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Stochastic resonance is applied to quantitative analysis for weak chromatographic signal of Sudan I

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Abstract

Based on the algorithm of stochastic resonance, a new method improved the signal-to-noise ratio (SNR) of weak chromatography signal remarkably. An excellent quantitative relationship can be obtained between concentration and weak chromatography signals of Sudan I which was embedded in the noise background.
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Keywords: Stochastic resonance; Sudan I; Weak signal; HPLC-UV/VIS

1. Introduction

Noise has always been considered to be a source of disorder and a nuisance to be avoided. In order to avoid the effect of noise and improve the detection limit, chemometric methods, such as fast Fourier transform (FFT), wavelets transform (WT) and various smoothing and filtering algorithms, were widely used. In practice, these methods may result in tiny lost of useful information due to improper truncations. Stochastic resonance (SR), which was first introduced by Benzi and his co-workers to explain the periodicity of Earth's ice age, renders an entirely new way for detecting weak chromatographic signal [1]. SR is a phenomenon that manifests in nonlinear systems, whereby generally feeble input information (such as a weak signal) can be amplified and optimized by the assistance of noise [2]. For a system well characterized by linear-response theory (that is, with linear or "mildly" nonlinear internal dynamics) the signal-to-noise ratio (SNR) at the output must equal the SNR at the input, and any increase in the input noise will result in a decrease in the output SNR. In contrast, the signature of stochastic resonance is an increase in the output SNR with increased input noise [3]. Over the last two decades, SR has continuously attracted considerable attention. Typical SR behaviors have been found in many physical systems [4,5] and complex systems such as chemical reaction [6,7] and quantitative structure–activity relationship (QSAR) [8]; however, its application in the analysis field is seldom reported. In this Letter, based on the theory of stochastic resonance, output signal was enhanced by optimizing the parameters a and b, and the detection sensitivity of Sudan I with high performance liquid chromatography with ultraviolet/visible detection (HPLC-UV/VIS) was increased significantly.

Sudan I (1-phenylazo-2-naphthol, CAS 842-07-09) (Fig. 1) is an azo dye that causes tumors in the liver or bladder of rats, mice and rabbits. It is considered a possible human carcinogen and mutagen, and is classified as category 3 carcinogen by

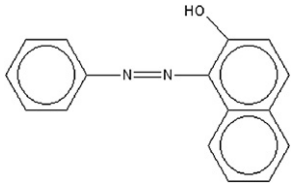

Fig. 1. Structure of Sudan I (1-phenylazo-2-naphthol, CAS 842-07-09).

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the International Agency for Research on Cancer (IARC). In some countries, the harmful contaminant is usually added to help retain the typical reddish colour of pepper-based products and meat derivatives, but this particular application is not allowed in the European Union and many other countries [9,10]. Based on the method published by European Commission (*Corrected method for the detection of Sudan, NEWS notification: 03/99*), Sudan I was extracted by acetonitrile and the extract was analyzed by HPLC in reversed phase (RP) after filtration. A variable UV/VIS detector is used for quantification, and as a result, the limit of quantization (LOQ) and limit of detection (LQD) were originally 0.100 and 0.030 μg/mL. After the application of SR, the LOQ and LOD were improved to 0.020 and 0.006 μg/mL, respectively. So SR can remarkably improve the signal-to-noise ratio (SNR) of HPLC-UV/VIS and make it possible to perform the trace analysis of Sudan I in some kinds of pepper-based products.

2. Theory and algorithm

Nonlinear Langevin equation has been applied to describe the phenomenon of SR. It is defined as follows [1,11,12]:

$$\frac{dx}{dt} = -U'(x) + MI(t) + C\xi(t), \tag{1}$$

where $I(t) = S(t) + N(t)$ denotes an input signal $S(t)$ and the intrinsic noise $N(t)$; $\xi(t)$ is the external noise, M and C are the adjustable parameters. $U(x)$ is the simplest double-well potential with the constants a and b characterizing the system

$$U(x) = -\frac{1}{2}ax^2 + \frac{1}{4}bx^4. \tag{2}$$

The symmetric double-well shows that the minima are located at $\pm x_m$, where $x_m = (a/b)^{1/2}$. A potential barrier separated the minima with the height given by $\Delta U = a^2/4b$. The barrier top is located at $x_b = 0$ [2]. When the input signal, noise and nonlinear system work coherently, the potential barrier can be reduced and the particle, which stays in one of the potential, may surmount the energy barrier and enter another potential well. Thus, the intensity of signals will increase and the detection of weak signal from noise background will be possible.

Suppose the input signal is a sinusoid, $I(t) = A\sin(\varpi_0 t)$, where A is the intensity of input signal, ϖ_0 is frequency of the input signal. Based on the adiabatic theory, the SNR can be described approximately as [1,13]

$$\mathrm{SNR} = \frac{\sqrt{2}\mu^2 A^2 e^{-\mu^2/4D}}{4D^2} = \sqrt{2}\Delta U\left(\frac{A}{D}\right)^2 e^{-\Delta U/D}. \tag{3}$$

The equation shows that the potential barrier ΔU and the noise intensity D decide the SNR of output signal. According to the theory, SR can be observed by adjusting input noise intensity D and the potential barrier ΔU. In previous literature [1], noise in analytical signals is often assumed to be Gaussian white noise, but added external noise, which is usually simulated, is somewhat colored. The addition of external colored noise will damage the characteristic of the intrinsic noise and result in the serious distortion of the obtained signals. In order to perform quantitative determination, in this Letter, M and C in Eq. (1) were set to 1 and 0, respectively, to keep the property of noise and reduce variable factors in SR algorithm, which means that the input signal will not be adjusted nor external noise will be added. Only the parameters of the system are modulated to match the input signal including real signal and intrinsic noise to achieve SR.

Eq. (1) is solved by a fourth-order Runge–Kutta method ($M = 1$ and $C = 0$). The input signal is first prepared by normalizing in $[-1, 1]$. The algorithm can be described as follows [1,12]:

$$x_{n+1} = x_n + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4), \quad n = 0, 1, \ldots, N-1,$$
$$k_1 = ax_n - bx_n^3 + u_n,$$
$$k_2 = a(x_n + k_1/2) - b(x_n + k_1/2)^3 + u_n,$$
$$k_3 = a(x_n + k_2/2) - b(x_n + k_2/2)^3 + u_{n+1},$$
$$k_4 = a(x_n + k_3/2) - b(x_n + k_3/2)^3 + u_{n+1},$$

where $u_n = I_n + \xi_n$, X is output signal. The final results can be obtained by inverse normalization of the output signals.

In this Letter, the algorithm was implemented in MATLAB 6.5 by the authors and the programs were performed on PIII.

3. Experimental

3.1. Chromatographic and detection conditions

The HP1090 system was equipped with SPD-10A VP UV-VIS detector. The N2000 chromatography data system (Zhejiang University Star Instrument Technology Co. Ltd.) was used with sampling frequency of 10 Hz. The samples were separated on a Lichrospher C_{18} (150 mm × 4.6 mm ID, 5 μm) column. The mobile phase was a mixture of acetonitrile-acidified water (165 ml acetic acid plus 1000 ml water) (20 : 80, V/V) at a flow-rate of 1.0 mL/min. The wavelength was set at 478 nm.

3.2. Reagents

Sudan I (1-phenylazo-2-naphthol) standard was purchased from Dr. Ehrenstorfer (Augsburg, Germany) (Lot 40517, Dye content 97.5%). Acetonitrile was HPLC-grade solvents and obtained from Merck (Darmstadt, Germany).

3.3. Sudan I solution preparation

Primary stock solution of Sudan I was made up to 100 μg/mL with the acetonitrile, and working solutions of 0.004, 0.006, 0.010, 0.020, 0.030, 0.040, 0.050, 0.080, 0.100 μg/mL were prepared by diluting the appropriate volumes of the primary stock solution in acetonitrile.

3.4. Sample preparation

The pepper-based products (chilli powder, pepper paste and chorizo) used in this experiment were proved free of Sudan I by HPLC-UV/VIS method.

3.4.1. Chilli powder

In a 10 mL centrifuge tube, 1.0 g of chilli powder was spiked with the primary stock solution of Sudan I. 5 mL acetonitrile was added to the tubes and then vortex mixed for 3 minutes. After centrifugation at 4000 rpm for 10 min, the organic phase was then filtered on filter paper (0.45 μm).

3.4.2. Pepper paste

In a 10 mL centrifuge tube, 1.0 g of pepper paste was spiked with the primary stock solutions of Sudan I, and then operated as the "chilli powder" sample preparation process following the step of "5 mL acetonitrile".

3.4.3. Chorizo

In a 10 mL centrifuge tube, 1.0 g of dispersed chorizo was spiked with the primary stock solutions of Sudan I, and then operated as the "chilli powder" sample preparation process following the step of "5 mL acetonitrile".

4. Results and discussion

4.1. Optimization of system parameters a and b

In Eq. (2), the parameters a and b not only define the height of the potential barrier ($\Delta U = a^2/4b$), but affect the profile of the potential well. When the input signal was fixed, the parameters a and b affected the quality of final output signal directly. Therefore, it is necessary to optimize the parameters a and b in order to get a good output result. According to previous literature [1], taking into account the shape of the output signal, the quality of final output signal can be evaluated by the ratio of peak height to half-width. The optimization method used in the published papers [14,15] and the satisfied value of the two parameters can be obtained ($a = 2.5 \times 10^{-2}$ and $b = 1 \times 10^{-5}$). Although all samples have different strengths in different concentrations, the same parameter set will be used for them to keep the quantitative relationship of the output signals.

4.2. Limit of detection and limit of quantification

10 μL of Sudan I working solution was injected into the chromatography and a UV/VIS detector was used. As a result, the LOD and LOQ of Sudan I solutions were originally 0.100 and 0.030 μg/mL. The chromatograph of Sudan I solution at the concentration of 0.006 μg/mL was showed in Fig. 2(a) and (b), and it was too weak to meet the requirement of analysis. So it is impossible to detect Sudan I accurately in this condition. Therefore, a new and effective method of dealing with data of the chromatograph signal should be adopted. The retention time of Sudan I is 7 min, so we choose a section of signals during the period of 6–8 minutes to perform stochastic resonance ($a = 2.5 \times 10^{-2}$ and $b = 1 \times 10^{-5}$). Fig. 2(c) showed the signal of Sudan I was amplified obviously through SR and the detection can be practiced accurately. After the application of SR, the LOQ and LOD were improved to 0.020 and 0.006 μg/mL, respectively.

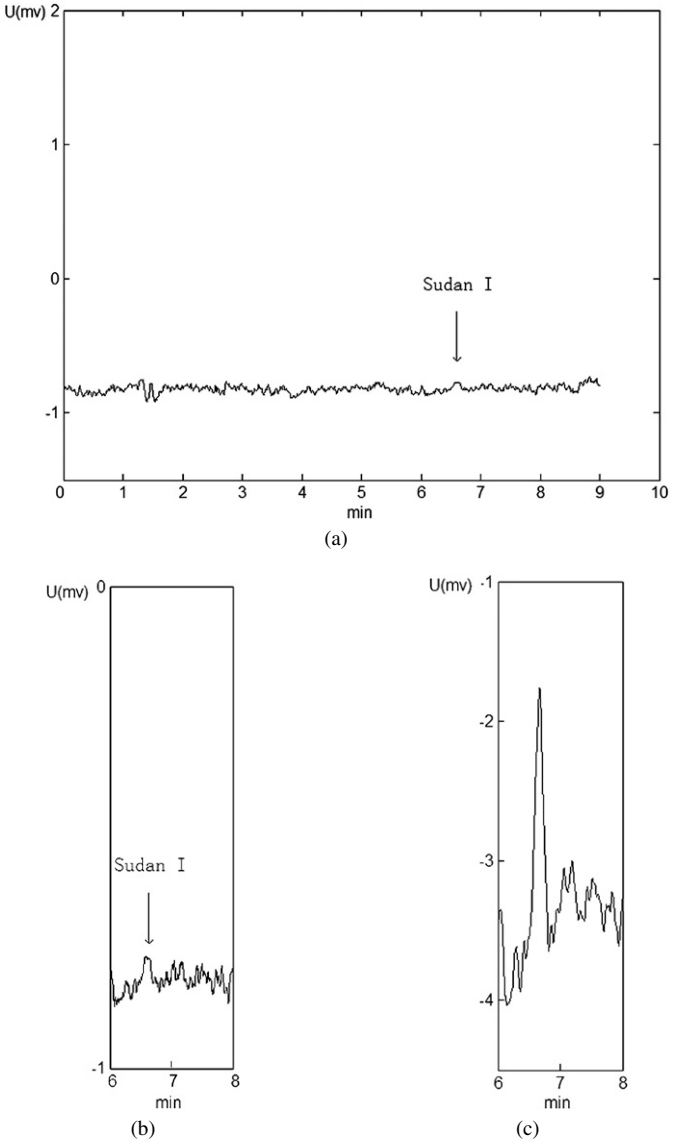

Fig. 2. (a), (b) Chromatograph of 0.006 μg/mL Sudan I solution; (c) chromatograms of 0.006 μg/mL Sudan I solution obtained by SR.

Table 1
Calibration curve of Sudan I

Concentration (μg/mL)	0.020	0.040	0.050	0.080	0.100
Peak area acquired by SR	38763.6	74601.2	103433.8	162453.1	194442.5
Linear regression curve	$y = 1984.6x - 369.04$				
r	0.9977				

4.3. Calibration curve

A set of Sudan I calibration solutions was prepared at concentrations of 0.020, 0.040, 0.050, 0.080, 0.100 μg/mL by diluting the appropriate volumes of the primary stock solution in acetonitrile. Separately inject equal volumes (10 μL) into the chromatography and record the chromatogram. Choose the signal during the period of 6–8 minutes to perform stochastic resonance ($a = 2.5 \times 10^{-2}$ and $b = 1 \times 10^{-5}$). As shown in Table 1 and Fig. 3, Sudan I solutions had good linearity between

Table 2
Recoveries

Kinds of pepper-based	Mean (%) $n = 5$			RSD (%)		
	0.100 μg/g	0.250 μg/g	0.500 μg/g	0.100 μg/g	0.250 μg/g	0.500 μg/g
Chilli powder	92.16	92.34	91.12	9.31	7.08	5.37
Pepper paste	93.26	93.65	92.30	8.68	7.78	6.26
Chorizo	93.57	91.96	92.76	8.44	6.61	5.76

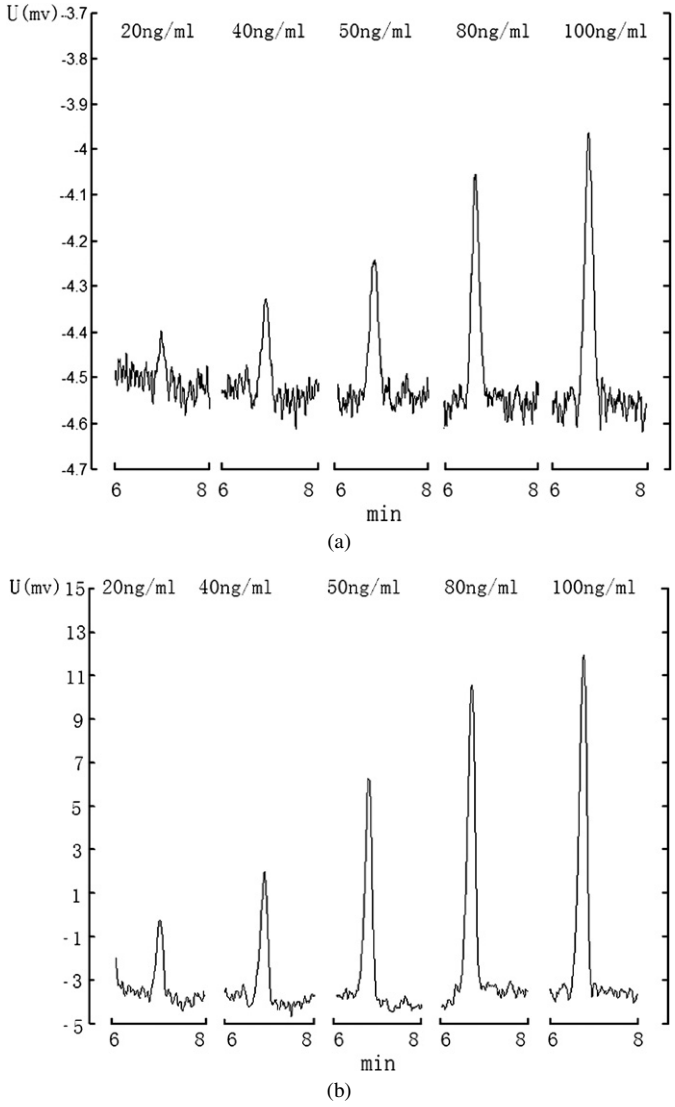

Fig. 3. (a) Original chromatograms of Sudan I; (b) chromatograms of Sudan I obtained by SR.

concentration and peak area acquired by SR, over the concentration range 0.020–0.100 μg/mL.

4.4. Precision

Precision experiment was performed at the concentration of 0.050 μg/mL and the result showed a good precision (RSD = 5.46%, $n = 6$).

4.5. Recovery of Sudan I in chilli powder, pepper paste and chorizo

In different kinds of pepper-based products the recovery experiment was performed at the concentration of 0.100, 0.250, 0.500 μg/g (equal to the concentration of 0.020, 0.050, 0.100 μg/mL) and the sample was prepared as the "sample preparation". According to the different kinds of pepper-based products, choose the signal during the period of 6–8 minutes to perform stochastic resonance ($a = 2.5 \times 10^{-2}$ and $b = 1 \times 10^{-5}$) and the result of recovery was shown in Table 2.

5. Conclusions

The quantitative analysis of Sudan I in some kinds of pepper-based products showed that SR could not only improve the detection limit and quantification limit but kept a good quantitative linearity between concentration and peak strength acquired by SR. The method presented in this Letter can enhance the sensitivity of instruments and make it possible to detect the weak signal accurately, which could not be detected effectively before. With the deep research of the theory of stochastic resonance and improvement of the new method, it will be a promising tool in micro and trace analysis.

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