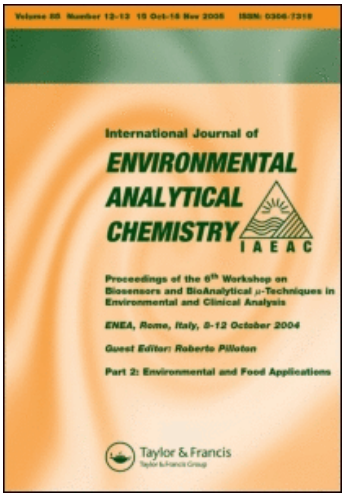

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The phenomenon of stochastic resonance (SR), which was discovered in recent years, rendered an entirely new way for the detection of weak signals, and it has been widely studied in many different science fields. This phenomenon is manifest in nonlinear systems whereby a weak signal can be amplified when the noise, signal and nonlinear system attain the proper cooperation. The introduced algorithm was employed to detect pyrene in drinking water samples with solid-phase extraction–liquid chromatography. The weak chromatographic peak of the analyte was amplified significantly, and the profiles of the peaks were also satisfactory. The limit of detection and the limit of quantification were improved from $0.022\,\mathrm{ng\,mL^{-1}}$ and $0.08\,\mathrm{ng\,mL^{-1}}$ to $0.004\,\mathrm{ng\,mL^{-1}}$ and $0.01\,\mathrm{ng\,mL^{-1}}$, respectively. The results showed an excellent quantitative relationship between concentrations and chromatographic responses. It is expected that the SR will be an effective tool to detect weak chromatographic peaks quantitatively in trace analysis.

Keywords: stochastic resonance; weak signal; PAHs; pyrene; water sample

1. Introduction

Stochastic resonance (SR) was first introduced by Benzi *et al*. [1,2] to explain the periodicity of Earth's ice ages. In recent decades, SR has received increasing interest since weak signals can be amplified significantly in a nonlinear system by the assistance of noise. SR is a nonlinear phenomenon whereby the noise can enhance the detection of a weak signal. It generally occurs in bistable dynamical systems attacked by a weak signal corrupted by noise through the nonlinear internal dynamics of the system, the small signal can be amplified by the assistance of noise [3]. It has been shown in numerous research works that the strength of signals will increase and that of noise will decrease by the cooperation of proper noise, weak signals and nonlinear system with a threshold [4–6]. Typical stochastic resonance phenomena have been found in many simple physical systems [7–8] and complex chemical systems [9–10]. Its application in chromatographic analysis was first found in Pan *et al*.'s work [11]. And in our previous studies, SRA was used to determine phenazopyridine,

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glyburide and roxithromycin in plasma [12–14]. Also, it was used to determine Sudan I in pepper-based products [15] and chloramphenicol residues in milk [16]. However, the theory of stochastic resonance is seldom employed to deal with the problems in environmental science.

Safety of water resources threatened by persistent organic pollutants is of great concern in all countries. The USA Environmental Protection Agency (EPA) presented 16 kinds of Polycyclic Aromatic Hydrocarbons (PAHs) for the cancer risk and genotoxicity, such as naphthalene, acenphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluor anthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluor anthene, benzo[a]pyrene, dibenzo[a, h]anthracene, benzo[g, h, i]perylene and indeno[1, 2, 3-cd]pyrene. PAHs in the environment are widespread; they will cause pollution of drinking water sources, then enter the human body through drinking water. Therefore, it is of great significance to analyse the PAHs of cancer risk in drinking water. Pyrene is one of the PAHs, and it is commonly found in a variety of semi-volatile organic compounds in water, which is monitoring the environmental quality of priority targets. It is flammable, toxic and can be decomposed at high temperature. The maximum allowable concentration of pyrene in the drinking water was 0.01 ng mL^{-1}, and the documents have reported that the limit of quantification of HPLC is 0.08 ng mL^{-1} in pyrene solution, which can not meet the state standards.

In this paper, stochastic resonance algorithm was at first applied to the chromatographic signals of pyrene detected by direct injection of the solutions into the HPLC/UV system. The weak chromatographic peak of the pyrene was enhanced significantly, and the profiles of the peaks were also satisfactory. The sensitivity was improved by stochastic resonance algorithm (SRA) without additional cost and complexity of experiment. The results showed an excellent quantitative linearity between concentration and peak strength. Linearity, precision and recoveries were also determined.

2. Theory and algorithm

In order to enhance detectability, a great number of chemometrics techniques have been employed to improve analytical instruments. Traditional methods (such as wavelet transform and Flourier transform) filter out the noise to improve analytical signals, but they may result in the tiny loss of useful information. However, stochastic resonance shows the conductive aspect of noise and renders a seemingly counterintuitive but much better approach for solving the problem due to utilising noise to amplify a weak input signal. Frequently used filtering and smoothing methods eliminate the 'useless' part or noise from the signal, but SR transfers its energy to real useful signal and remains the integrity of the signal. The nonlinear Langevin equation has been frequently employed to describe the phenomenon of SR. It has the following formula [17–20]:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -U'(x) + MI(t) + C\xi(t) \tag{1}$$

where $I(t) = S(t) + N(t)$ denotes an input signal $S(t)$ and the intrinsic noise $N(t)$, x is the particle displacement, and $\xi(t)$ 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 characterising the system:

$$U(x) = -\frac{a}{2}x^2 + \frac{b}{4}x^4. \tag{2}$$

The symmetric double well shows that theminima are located at $\pm x_m$, where $\pm x_m = (a/b)^{1/2}$. A potential barrier separates the minima with the height given by $\Delta U = a^2/4b$. The barrier top is located at $x_b = 0$ [21]. 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.

In previous literature [17], noise in analytical signals is often assumed to be Gaussian white noise, but added external noise, which is usually simulated, is somewhat coloured. The addition of external coloured 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, M and C in Equation (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 will external noise be added. Only the parameters of the system are modulated to match the input signal including real signal and intrinsic noise to achieve SR.

Equation (1) is solved by a fourth-order Runge–Kutta method ($M = 1$ and $C = 0$). The input signal is first prepared by normalising in $[-1, 1]$. The algorithm can be described as follows [17,19]:

$$
\begin{aligned}
k_1 &= a x_n - b x_n^3 + I_n \\
k_2 &= a(x_n + k_1/2) - b(x_n + k_1/2)^3 + I_{n+1} \\
k_3 &= a(x_n + k_2/2) - b(x_n + k_2/2)^3 + I_{n+1} \\
k_4 &= a(x_n + k_3) - b(x_n + k_3)^3 + I_{n+2}
\end{aligned}
$$

x is output signal, a and b are constants of the symmetric double-well potential function. The final results can be obtained by inverse normalisation of the output signals.

In this paper, the algorithm was implemented in MATLAB 7.0 by Zhangwei from the Center for Instrumental Analysis at China Pharmaceutical University.

3. Experimental

3.1 *Material*

Pyrene (99% purity) was obtained from the Johnson Matthey Company. Acetonitrile (HPLC-grade) was purchased from Merck (Darmstadt, Germany). The solid phase extraction was from SUPELCO (USA). Diethyl ether was analytical grade and originated from Nanjing Chemical Reagent Co. (Nanjing, China). Distilled water was used throughout the study.

3.2 *HPLC/UV system*

The chromatographic system was the Shimadzu HPLC LC-10ATVP series (Tokyo, Japan) equipped with a LC-10 ATVP pump, a 7725 manual injector, a SPD-10 AVP detector, and a N2000 workstation (Zhejiang University). Separation was carried out at room temperature on a reversed-phase Agilent C18 (100 mm × 4.6 mm i.d., 5 μm) column. The mobile phase consisted of acetonitrile and distilled water (60:40, *V*/*V*). The flow rate was 1.0 mL min^{-1}, the detection wavelength was 240 nm and the injection volume was 20 μL.

3.3 *Pyrene solution preparation*

Primary stock solution of pyrene was made up to 1 mg mL^{-1} with the acetonitrile and working solutions 0.001 mg mL^{-1}, 0.01 mg mL^{-1} and 0.1 mg mL^{-1} were prepared by diluting the appropriate volumes of the primary stock solution in acetonitrile.

3.4 *Solid phase extraction procedure*

Aliquots (500 mL) of water samples were extracted using C18 (60 mg) cartridges (SUPELCO, USA) that were pre-equilibrated with 2 mL of methanol followed by 2 mL of methanol in water (50%). Following loading of the sample, cartridges were washed with 4 mL water and 2 mL 95% methanol, and analytes were eluted with 10 mL diethyl ether at a flow rate of 0.5 mL min^{-1}. Extracts were dried under nitrogen at 40°C and reconstituted in 100 μL of mobile phase.

4. Results and discussion

4.1 *The section of chromatogram*

Typical chromatogram of pyrene is presented in Figure 1(a). The retention time of pyrene was around 10.5 minutes. The enhancement of the peak of interest might be affected by other peaks present in the chromatogram (which will also absorb energy from noise), and so if these other peaks are included in the input, the output peaks of interest may not be ideal. Therefore, only the section from each chromatogram that included the weak peak signal of interest and the noise around it was chosen as the input signal for the algorithm. The chromatogram of 9–12 minutes was selected as the input signal.

4.2 *Optimisation of system parameters* a *and* b

When a quantitative determination is performed in practice, the optimisation of system parameters was essential and complicated. Although all sample included in a series had different strengths in different concentrations, the same parameter set would be used for them to keep the quantitative relationship of the output signals of the series. When the input signal was fixed, the selection of nonlinear system parameters a and b affected the quality of final output signal directly. Therefore, system parameters a and b must be optimised to obtain satisfactory output signal. The signal-to-noise ratio (SNR) was always adopted as an indicator of optimisation for evaluating the quality of output signal in previous literatures [22]. SNR is defined as a ratio of the standard deviation of peak area in the output signal to that of baseline area. This method took into consideration the relationship between chromatographic peak and noise in output signal. The optimised values of the two parameters ($a = 0.5304$ and $b = 0.05298$) can be obtained by optimisation with SNR.

4.3 *The limit of detection and the limit of quantification*

The previous literature has reported that the limit of detection and the limit of quantification was 0.022 ng mL^{-1} and 0.08 ng mL^{-1}, respectively, by high performance liquid chromatograph. Figure 2(a) was chromatogram of 0.01 ng mL^{-1} pyrene solution

and the peaks are too small to meet the quantitative requirements. The signal was significantly enhanced by SRA and presented in Figure 2(b). The limit of detection and the limit of quantification reached 0.004 ng mL^{-1} and 0.01 ng mL^{-1}.

4.4 *Calibration curve*

A set of pyrene calibration solutions was prepared at concentrations of 0.04, 0.08, 0.1, 0.2, 0.4 ng mL^{-1} by diluting the appropriate volumes of the primary stock solution in acetonitrile. Separately inject equal volumes (20 μL) into the chromatography and record

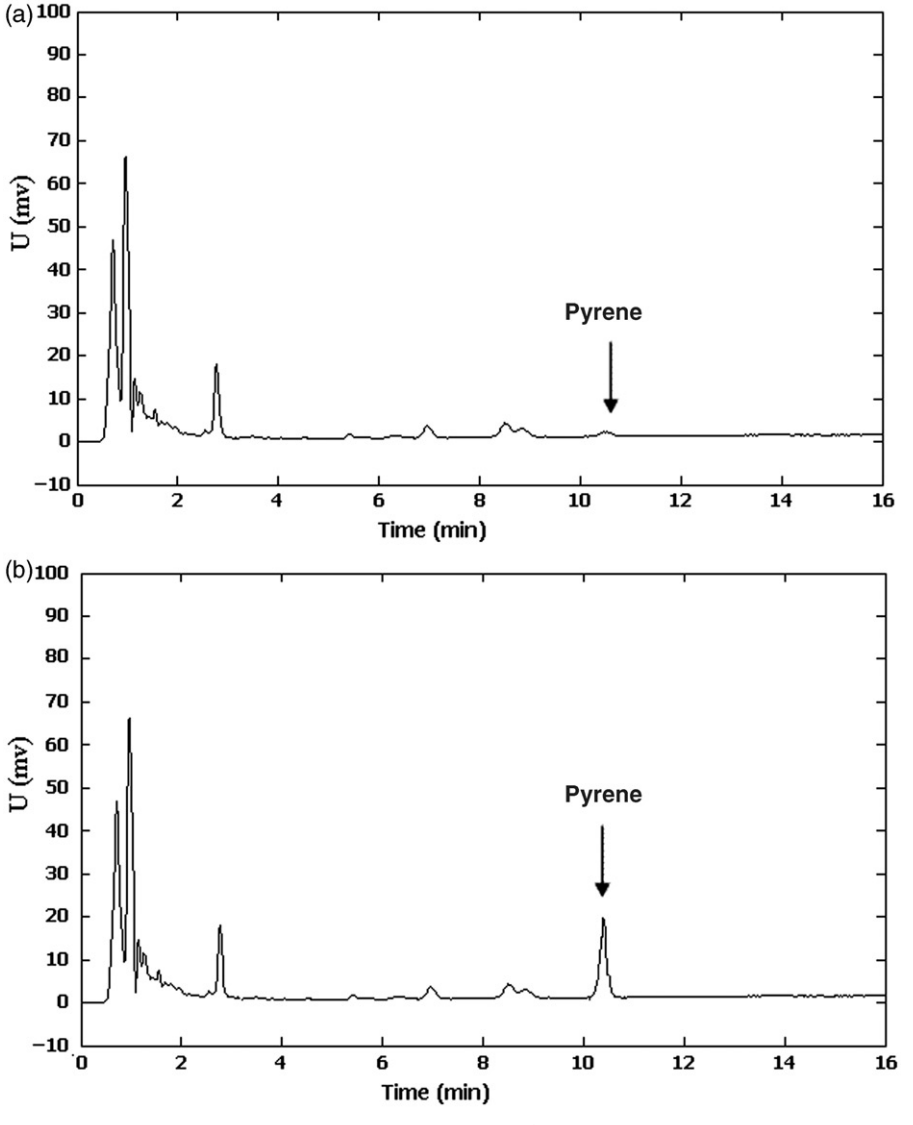

Figure 1. (a) The original chromatograms of 0.01 ng mL^{-1} pyrene. (b) The chromatograms obtained by SRA.

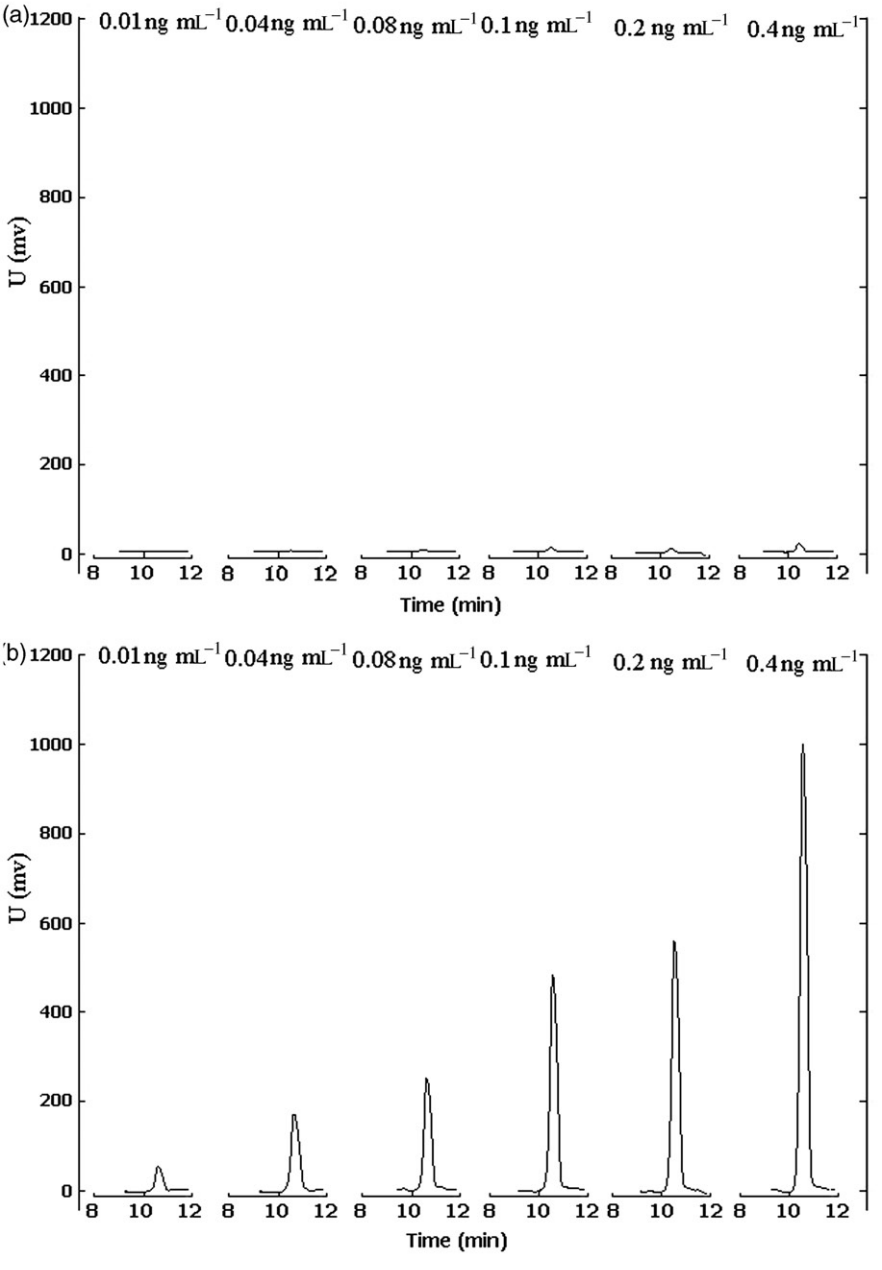

Figure 2. The chromatograms of calibration of pyrene in water. (a) The original chromatograms of pyrene. (b) The chromatograms obtained by SRA.

the chromatogram. Choose the signal during the period of 9–12 minutes to perform stochastic resonance ($a = 0.5304$ and $b = 0.05298$). As shown in Figure 2 and Figure 3, the results show good linearity between concentration and peak area acquired by SR over the concentration range from 0.04 to 0.4 ng mL^{-1}.

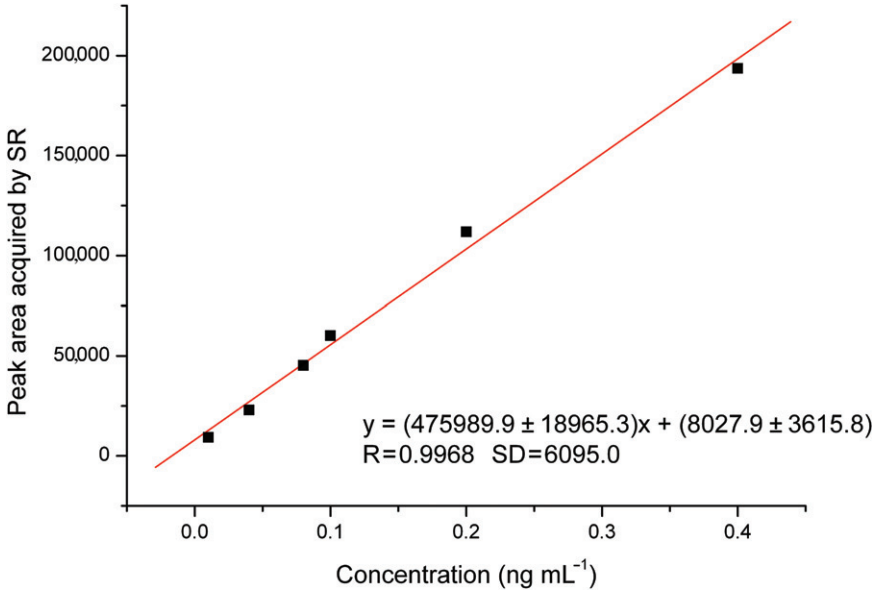

Figure 3. Calibration curve of pyrene.

Table 1. Repeatability of pyrene.

Added concentration ($ng\,mL^{-1}$)	Measured average concentration ($ng\,mL^{-1}$)	RSD (%)
Intra-day precision ($n=5$)		
0.04	0.0436	8.52
0.08	0.0816	7.34
0.2	0.2126	6.92
Inter-day precision ($n=15$)		
0.04	0.0433	9.16
0.08	0.0786	7.98
0.2	0.2235	7.35

4.5 *Precision*

Precision experiment was performed at the concentrations of 0.04, 0.08, $0.4\,ng\,mL^{-1}$. Intra-day precision was determined by repeated analysis of prepared samples on one day ($n=5$), and inter-day precision was determined by repeated analysis of prepared samples on three different days ($n=5$ series per day). Intra-day and inter-day assays are summarised in Table 1 and the results indicate that precision of the assay are acceptable.

4.6 *Recovery*

The assay method was validated in terms of recovery. It was evaluated by processing three different concentration levels of the sample (each level analysed five times). The data are

Table 2. Recovery of pyrene.

Concentration ($ng\,mL^{-1}$)	0.04	0.08	0.2
Recovery (%)	103.90	98.25	101.5
R.S.D. (%)	8.71	7.49	7.11

given in Table 2, and the results showed that recoveries met the requirements of quantitative analysis.

5. Conclusions

The nonlinear stochastic resonance algorithm has an important academic value and practical significance in detecting weak chromatographic peak. The stochastic resonance algorithm for the detection of weak chromatographic peaks can be used to increase sensitivity of conventional laboratory equipment. For example, the sensitivity of low-cost HPLC-UV chromatography combined with SRA will have the same level with that of LC-MS, while sensitivity of LC-MS can be further improved by SRA. Therefore there are broad prospects for application. It is expected to solve the conflict between the sensitivity of detector and the requirements of analysis via use of SRA in trace pollutants, pesticide residues and drug residues.

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