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A Novel Approach to Improve the Detectability of CO_2 by GC Analysis

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Abstract: A novel stochastic resonance algorithm was employed to enhance the signal-to-noise ratio (SNR) of signals of analytical chemistry. By using a gas chromatographic data set, it was proven that the SNR was greatly improved and the quantitative relationship between concentrations and chromatographic responses remained simultaneously. The linear range was extended beyond the instrumental detection limit.

Keywords: Stochastic resonance, detectability, gas chromatography.

For a long time, noise was considered to be a nuisance in GC analysis. Especially in trace and ultratrace analysis, noise was the primary obstacle for enlarging instrumental detectability. Many methods, such as fast Fourier transform[1] (FFT), wavelet transform[2] (WT) and other smoothing algorithms, filtering algorithms, were widely employed to reduce noise level, although they can possibly result in loss of useful information. However, stochastic resonance[3,4] (SR) shows the conductive aspect of noise and renders a seemingly counterintuitive but much better approach for solving the problem.

SR is a phenomenon wherein noise, signal and system cooperate each other and consequently the signal-to-noise ratio is enhanced in nonlinear system by optimizing the noise level or modulating the system's characteristic parameters. Various applications of the phenomenon have been explored in different areas. In our laboratory it has been successfully employed in spectrum analysis[5,6,7]. However, due to the stochastic performance of the system, the application in quantitative analysis did not turn out a satisfying result up to now.

In this work, a bistable system was employed with the input signal to construct the nonlinear system:

$$\frac{dx}{dt} = -v'(x) + input(t) \tag{1}$$

Here $v(x) = 0.5\mu x^2 - 0.25x^4$, is the bistable potential function; μ is a positive constant

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characterizing the system; $input(t) = S(t) + \xi(t)$, with $S(t)$ the signal and $\xi(t)$ the noise. The improved output signal $x(t)$ can be obtained by integrating **Eq. 1**. Generally, SR was realized by modulating the parameter μ and adding properly strong noise $\xi(t)$. The added noise, however, had different properties from the intrinsic noise of the signal. Thus, the external noise had negative effects on the output signal. In this work, SR will be achieved only by modulating the parameter μ. For the weak analytical signal, we presume the noise level of the studied signal is invariable in analysis time interval. That means the continuously analyzed samples have the same noise level. Under the same optimized parameter μ and the same noise level, the performance of nonlinear system was not random but definitive. Therefore, quantitative analysis becomes possible.

SR was applied to micro analysis of carbon dioxide (CO_2) by gas chromatogram in this work. The experiment was performed on SP-2000 gas chromatograph system with TCD detector monitoring bridge current at 110 mA, temperature at 110 ε , and attenuation factor at 32. Carrier gas was nitrogen (N_2) at a flow-rate of 20 mL min^{-1}. Oven temperature was set at 100 ε . A 502 bonding silica-gel column was used. The pure gas of CO_2 was analyzed in the experiment. The retention time of CO_2 was 5.0 minutes under this condition. Series of sample was made of 0.40 μL, 0.50 μL, 0.70 μL, 0.80 μL, 0.90 μL, and 1.00 μL CO_2. **Figure 1** shows the chromatographic series. Obviously, it is impossible to accurately determine the concentration of CO_2 under so heavy noise. The results obtained from SR under the same condition of $\mu = 0.31$ are shown in **Figure 2**.

It can be observed from **Figure 2** that the noise level was greatly reduced. It can be also found that the profiles of the obtained chromatographic peaks were distorted because of the limitation of the method, but the location was not effected and the proportional relationship among the peak heights was kept. Therefore, the quantitative analysis was performed by using the chromatographic height. In order to evaluate the reliability of this result, a linear regression was implemented with the response heights to volumes of CO_2. **Table 1** summarized the related values.

Table 1 The chromatographic peak intensities to the volumes of CO_2 (at 0.5 minutes)

Volume (μL)	0.40	0.50	0.70	0.80	0.90	1.00
Intensity	0.04011	0.05048	0.07035	0.08153	0.09283	0.10408

The regression equation was given as **Eq. 2**. The correlation coefficient (R) is 0.9996, and the standard deviation (SD) is 0.00078. The regression line was presented in **Figure 3**. It is clearly that the quantitative relationship between different quantities of CO_2 and their heights was accurately kept.

$$I = 0.10618(\pm 0.00151)V - 0.00286(\pm 0.00113)$$
$$R = 0.9996, \qquad SD = 0.00078 \tag{2}$$

where I and V denote the chromatographic response height and injection volume of CO_2 respectively.

Figure 1 Experimental chromatogram

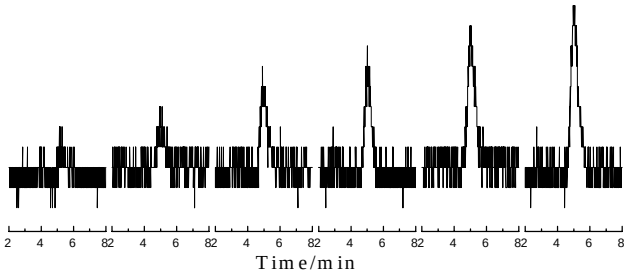


Figure 2 Obtained chromatogram by SR ($\mu = 0.31$)

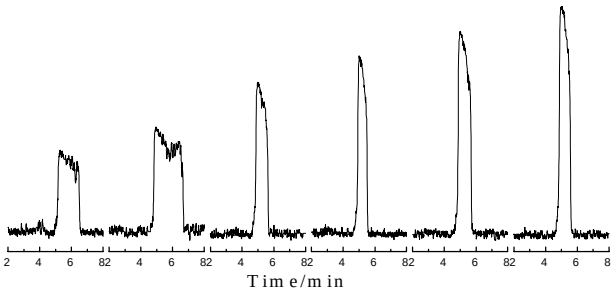
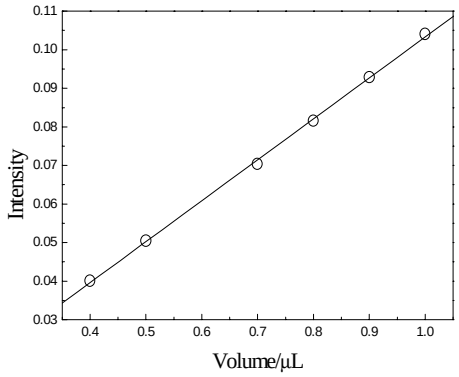


Figure 3 The correlation plot of obtained intensity *vs* volume



In conclusion, by controlling the randomness of nonlinear system, a new stochastic resonance algorithm was achieved. The successful application to the gas chromatogram analysis of micro quantity CO_2 corroborated the new algorithm. The experiment proved

that not only the SNR of the studied signal was remarkably improved, but the proportion relationship between response intensities resulting from different concentrations was simultaneously kept as well. In spite of SR has its imperfection, it can greatly enhance instrumental detectability and the analytic accuracy of the trace analysis. By the means, the instrumental detection limit can be improved and the linear range can be extended. SR is a new effective chemometrics method to micro or trace analysis.

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