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SHORT COMMUNICATION

Rapid analysis of piperazine ferulate tablets by optic-fiber sensing technology and the similarity of ultraviolet spectra

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Abstract A rapid analysis method of piperazine ferulate tablets by optic-fiber sensing technology with UV–vis absorption spectrum was established. Qualitative and quantitative data were obtained and compared by maximum and minimum wavelength, absorbance and contrast spectra. Similarity method was used to identify authenticity of drugs. The difference of contents measured by this method and UV determination method in China Pharmacopoeia showed no statistical significance ($P > 0.05$), while the similarity can be used as a parameter to identify the authenticity of drugs.

1. Introduction

With drug seized-me-fast, drug quickly seized vehicles and other equipment, the quality of drugs can be rapidly identified. Nevertheless, these methods need development and improvement [1]. Over the past years, we have been studying the application of optic-fiber sensing technology to drug detection [2,3]. Optical-fiber is suitable for spot analysis and rapid drug test because of its special characteristics of being small, flexible and portable as well as low transmission loss [4–6]. In this paper, optic-fiber sensing technology is used to rapidly identify and analyze the content of piperazine ferulate tablets. In order to obtain more parameters from the ultraviolet spectra, this paper tries to explore a new method to identify the authenticity of drugs by comparing the similarity of full ultraviolet spectra between the sample map and the standard one.

2. Materials and methods

2.1. Reagents and drugs

Piperazine ferulate reference standard (Batch no.100834-200701) was obtained from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China); piperazine ferulate tablets (Hunan CommScope Pharmaceutical Ltd. 50 mg, Batch no. 091101,100601,100301) were purchased from the market.

2.2. Instrumentation

Optic-fiber chemical sensing device (FODT) was developed by Xinjiang Medical University and Xinjiang FOCS Biotech

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Development Co. Ltd.; UV–visible spectrophotometer (Cintra-40, GBC Scientific Equipment Pty Ltd., Australia) was utilized for the offline control UV determination.

2.3. Stock solution preparation

2.3.1. Configuration of the standard stock solution

A precisely weighed piperazine ferulate reference standard was dissolved in purified water and diluted quantitatively to obtain a 252.0 μg/mL standard stock solution.

2.3.2. Configuration of the sample solution

A crushed piperazine ferulate tablet was put, into a 1000 mL volumetric flask and diluted with purified water to the scale.

2.4. Qualitative identification of UV spectra on the optic-fiber sensing device

An accurate volume of 5 mL standard stock solution was diluted to 25 mL with purified water in a volumetric flask to obtain a 50.4 μg/mL solution. The standard ultraviolet absorption spectrum of the piperazine ferulate can be obtained by determining on the optic-fiber sensing device (0.5 mm probe, scanning wavelength range 220–500 nm). According to the requirement of software, the information of piperazine ferulate reference standard was entered and saved into the standard map database as a standard map of piperazine ferulate. Under the same condition, we determined the sample solution and obtained the ultraviolet absorption spectra of the sample tablet.

2.5. Quantitative determination on the optic-fiber sensing device

Based on the methods of determination in Section 2.4 and configuration of the sample solution in Section 2.3.2, we determined the piperazine ferulate sample solution. For accurate monitor in situ without any physical or chemical separation, dual-wavelength method was adopted on the optic-fiber sensing device. In this study, we chose 500 nm as the second detection wavelength because the piperazine ferulate solution cannot absorb light at 500 nm, but only the accessories can. Therefore, we can only eliminate the interference of accessories and directly get the absorbance and the concentration of solution using the reference standard method, which the software system requires. We selected three batches of piperazine ferulate tablets and determined six tablets of each batch to obtain results of their contents.

2.6. Quantitative comparison

Accurately weighed powder was dissolved in purified water, transferred to a 50 mL volumetric flask and diluted to the mark. A probe of 0.5 mm was directly inserted into the sample solution of piperazine to obtain the absorbance from the software system. At the same time, the solution was diluted 10 times and measured by the UV spectrophotometer [7]; then the concentration was calculated and paired *t*-test was carried out.

2.7. Identification of true, false and inferior drugs using similarity method

Sample preparation: We took one piperazine ferulate tablet ground it into powder, dissolved with purified water and diluted to 1000 mL in a volumetric flask (five repetitions), making "qualified drug" 5 copies of the sample solution. We took an appropriate amount of piperazine ferulate powder, dissolved and diluted it with purified water to compound series of solution with certain concentrations, making "inferior drug" 5 copies of the sample solution. The solution without piperazine ferulate was prepared, making "fake drug" 5 copies of the sample solution [8].

This study used two algorithms, namely, correlation coefficient method and similarity method. The equations are as follows:

1. Similarity method [9,10]

$$S = 1 - \frac{1}{n}\sum_{i=1}^{n}\left|\frac{X_i + Y_i}{X_i - Y_i}\right|$$

2. Correlation coefficient method [11]

$$R = \frac{\left[\sum_{i=1}^{n} X_i \times Y_i - \left(\frac{\sum_{i=1}^{n} X_i \times \sum_{i=1}^{n} Y_i}{n}\right)^2\right]^2}{\left[\sum_{i=1}^{n} X_i^2 - \left(\frac{\sum_{i=1}^{n} X_i \times \sum_{i=1}^{n} X_i}{n}\right)^2\right]\left[\sum_{i=1}^{n} Y_i^2 - \left(\frac{\sum_{i=1}^{n} Y_i \times \sum_{i=1}^{n} Y_i}{n}\right)\right]}$$

where X_i and Y_i are the absorbance of reference standard and sample determined at the same wavelength, respectively; n represents the number of scanning data points.

3. Results

3.1. Qualitative identification of the sample

The results showed that the max absorbance of standard UV absorption spectrum was at 286.2 nm and 309.5 nm, and the min absorbance at 253.4 nm; the max absorbance of sample UV absorption spectrum was at 286.8 nm and 310.7 nm, and the min absorbance at 253.2 nm. Both the λ_{max} of two solutions were within the range of Pharmacopoeia (268 ± 2 nm, 310 ± 2 nm), which indicated that the piperazine ferulate tablets could be identified by this optic-fiber sensing technology.

3.2. Quantitative identification of the sample

The results of three batches of piperazine ferulate tablets are shown in Table 1. All were within the range of labeled amount of Chinese Pharmacopoeia from 90% to 110%.

Table 1 Determination results of three batches of piperazine ferulate tablets (%).

Batch no.	1	2	3	4	5	6	RSD (%)
100301	104.2	103.2	104.9	103.8	104.9	96.2	3.02
091101	104.2	96.2	98.7	101.4	98.0	98.3	
100601	101.1	101.4	99.0	99.7	98.0	97.3	

3.3. Quantitative comparison of the new method and the reference method

Matched with t test, there was no significant difference between the two groups of data ($P>0.05$), both within the specified qualification range in "Chinese Pharmacopoeia" as shown in Table 2.

3.4. The results of identification by similarity

The results of two algorithms are listed in Tables 3 and 4. According to Table 3, the similarity of "qualified drug" was greater than 0.999 while the similarity of "fake drug" was less than 0.020. In Table 4, the similarity of "qualified drug" was greater than 0.980 and the similarity of "fake drug" was less than 0.5.

Table 2 Comparison of the two methods for the assay of piperazine ferulate tablets (%).

No.	Batch no.	Optic	RSD (%)	UV	RSD (%)
1	091101	102.8	0.4	102.3	0.6
2	100301	100.3	0.7	100.4	1.3
3	100601	102.2	0.9	101.8	1.2

Table 3 Similarity calculated by correlation coefficient.

Sample	1	2	3	4	5
Qualified	0.9998	0.9992	0.9997	0.9997	0.9990
Inferior	0.9899	0.9916	0.9929	0.9938	0.9963
Fake	0.0070	0.0192	0.0722	0.0526	0.0786

Table 4 Similarity calculated by the similarity system theory.

Sample	1	2	3	4	5
Qualified	0.9888	0.9838	0.9855	0.9954	0.9874
Inferior	0.3793	0.6606	0.8012	0.9379	0.8497
Fake	0.1686	0.1930	0.4253	0.0689	0.0310

3.5. Validation of the method

3.5.1. Linearity

The linearity of the piperazine ferulate reference standard was constructed by preparing a six-point calibration curve at different concentrations of 9.98, 19.96, 29.94, 39.92, 49.90, and 59.88 μg/mL by absorbance against the concentration of piperazine ferulate reference standard solution. The calibration curve indicates a good linearity ($r>0.9999$): $A=0.0064C+0.0008$ ($r=0.9999$, $n=6$).

3.5.2. Precision

The parameter was investigated at three levels of the sample (10.0, 40.0 and 60.0 μg/mL) for precision, namely, intra-day (three repetitions of each concentration, within one day) and inter-day repeatabilities (three repetitions of each concentration, on three consecutive days). The intra-day precision (RSD) of three levels of the sample solution was 3.13%, 0.75% and 0.59%, while inter-day precision (RSD) was 2.00%, 3.14% and 5.08%. The results indicated that the precision for this method was acceptable.

3.5.3. Recovery

Recovery was determined by adding three different volumes of standard solution to a certain amount of unfiltered sample solution. The results are shown in Table 5. The mean recovery of the three markers was 100.67%, 99.33% and 99.80% respectively, and the RSD was 0.70%, 0.47% and 0.30%.

4. Discussion

Determination of piperazine ferulate tablets on the optic-fiber sensing device proved that this method was in good accordance with UV determination method. Although the UV determination method is widely used for piperazine ferulate tablets, it involves sample solution filter, dilution, several removals and manipulations, which may become the potential sources of errors. For the optic-fiber sensing device, there is no need to filter, dilute several times and remove the sample solution, but just need to insert the probe directly into the solution when measured. Through the mathematical separation model of dynamic dual-wavelength spectrophotometer, the interference from accessories was eliminated. By choosing the different specifications of probes to change the optical path length, the determination analysis of high concentration can be made on the optic-fiber sensing device. Therefore, this

Table 5 Recovery test of piperazine ferulate.

No.	Initial amount (mg)	Added amount (mg)	Found amount (mg)	Recovery (%)	Average recovery (%)	RSD (%)
1	0.247	0.250	0.497	100.0	99.9	0.74
2	0.247	0.250	0.504	101.4		
3	0.247	0.250	0.500	100.6		
4	0.247	0.749	0.992	99.6		
5	0.247	0.749	0.992	99.6		
6	0.247	0.749	0.984	98.8		
7	0.247	1.248	1.492	99.8		
8	0.247	1.248	1.496	100.1		
9	0.247	1.248	1.488	99.5		

method reduces the operating time and steps, just as the original intention of rapid test.

In this study, the UV spectra similarity method was used to identify the authenticity of chemical drugs. If the correlation coefficient method was used to calculate the similarity, both the similarities of ''qualified drugs'' and ''inferior drugs'' were greater than or equal to 0.990 and the similarity of ''fake drugs'' was less than 0.080. When the system theory method was used, there were significant differences between the similarity of ''qualified drugs'' and ''inferior drugs''. Therefore, this study chose to combine the two methods of calculating the similarity as one of the parameters for identifying genuine, counterfeit and inferior drugs.

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