neurotransmitter serotonin [1], and played an important role in brain function and related regulatory mechanisms [2–4]. Up to now, several analytical methods for the determination of tryptophan, including voltammetry [5,6], HPLC [7,8], spectrofluorimetry [9], spectrophotometry [10] and capillary electrophoresis [11] had been reported.

Because of high analytical frequency, simple and inexpensive instrumentation, chemiluminescence had extensively been used to the analysis of a wide variety of inorganic and organic substance [12,13]. In the last two decades, several chemiluminescence methods had been exploited for the determination of tryptophan. One kind of the known chemiluminescence methods was based on the oxidization reaction of tryptophan with acidic cerium (IV) [14] or permanganate [15,16] and with basic hydrogen peroxide in the presence of iron (III) or copper (II) as catalyst [17,18]. However, the chemiluminescence method based on homogeneous chemical redox reactions mentioned above suffered from high interference from reducible substances such as cysteine [14], ascorbic acid [19] and protein [20,21], respectively, which were limited to the determination of tryptophan in pharmaceutical preparations. Another method was electrogenerated chemiluminescence method, which was based on the reaction of hydrogen peroxide with an oxidation product of tryptophan at a Pt electrode [22]. But the electrogenerated chemiluminescence method showed poor reproducibility due to electrode fouling [23]. Still, a simple and selective method to measure tryptophan with high sensitivity would be highly desirable.

The peroxynitrous acids (*cis*-peroxynitrous acid, *trans*-peroxynitrous acid and the excited-state peroxynitrous acid) are superior in chemiluminescence analysis to such oxidant as cerium (IV), permanganate and hydrogen peroxide. Peroxynitrous acids are both powerful oxidizing and peroxidizing agents in acid medium [24,25]; they can oxidize and peroxidize a large number of organic and inorganic substances such as quinolines and carbonate to produce intense chemiluminescence [26,27]. Moreover, excited-state peroxynitrous

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acid ($ONOOH^*$) can also emit a weak chemiluminescence during its isomerization into nitrate [28,29]. The energy of $ONOOH^*$ can easily transferred to a fluorophore intentionally added to the weak chemiluminescence system, so that in the presence of fluoroquinolones the chemiluminescence intensity is enhanced [30]. In addition, peroxynitrous acids can be conveniently synthesized on-line by mixing acidic hydrogen peroxide with nitrite in a simple flow-injection system [31]. However, to the best of our knowledge, no work concerned peroxynitrous acids application in biological analysis area.

In this paper, an intense chemiluminescence emission was observed when tryptophan–sodium nitrite mixed solution was injected into acidic hydrogen peroxide solution. The chemiluminescence mechanism was discussed. In addition, a high selective flow-injection chemiluminescence method was proposed for the determination of tryptophan in pharmaceutical preparations and human serum.

2. Experimental

2.1. Chemicals

L-Tryptophan was of biochemical-reagent grade and was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The stock standard solution of tryptophan (1.00×10^{-3} mol l^{-1}) was prepared by dissolving 0.0204 g of L-tryptophan in water, and diluting to 100 ml with water. The solution was kept in the refrigerator at 4 °C. Standard working solutions were prepared daily by appropriate dilution of the stock solution with water. All other reagents were of analytical reagent grade. The hydrogen peroxide used was purchased from Xi'an Chemical Reagent Plant (Xi'an, China). The H_2O_2 solution (0.25 mol l^{-1}) was standardized with standard potassium permanganate. Twice distilled water was used throughout the experiments.

2.2. Apparatus

The flow-injection system, as shown in Fig. 1, was an IFFM-D-FI-CL analysis system (Xi'an Remax Electronic Science-Tech Co. Ltd., China). The flow-injection system used consisted of two peristaltic pumps and a six-way injection valve. PTFE tube (0.8 mm i.d.) was used to connect all components in the flow system. One peristaltic pump was used to deliver sodium nitrite and sample solutions. The two solutions were mixed in a Y-shaped mixing element (Y1) and then the mixed solution was injected into carrier solution using a six-way valve equipped with a 120 μl sample loop. The other peristaltic pump was used to deliver the carrier (sulfuric acid) and hydrogen peroxide solutions. The second Y-shaped mixing element (Y2) was used for mixing carrier (sulfuric acid) and hydrogen peroxide solutions. A mixing coil (glass tubing, 100 mm × 1 mm i.d.) after the second Y-shaped mixing element (Y2) was used as flow cell, and was placed in front of the photomultiplier tube (PMT) (Model R105UH, Hamamatsu, Japan). The chemiluminescence signal produced in the flow cell was collected with the PMT and recorded with a computer equipped with chemiluminescence analysis system software (Xi'an Remax Electronic Science-Tech Co. Ltd., China). The PMT was operated at −900 V. The fluorescence spectra were monitored using RF-540 fluorescence spectrometer (Shimadzu, Japan).

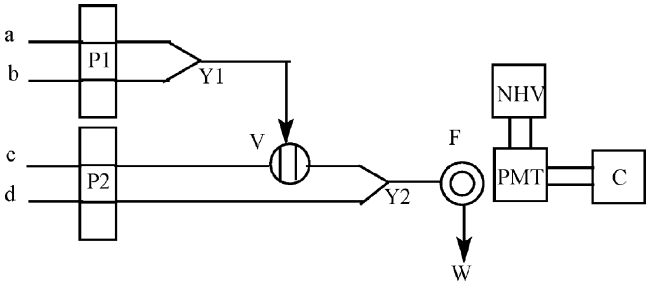


Fig. 1. Schematic diagram of the flow-injection chemiluminescence manifold used for the determination of tryptophan: P1 and P2, peristaltic pump; Y1 and Y2, three-way pipe; V, six-way valve; F, flow cell; W, waste; NHV, negative high voltage; PMT, photomultiplier tube; C, computer; a, sample stream; b, sodium nitrite stream; c, sulfuric acid carrier stream; d, hydrogen peroxide stream.

2.3. Procedure

2.3.1. General procedure

As shown in Fig. 1, flow lines were inserted into the sample (or standard) solution, sodium nitrite solution, sulfuric acid solution and hydrogen peroxide solution, respectively. By keeping the valve in washing position, sulfuric acid and hydrogen peroxide solutions were continuously pumped into the manifold until the baseline was established on the recorder. Then a mixture of the sample solution and sodium nitrite solution was injected into the sulfuric acid carrier solution. The carrier solution was then merged with hydrogen peroxide solution in the second Y-shaped mixing element (Y2) before the flow cell. When the mixed solution flowed into the cell, chemiluminescence signal was recorded. Calibration graphs were constructed by plotting the chemiluminescence intensity (peak height) versus the concentration tryptophan.

2.3.2. Procedure for the determination of tryptophan in pharmaceutical preparations and human serum

The compound amino acids injection that contained 18 amino acids injection was diluted with water so that final concentration was in the working range. Healthy human serum specimen, obtained from the hospital of Northwest University, Xi'an, was stored in refrigerator at 4 °C until assay. The human serum was diluted 20 times with water. Other measurements were performed as general procedure mentioned above.

2.3.3. Procedure for chemiluminescence kinetic profiles

The chemiluminescence kinetic profiles were obtained using batch method. Five milliliters of mixed solution of hydrogen peroxide and sulfuric acid was added to a reaction cell which was placed in front of the PMT. Then 5.0 ml of tryptophan solution, sodium nitrite–tryptophan mixed solution or sodium nitrite solution was rapidly injected into the reaction cell through a fill orifice by an injector, respectively. The chemiluminescence signal produced in the reaction cell was recorded.

2.3.4. Procedure for chemiluminescence spectrum

The chemiluminescence spectrum was achieved with a set of interference filters. The filters were set between the flow cell and the PMT. Other procedures described as general procedure were adopted to obtain the chemiluminescence intensity at different wavelength bands.

3. Results

3.1. Characteristics of chemiluminescence

Experiments showed that a weak chemiluminescence was observed when nitrite reacted with hydrogen peroxide in sulfuric acid medium (Fig. 2(b)). The chemiluminescence reaction resulted from excited-state $ONOOH^*$ as shown by previous studies [24–31]. The internal time between the beginning of the chemiluminescence and the achievement of its maximum signal value was 2.5 s. The lingering time was due to the requirement of conversion from *cis*-ONOOH to $ONOOH^*$ [32]. When tryptophan was added in the weak chemiluminescence system, the time that peak appeared was 1.6 s that was shorter than 2.5 s, and the peak height (chemiluminescence intensity) increased greatly (Fig. 2(c)).

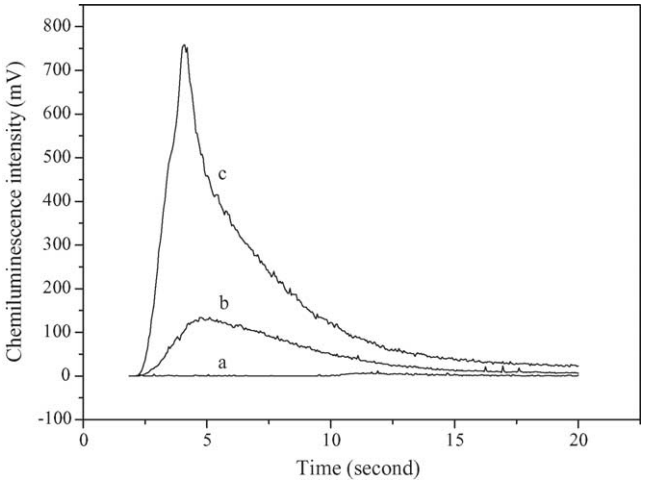


Fig. 2. Chemiluminescence dynamic response curves of chemiluminescence reaction of 0.25 mol l^{-1} hydrogen peroxide–0.20 mol l^{-1} sulfuric acid with (a) 2.0×10^{-6} mol l^{-1} tryptophan, (b) 0.10 mol l^{-1} sodium nitrite and (c) 0.10 mol l^{-1} sodium nitrite and 2.0×10^{-6} mol l^{-1} tryptophan in batch mode.

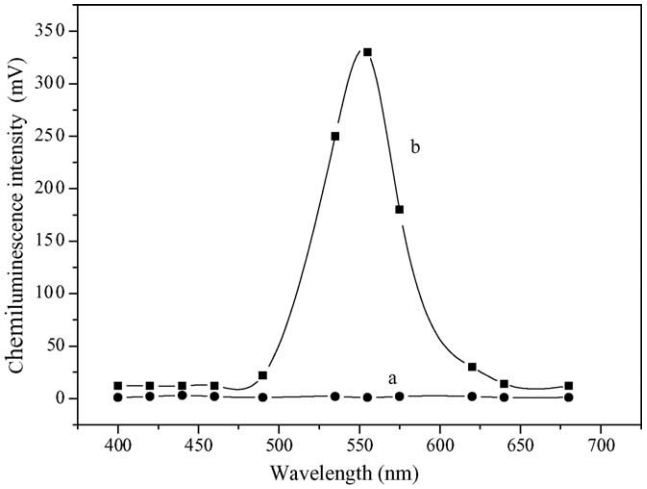


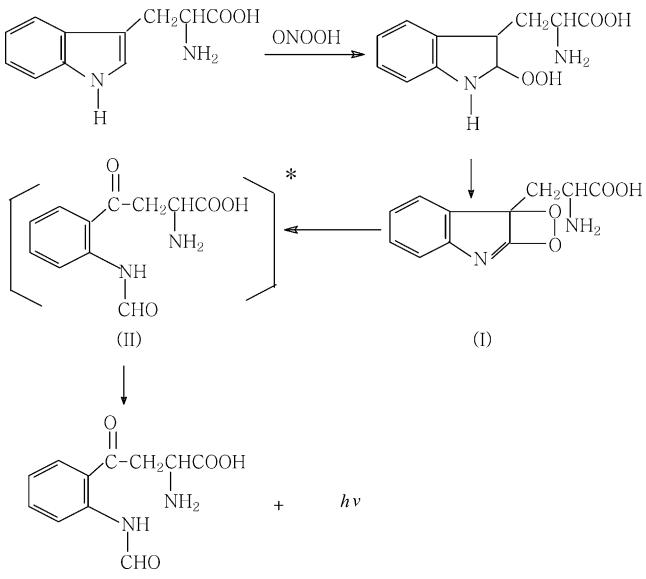
Fig. 3. Chemiluminescence spectra in 0.25 mol l^{-1} hydrogen peroxide–0.10 mol l^{-1} sodium nitrite–0.20 mol l^{-1} sulfuric acid system in the absence (a) and the presence (b) of 1.0×10^{-5} mol l^{-1} tryptophan.

The fluorescence and chemiluminescence spectra were examined in order to obtain more information about the chemiluminescence mechanism. The fluorescence spectra were recorded in the range of 300–700 nm in tryptophan–sulfuric acid solution. Only one fluorescence peak (λ_{max} = 355 nm) was observed. The fluorescence peak was from tryptophan itself [33]. After hydrogen peroxide or sodium nitrite was separately added into the tryptophan–sulfuric acid solution, the maximum wavelength and the peak intensity (λ_{max} = 355 nm) hardly changed. However, after adding small amount of sodium nitrite into tryptophan–hydrogen peroxide–sulfuric acid solution, the fluorescence peak (λ_{max} = 355 nm) disappeared and no any fluorescence emission was observed. These results indicated that tryptophan was oxidized by peroxynitrous acids to be some non-fluorescence products. That is, the chemiluminescence did not originate from the so-called energy transfer from the $ONOOH^*$ to tryptophan.

The chemiluminescence spectra in hydrogen peroxide–nitrite–sulfuric acid solution in the absence and the presence of tryptophan were also recorded in the range of 400–680 nm using flow-injection method. When tryptophan was absent, no obvious chemiluminescence spectrum was observed (Fig. 3(a)). The reason was that the CL from $ONOOH^*$ was too weak to penetrate the interference filters. The chemiluminescence spectrum in the presence of tryptophan only showed one peak band (490–620 nm) (Fig. 3(b)), which was in good agreement with the chemiluminescence spectra that was produced by oxidization of tryptophan by peroxynitrite in alkaline solution [34]. Moreover, it was also reported that the reaction of tryptophan with singlet oxygen also accompanied a chemiluminescence [35]. These chemiluminescence phenomena were considered as they originated from peroxidation and epoxidation of tryptophan by singlet oxygen and peroxynitrite [36,37]. Thus, The emitting species should be excited-state oxidation product resulted from decomposition of the formed dioxetane, epoxidized product of tryp-

tophan by peroxynitrous acid [38,39], rather than the weak chemiluminescence of excited-state ONOOH* enhanced by tryptophan.

Based on above discussion, the possible chemiluminescence mechanism was suggested as follows. In acid solution, hydrogen peroxide reacted with nitrite produced peroxynitrous acids. Then the peroxynitrous acids oxidized tryptophan to form a transient dioxetane (I) [17]. The dioxetane decomposed to an excited intermediate (II) [40]. An intense chemiluminescence was observed when the excited intermediate (II) went back to its ground state. In its simple form, the intense chemiluminescence mechanism stated above was attributed to the following reactions:



3.2. Optimization of the experimental conditions

A series of experiments were conducted to establish the optimum analytical conditions. The parameters optimized included selection of carrier solution, nitrite and hydrogen peroxide concentrations, as well as the flow rate for the FIA system.

3.2.1. Selection of carrier solution

Because of no peroxynitrous acids forming in alkaline or neutral solution [41], neither the weak chemiluminescence from ONOOH* nor the intense chemiluminescence from tryptophan–sodium nitrite–hydrogen peroxide solution was observed in alkaline or neutral solution. The weak chemiluminescence and the intense chemiluminescence were observed when such inorganic acids as HCl, H_2SO_4, HNO_3 and H_3PO_4 were used as carrier solution. When sulfuric acid was used as carrier solution, not only was the maximum ratio of the intense chemiluminescence signal to blank chemiluminescence signal from the reaction of nitrite with hydrogen peroxide obtained, but also the best reproducibility for monitoring tryptophan was achieved. Thus, sulfuric acid was selected as carrier solution for the determination of tryptophan in the proposed chemiluminescence system.

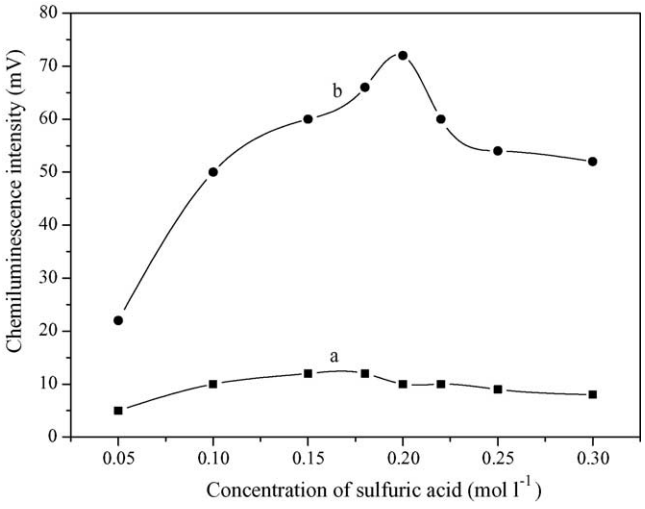


Fig. 4. Effect of sulfuric acid concentration on the chemiluminescence intensity in 0.10 mol l^{-1} sodium nitrite–0.25 mol l^{-1} hydrogen peroxide in the absence (a) and the presence (b) of 2.0×10^{-6} mol l^{-1} tryptophan.

The effect of sulfuric acid concentration on the chemiluminescence intensity in the presence of 2.0×10^{-6} mol l^{-1} tryptophan was shown in Fig. 4. The most intense chemiluminescence intensity was obtained at 0.20 mol l^{-1} sulfuric acid. Therefore, 0.20 mol l^{-1} sulfuric acid was used throughout the experiments.

3.2.2. Effect of hydrogen peroxide concentration

The effect of hydrogen peroxide concentration on the chemiluminescence intensity in the presence of 2.0×10^{-6} mol l^{-1} tryptophan was investigated over the range of 0.04–0.36 mol l^{-1}. The chemiluminescence intensity increased as the hydrogen peroxide concentration was increased from 0.04 to 0.24 mol l^{-1}. With the hydrogen peroxide concentration increasing from 0.24 to 0.36 mol l^{-1}, the intensity reached a maximum value and kept constant (Fig. 5). Therefore, 0.25 mol l^{-1} hydrogen peroxide was used throughout the experiments.

3.2.3. Effect of sodium nitrite concentration

The effect of sodium nitrite concentration on the chemiluminescence intensity was examined by using 2.0×10^{-6} mol l^{-1} tryptophan. As shown in Fig. 6, the chemiluminescence intensity rose as the sodium nitrite concentration was increased from 0.03 to 0.10 mol l^{-1} and reached its maximum value at 0.10 mol l^{-1}. The raising of nitrite concentration over 0.10 mol l^{-1} caused the decrease of the chemiluminescence intensity. The decrease resulted from the fast reaction of nitrite with hydroxyl radical ($OH^{\bullet}$) ($k = 1 \times 10^{10}$ mol^{-1} l s^{-1}, rate constant) that was the decomposition product of *trans*-ONOOH [42,43]. Therefore, 0.10 mol l^{-1} sodium nitrite was used throughout the experiments.

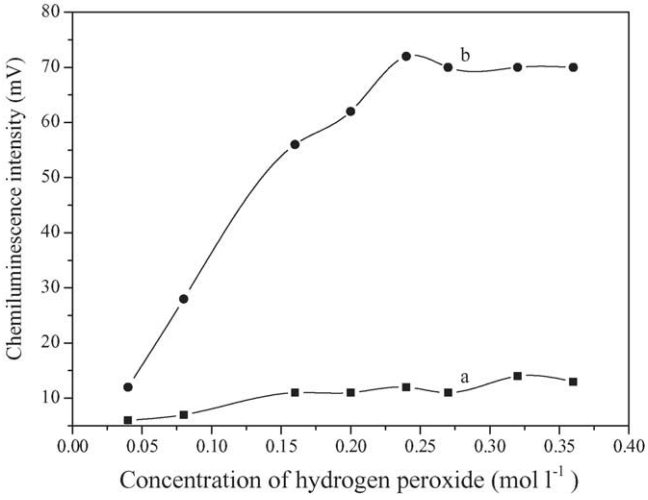


Fig. 5. Effect of hydrogen peroxide concentration on the chemiluminescence intensity in 0.10 mol l^{-1} sodium nitrite–0.20 mol l^{-1} sulfuric acid solution in the absence (a) and the presence (b) of 2.0×10^{-6} mol l^{-1} tryptophan.

3.2.4. Effect of flow rate

Pump P2 was used to deliver the carrier (sulfuric acid) and hydrogen peroxide solutions. Hydrogen peroxide solution and sulfuric acid carrier solution that contained nitrite and sample were first mixed at the second Y-shaped mixing element (Y2), and then the mixed solution was delivered by pump P2 to the flow cell placed in front of the PMT. Because peroxynitrous acid was short-lived species ($t_{1/2}$ ca. 1 s) [44,45], the raising of the amount of the on-line produced peroxynitrous acid reaching to the flow cell was favorable to raise the sensitivity of the proposed method. Except that the distance between Y2 and the flow cell was shorten as possible, the raising of the flow rate of pump P2 was the other way. The effect of the flow rate on the chemiluminescence intensity was examined in the range of 1.5–5.3 ml min^{-1}

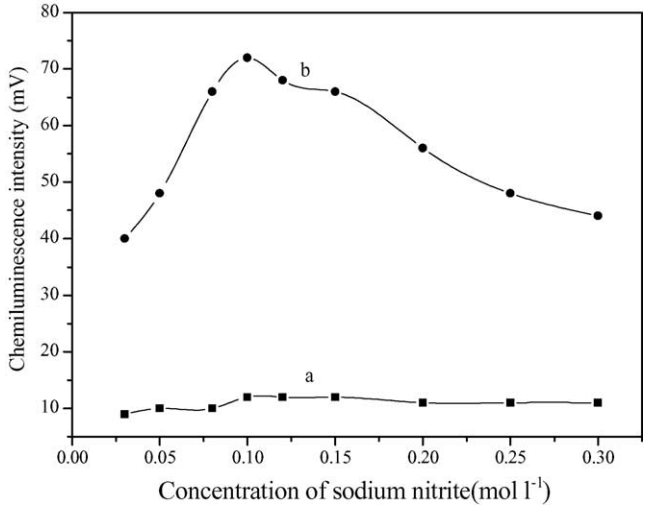


Fig. 6. Effect of sodium nitrite concentration on the chemiluminescence intensity in 0.25 mol l^{-1} hydrogen peroxide–0.20 mol l^{-1} sulfuric acid in the absence (a) and the presence (b) of 2.0×10^{-6} mol l^{-1} tryptophan.

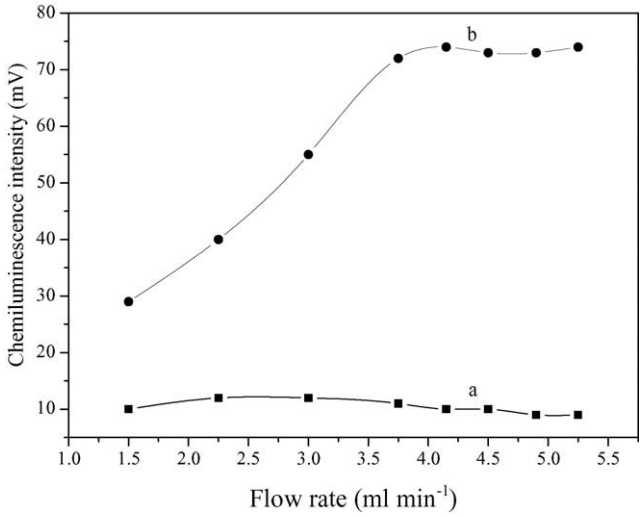


Fig. 7. Effect of flow rate on the chemiluminescence intensity in 0.10 mol l^{-1}sodium nitrite–0.25 mol l^{-1} hydrogen peroxide–0.20 mol l^{-1} sulfuric acid in the absence (a) and the presence (b) of 2.0×10^{-6} mol l^{-1} tryptophan.

(Fig. 7). The results showed that the chemiluminescence intensity rose sharply as the flow rate was increased from 1.5 to 4.2 ml min^{-1}. When the flow rate was increased from 4.2 to 5.3 ml min^{-1}, the chemiluminescence intensity reached a maximum value and kept constant. Thus 4.5 ml min^{-1} flow rate was used throughout the experiments.

3.3. Performance of the proposed method for tryptophan measurements

Under the selected experimental conditions, the chemiluminescence intensity was linear with tryptophan in the range of 6.0×10^{-7} to 3.0×10^{-5} mol l^{-1}. The detection limit was 1.8×10^{-7} mol l^{-1} (S/N = 3) and the relative standard deviation for 2.0×10^{-6} mol l^{-1} tryptophan ($n = 9$) was 1.1%. The linear regression equation was $I = 9.25 + 3.24 \times 10^{7}\, C$ (where I is chemiluminescence intensity and C the tryptophan concentration, units are mV and mol l^{-1}, respectively) with a correlation coefficient of 0.9995 ($n = 13$). The sample measurement frequency was calculated to be about 50 samples h^{-1}.

3.4. Interferences study

In order to assess the proposed method to the analysis of tryptophan in pharmaceutical dosage forms and biological samples, the interference of basic amino acids, commonly used excipients and additives, co-existing ions or the other compounds was examined. The solutions for this purpose contained 2.0×10^{-6} mol l^{-1} tryptophan and increasing amounts of interfering species. The tolerated limit for a foreign species was taken as the largest amount yielding a relative error less than 5% for the determination of tryptophan. The results of interference tests were listed in

Table 1
The tolerable concentration ratios of some interfering species to 2.0×10^{-6} mol l^{-1} tryptophan

Substance	Tolerable concentration ratio
Cation	
K^+, Na^+, Ca^{2+}, NH_4^+, Zn^{2+}	1000
Mg^{2+}, Mn^{2+}	500
Ni^{2+}, Al^{3+}, Pb^{2+}	100
Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}	5
Anion	
Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-	1000
Vitamin	
Thiamine hydrochloride (Vitamin B_1)	1000
Ascorbic acid (Vitamin C)	100
Riboflavin (Vitamin B_2), folic acid (Vitamin Bc)	50
Amino acid	
Valine, serine, arginine	500
Threonine, alanine, aspartic acid, phenylalanine	200
Histidine, cysteine, methionine, leucine, isoleucine	100
Glycine, glutamic acid, tyrosine, proline, lysine	50
Others	
Oxalic acid, urea	1000
Uric acid, starch, sorbitol	500
Glucose, sucrose, human serum albumin	200
Polyethylene glycol 6000, sodium lauryl sulfate, aniline	50
Indole-3-acetic acid	0.5

Table 1. The results showed that the proposed method has good selectivity. Although indole-based compound such as indole-3-acetic acid caused positive interference to a certain degree, which was due to the similarity of indole-3-acetic acid and tryptophan in chemical characteristics and molecular structure [38], dole-3-acetic acid at 0.5 times the tryptophan concentration was tolerable. Besides, 50 times aniline did not caused interference.

It was known that the major metabolites of tryptophan in human serum were indole and kynurenine derivatives [46]. The indole derivative included 5-hydroxytryptamine, 5-hydroxytryptophan, 5-hydroxyindoleacetic acid and 5-hydroxytryptophol. Among them, 5-hydroxytryptamine was staple and its content was far higher than the sum of other indole derivatives metabolites [46,47]. Moreover, the average content of tryptophan in healthy human serum was about 60 times higher than that of 5-hydroxytryptamine [48,49]. Therefore, the total indole derivatives concentration in healthy human serum was much lower than 0.5 times the tryptophan concentration. After human serum was diluted twenty times, the interference from indole derivatives metabolites of tryptophan could be neglected. On the other hand, the kynurenine derivatives metabolites, including kynurenine and 3-hydroxykynurenine, belonged to aniline derivative. It was reported that the total kynurenine derivatives concentration in healthy human serum was less than 0.05 times the tryptophan concentration [46,49,50], which was much lower than the tolerable concentration ratio of aniline to tryptophan. Therefore, the kynurenine derivatives metabolites in human serum had no effect on the determination of tryptophan.

3.5. Application

The method was applied to the determination of tryptophan in compound amino acid injection. The determination result of tryptophan in compound amino acid injection was shown in Table 2, which agreed well with that obtained by UV method [51]. Moreover, recovery studies were also carried out on sample solution to which known amounts of tryptophan standard solution were added. Each recovery was calculated by comparing the results obtained before and after the addition. As shown in Table 2, the recoveries were between 98 and 104% ($n = 5$).

The proposed method was also applied to the determination of tryptophan in human serum. The analysis results were listed in Table 3, which was within the normal range of

Table 2
Determination of tryptophan in compound amino acids injection

Sample	Proposed method[a] (mg)	UV method[a] (mg)	Added (10^{-6} mol l^{-1})	Found[a] (10^{-6} mol l^{-1})	Average recovery (%)
Injection (450 mg tryptophan in 500 ml)	459 ± 5	456 ± 7	1.00	1.04 ± 0.02	104
			4.00	3.97 ± 0.04	99
			8.00	7.85 ± 0.15	98

[a] Mean value ± S.D. ($n = 5$).

Table 3
Determination of tryptophan in human serum

Sample	Proposed method[a] (10^{-6} mol l^{-1})	Added[a] (10^{-6} mol l^{-1})	Found[a] (10^{-6} mol l^{-1})	Average recovery (%)
No. 1	52.1 ± 0.6	1.00	0.95 ± 0.02	95
		5.00	5.06 ± 0.08	101
No. 2	50.5 ± 0.5	1.00	0.98 ± 0.02	98
		5.00	4.94 ± 0.07	99
No. 3	47.8 ± 0.5	1.00	1.03 ± 0.03	103
		5.00	4.83 ± 0.08	97

[a] Mean value ± S.D. ($n = 5$).

25–53 mol l^{-1} [49,52]. At the same time, the standard addition recovery tests were taken in order to evaluate the validity of the proposed method for the determination of tryptophan in human serum. As shown in Table 3, the recoveries were between 95 and 103% ($n = 5$).

4. Conclusions

A flow-injection chemiluminescence method for the determination of tryptophan is described, which is based on the chemiluminescence reaction of peroxynitrous acid (ONOOH) with tryptophan in sulfuric acid solution. As compared with these known chemiluminescence methods in hydrogen peroxide –Fe^{3+} or Cu^{2+} alkaline solution, in acidic permanganate or cerium (IV) solution, the proposed method had superior selectivity, and avoided separation set-up. In addition, as peroxynitrous acid possesses both strong epoxidizing and peroxidizing ability, the chemiluminescence in hydrogen peroxide–nitrite–sulfuric acid medium may have potential application in pharmaceutical and biomedical analysis.

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