Stochastic Resonance Algorithm Applied to Quantitative Analysis for Weak Chromatographic Signals of Alkyl Halides and Alkyl Benzenes in Water Samples

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Abstract

The stochastic resonance algorithm is applied to the trace analysis of alkyl halides and alkyl benzenes in water samples. Compared to encountering a single signal when applying the algorithm, the optimization of system parameters for a multicomponent is more complex. In this article, the resolution of adjacent chromatographic peaks is first involved in the optimization of parameters. With the optimized parameters, the algorithm gave an ideal output with good resolution as well as enhanced signal-to-noise ratio. Applying the enhanced signals, the method extended the limit of detection and exhibited good linearity, which ensures accurate determination of the multicomponent.

Introduction

Noise is generally considered damaging to the detection of interested signals and various smoothing and filtering algorithms have been widely used to reduce the effect of noise. However, these methods may drop out a part of useful information that is regarded as useless noise. Different from frequently used filtering and smoothing methods, the stochastic resonance algorithm (SRA), which is developed on the theory of stochastic resonance, will transfer the energy of noise to the real useful signal when signal, noise, and nonlinear system match well, and stochastic resonance condition is reached. Consequently, the signal-to-noise ratio of the interested signal will be enhanced.

Stochastic resonance was first introduced by Benzi and his coworkers to explain the periodicity of Earth's ice ages (1,2). In recent decades, there has been increased interest in stochastic resonance because weak signals can be amplified significantly in a nonlinear system by the assistance of noise. Typical stochastic resonance phenomena have been found in many simple physical systems (3,4) and complex chemical systems (5,6). The application of SRA in chromatographic analysis was first found in Pan and his coworkers' work (7). In our previous studies, it was applied successfully to quantitative analysis for single weak chromatographic signals of phenazopyridine (8), roxithromycin (9), and granisetron (10) in plasma. However, its application to simultaneously analysis for a multicomponent was never reported.

Alkyl halides and alkyl benzenes are important pollutants in water because of their wide use in many industrial processes and the use of chlorination in waterworks. These pollutants are receiving increasing attention from aquatic environment monitoring programs due to the high toxicity. For this reason, a number of alkyl halides and alkyl benzenes are listed in the chemical aspects of World Health Organization Guidelines for Drinking-Water Quality (11). In the quantitative analysis of volatile organic compounds in liquid samples, many methods have been widely used, such as liquid–liquid extraction (12), solid-phase extraction (13), solid-phase micro-extraction, and purge-and-trap gas chromatography (GC), or GC–mass spectrometry (MS) analysis (14,15). However, in these methods a relatively large volume (generally several milliliters or even more) of organic solvent can be consumed, or special equipments (such as headspace equipment and purge-and-trap unit) and advanced detectors (mass spectrometric detection) are required. Headspace single-drop microextraction (headspace SDME) is a fast, inexpensive, and efficient extraction technique. It integrates sampling, extraction, and preconcentration in a single step with consumption of microliter solvent (16–18).

In this paper, headspace SDME was used to extract and condense the target analytes in a water sample, and the extracts were analyzed by GC–flame ionization dectector (FID). SRA was subsequently used to process the chromatographic signals of the multicomponent obtained from GC–FID. The optimization of system parameters for any multicomponent is more complex than for a monocomponent when applying SRA because the res-

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olution of adjacent chromatographic peaks after SRA is related to system parameters. So the resolution of adjacent peaks was considered in the optimization progress as well as signal-to-noise ratios. As expected, the output chromatogram of SRA was characterized with significantly improved signal-to-noise ratios and good resolutions, as well. By applying the algorithm, the trace analysis of alkylhalides and alkylbenzenes in the water sample was accomplished with FID, and the analysis result shows that the proposed method in this work is comparable with or better than those advanced analytical instruments in regards to sensitivity, accuracy, and reproducibility. The application of SRA in this work and the easy implement of the algorithm suggested that it is a promising approach for a common detector coupled with SRA to perform trace analysis of multicomponents.

Theory and Algorithm

The nonlinear Langevin equation has been frequently employed to describe the phenomenon of stochastic resonance. The equation is as follows (19):

$$dx / dt = -U'(x) + MI(t) + C\hat{\imath}(t) \qquad \text{Eq. 1}$$

where the variable x is the output of the nonlinear system, representing the position of signal. $MI(t)$ represents an input signal, where M is an adjustable coefficient, and $I(t) = S(t) + N(t)$ denotes a signal embedded in a noisy environment with the useful signal, $S(t)$, and the intrinsic noise, $N(t)$. $C\hat{\imath}(t)$ is usually added to induce the occurrence of stochastic resonance with the adjustable coefficient, C, and the external noise, $\xi(t)$.

The symmetric double-well potential, $U(x)$, that often used can be expressed as the following equation with the constants a and b characterizing the system:

$$U(x) = -(a/2)x^2 + (b/4)x^4 \qquad \text{Eq. 2}$$

The double-well potential has one maximum unstable point at $x = 0$ and two stable minimum points at $x = \pm\sqrt{(a/b)}$. There is a potential barrier between the two stable states with the height given by $\Delta U = a^2 / 4b$. The weak chromatographic signal that can be viewed as Brownian particle may rest in one stable point initially. As the input signal, noise and nonlinear system cooperate well, meaning the stochastic resonance condition is reached, the weak signal can surmount the energy barrier and hop from one potential well to the other with the assistance of noise. As a result, the signal will obtain an increased intensity. However, for the relative low energy, the noise is confined in the original well with the intensity suppressed by the nonlinear system. Therefore, the output signal of the system will be obtained with a better signal-to-noise ratio compared to the input. By applying the enhanced signal, it will be possible to carry out the detection of weak signals from a noisy background.

The $\xi(t)$ generally considered colored noise, which is different from the Gaussian white noise in chromatography, will damage the characteristic of intrinsic noise and result in serious distortion of the output signals (7). The adjustment of coefficient M complicates the algorithm. Moreover, it has been proven by previous work that stochastic resonance could be induced by modulating the potential $U(x)$ alone, namely, adjusting a and b. So in this work, M and C are set to 1 and 0, respectively, to maintain the integrity of the intrinsic noise and simplify the algorithm. Equations 1 and 2 can be solved by a fourth-order Runge-Kutta method (20). The calculation procedure starts with normalization of the input signal $I(t)$ to the interval (–1, 1), and the normalized signal is then operated on by the algorithm to give the output signal. The final results can be obtained by inverse normalization of the output signals.

Experimental

Chemicals, reagents, and aqueous samples

The alkyl halide and alkyl benzene compounds considered in this work were: dichloromethane, chloroform, 1,2-dichloroethane, benzene, toluene, ethylbenzene, and xylene. All the analytes mentioned previously were analytical-grade and obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). A standard stock solution of the alkyl halide compounds (at 10 mg/L concentration level) and the alkyl benzene compounds (at 1 mg/L concentration level) was prepared with double-distilled water. Working solutions were prepared by dilution of standard stock solution with double-distilled water. All solutions were stored in the refrigerator at 4°C.

GC-grade phenylmethanol was purchased from Sinopharm Chemical Reagent (Shanghai, China). Analytical-grade cyclohexane, used as the internal standard (IS), was obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China).

The natural water samples included tap water obtained from three supply sites of the main water-supply network of Nanjing (China), and the water from the Yangtze River and Xuanwu Lake in Nanjing (China).

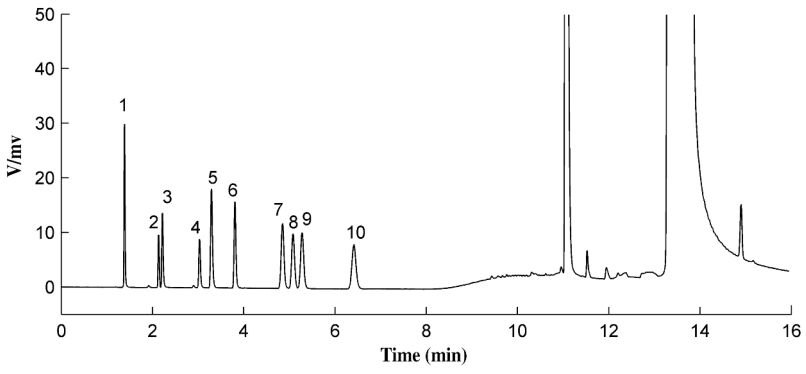

Figure 1. Typical chromatogram of IS and nine target analytes. The alkyl halides were at 500 µg/L concentration level, and the alkyl benzenes were at 50 µg/L concentration level. Peak designation: IS, 1; dichloromethane, 2; benzene, 3; chloroform, 4; toluene, 5; 1,2-dichloroethane, 6; ethylbenzene, 7; *p*-xylene, 8; *m*-xylene, 9; *o*-xylene, 10.

Sample preparation

The water sample was prepared by headspace SDME in the present work. Several factors would influence the performance of headspace SDME, such as extraction solvent, microdrop volume, sample temperature, extraction time, and stirring rate. These factors were optimized in this work, and the final extraction conditions were: 2 µL of phenylmethanol containing cyclohexane (0.1%, v/v) as IS, was suspended at the tip of a microsyringe in the headspace in a 10-mL vial containing 5 mL of water sample. Then the analytes partitioned between the headspace and the organic phase at 25°C and at a stirring rate of 800 rpm for 7 min. After extraction, 1 µL of solvent was retraced into the microsyringe and introduced into the GC inlet for analysis.

GC–FID analysis

All analyses were performed on a HP 5890 GC system (Hewlett Packard, Palo Alto, CA). Compounds were separated by a 30 m 0.32 mm i.d. capillary column coated with a 0.25 µm EC-1000 stationary phase (Alltech Associates, Inc., Bannockburn, IL). Nitrogen (> 99.99%) was used as the carrier gas at a flow rate of 1.6 mL/min. The injector temperature was 220°C, and all injections were made in split mode with a split ratio of 20:1. The FID temperature was set at 250°C. The column oven temperature was initially set at 50°C and held for 8 min, and then programmed to 200°C at a rate of 50°C/min and maintained for 15 min. Under this chromatographic condition, all of the nine target analytes and IS were separated well (Figure 1).

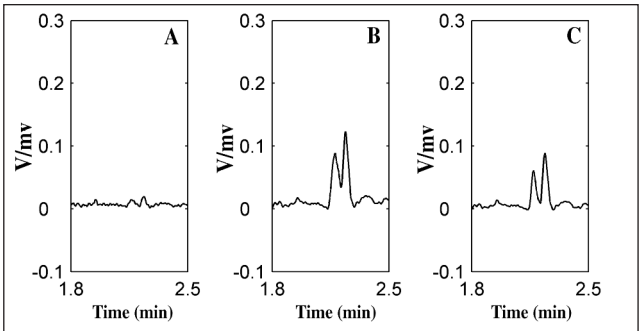

Figure 2. The close eluting peaks of dichloromethane and benzene processed by SRA. The original chromatogram (A); the chromatogram obtained by SRA with $a = 0.045$, $b = 1.1 \times 10^{-5}$ (B); and the chromatogram obtained by SRA with $a = 0.032$, $b = 7 \times 10^{-6}$ (C).

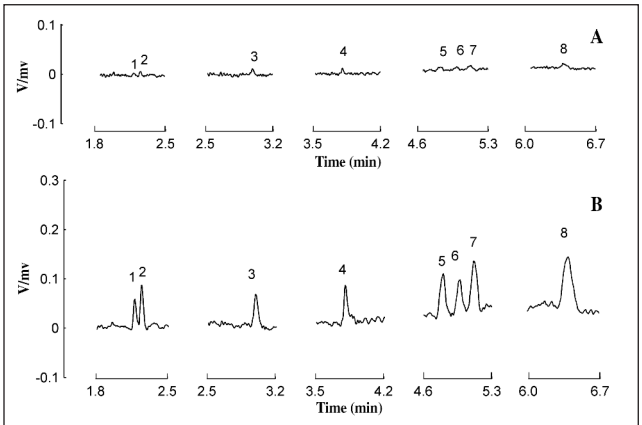

Figure 3. The chromatogram of LODs before (A) and after (B) the process of SRA. Peak designation and spiked concentration: dichloromethane at 2.1 µg/L, 1; benzene at 0.2 µg/L, 2; chloroform at 2.2 µg/L, 3; 1,2-dichloroethane at 1.0 µg/L, 4; ethylbenzene at 0.1 µg/L, 5; *p*-xylene at 0.1 µg/L, 6; *m*-xylene at 0.1 µg/L, 7; *o*-xylene at 0.2 µg/L, 8.

Results and Discussion

The selection of the system parameters

According to Equation 2, the parameters *a* and *b* of the nonlinear system define the profile of the potential well and the height of the potential barrier. When an input signal is fixed, the two parameters will affect the quality of the output signal. Therefore, it is necessary to optimize the parameters in order to obtain a satisfactory output result. For the noises in different sections of a chromatogram that have the similar characteristics, it is possible to perform SRA for multicomponents simultaneously with the same parameters. So in this paper, we picked up the 1.5–7.0 min section of the chromatogram consisting of all the target peaks of interest as the input of the algorithm for choosing the proper parameters.

The optimized method of parameters for single chromatographic peak has been discussed in our previous work (8–10), whereas optimization of parameters for multiple analytes, especially those with very close retention time, has not been encountered. In the case of multiple analytes, the optimization with the signal-to-noise ratio as an evaluating indicator sometimes may result in an unsatisfactory output. Those close eluting peaks, whose baseline originally separated, may begin to overlap after the process of SRA with improper parameters. For instance, when $a = 0.045$ and $b = 1.1 \times 10^{-5}$, the output chromatogram is characterized with a maximal signal-to-noise ratio but a poor resolution between the two peaks around 2 min (Figure 2B). So, in order to avoid improper parameter value, a threshold for resolution was set in the optimization of parameters. Basically, the resolutions of every two adjacent peaks are calculated, and the parameters yielding one or more resolutions lower than the threshold will be eliminated. For adjacent peaks with similar

Table I. Guideline Values, LODs, and LOQs of the Target Analytes With and Without SRA

		With SRA		Without SRA	
Analyte	Guideline value (µg/L)*	LOD (µg/L)	LOQ (µg/L)	LOD (µg/L)	LOQ (µg/L)
Dichloromethane	20	2.1	5.4	6.4	15.0
Chloroform	200	2.2	5.5	6.6	15.4
1,2-Dichloroethane	30	1.0	2.5	3.0	12.0
Benzene	10	0.2	0.6	0.6	2.4
Toluene	700	n.a.†	n.a.	n.a.	n.a.
Ethylbenzene	300	0.1	0.4	0.4	1.2
p-Xylene	500	0.1	0.4	0.4	1.3
m-Xylene	500	0.1	0.4	0.4	1.3
o-Xylene	500	0.2	0.4	0.6	1.3

* Guideline value for chemicals listed in WHO Guidelines for Drinking-Water Quality (11).
† Not analyzed.

peak area, resolution reach to 1.0 with an overlapped peak area of 2% is considered basic separation, which could seem to be accurate peak integration (21). While resolution of less than 1.0 will result in inaccuracy of area integration; on the other hand, a threshold of > 1.0 for resolution will lead to excessive elimination in the procedure of parameter optimization. Therefore, a threshold of 1.0 for resolution was finally introduced to the optimization procedure. According to experience in our previous work, the optimization of parameters was carried out within the range of 0 to 0.1 for *a* and 0 to 0.001 for *b*. Taking into account the signal-to-noise ratio and resolution of all the target compounds, the parameters *a* and *b* were finally set to 0.032 and 7×10^{-6}, respectively (Figure 2).

Table II. Calibration Curve and Repeatability of the Target Analytes by SRA

Analyte	Linear regression curve*	Standard error	Correlation coefficient (r^2)	Repeatability (%RSD)
Dichloromethane	$f = 0.008C (\pm 0.0001) + 0.067 (\pm 0.030)$	0.055	0.997	3.73
Chloroform	$f = 0.011C (\pm 0.0002) - 0.080 (\pm 0.048)$	0.089	0.998	8.15
1,2-Dichloroethane	$f = 0.016C (\pm 0.0002) + 0.076 (\pm 0.037)$	0.068	0.999	7.75
Benzene	$f = 0.112C (\pm 0.002) - 0.083 (\pm 0.048)$	0.088	0.998	4.52
Toluene	$f = 0.246C (\pm 0.004) + 0.289 (\pm 0.079)$	0.147	0.998	4.22
Ethylbenzene	$f = 0.215C (\pm 0.003) + 0.035 (\pm 0.061)$	0.112	0.999	6.37
p-Xylene	$f = 0.206C (\pm 0.004) + 0.115 (\pm 0.094)$	0.174	0.998	2.91
m-Xylene	$f = 0.197C (\pm 0.005) + 0.091 (\pm 0.110)$	0.204	0.995	7.69
o-Xylene	$f = 0.218C (\pm 0.002) + 0.082 (\pm 0.047)$	0.087	0.999	4.57

* The independent variable (C) denotes the concentration of target analyte and the dependent variable (f) denotes the area ratio of target analyte to IS.

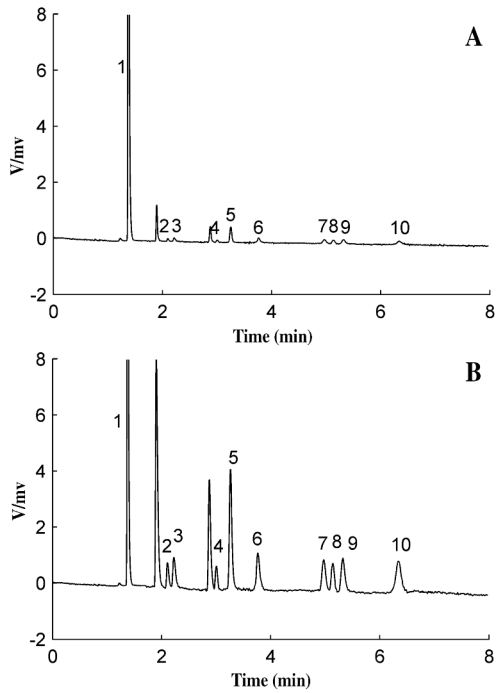

Figure 4. The chromatogram of all target analytes before (A) and after (B) the process of SRA. Peak designation: IS, 1; dichloromethane, 2; benzene, 3; chloroform, 4; toluene, 5; 1,2-dichloroethane, 6; ethylbenzene, 7; *p*-xylene, 8; *m*-xylene, 9; *o*-xylene, 10.

Method validation

Generally, signal-to-noise ratio of 3 and 10 are taken as limit of detection (LOD) and limit of quantification (LOQ), respectively. The application of SRA can lower the LODs and LOQs of the analytes (i.e., improve the detection sensitivity) remarkably. Take benzene, for instance, the LOD and LOQ were originally 0.6 µg/L and 2.4 µg/L, respectively. After the process of SRA, the LOD and LOQ of benzene were improved to 0.2 µ/gL and 0.6 µg/L, respectively. Figure 3 shows that LODs of all target compounds are significantly improved by SRA, except toluene. The LOQs of the interested analytes decrease notably as well, except toluene, and the LOQs are far below the guideline values of these chemicals listed in WHO Guidelines for Drinking-Water Quality (11). The LOD and LOQ of toluene were not evaluated because a small amount of toluene exists in the extraction solvent phenylmethanol. Fortunately, the systematic error it caused did not affect the quantitation relationship between the peak strength and the concentration of toluene in the water sample. The data about LODs, LOQs, and guideline values of these compounds are listed in Table I.

The calibration curves (a series of six different concentration solutions) were prepared and assayed in duplicates with the concentration range from 10 µg/L–500 µg/L for alkyl halides and from 1.0–50 µg/L for alkyl benzenes. The chromatogram during the period of 1.5–7.0 min including the signals of all target analytes was then chosen as the input of SRA. As described in previous work (8–10), the peak of IS was not taken into the process of SRA. Then the linearities of all the target compounds were evaluated with the peak area ratio of target analytes (after SRA) to the IS. The calculated calibration curves displayed good linearity for all target analytes with correlation coefficients (r^2) ranging from 0.995–0.999 (Table II). Figure 4 compares the chromatograms obtained by SRA with the original at the 10 µg/L concentration level of alkyl halides and 1 µg/L of alkyl benzenes. As shown in Figure 4A, the original strengths of the target chromatographic peaks cannot satisfy the determination requirements (with the exception of toluene, the signal-to-noise ratios of other eight compounds are lower than 10), so these analytes at this concentration level cannot obtain an accurate analysis. With the application of SRA, the strengths of all analytes were obviously amplified and characterized by better signal-to-noise ratio (Figure 4B). As a result, the calibration curves were extended compared to the method without SRA.

The investigation of repeatability was carried out with spiked preparations at a middle concentration level (six replicates), namely alkyl halides at a concentration of 100 µg/L and alkyl benzenes at that of 10 µg/L. Relative standard deviations (RSD) reveal that the present method has good repeatability (Table II).

The accuracy of the present method was investigated at three different concentration levels, and each level was analyzed five times. Table III shows the proposed method has satisfactory accuracy for each of the nine compounds.

Table III. Accuracy of the Target Analytes by SRA

Analyte	Low conc. (%)*		Middle conc. (%)†		High conc. (%)‡	
	Accuracy	RSD	Accuracy	RSD	Accuracy	RSD
Dichloromethane	94.6	10.26	98.8	7.21	96.1	6.68
Chloroform	102.2	8.59	94.5	4.65	99.1	5.07
1,2-Dichloroethane	96.4	6.06	98.1	5.68	97.4	2.39
Benzene	98.7	8.33	104.3	7.54	102.1	6.14
Toluene	102.9	6.21	98.4	6.55	97.0	4.64
Ethylbenzene	100.5	7.75	102.7	4.31	98.7	4.22
p-Xylene	93.6	7.98	99.0	7.46	100.4	4.78
m-Xylene	96.8	9.12	99.6	7.08	101.8	5.15
o-Xylene	99.3	5.34	96.3	5.58	96.5	3.38

* Alkyl halides were at 20 µg/L concentration level, and alkyl benzenes at 2 µg/L concentration level.
† Alkyl halides were at 100 µg/L concentration level, and alkyl benzenes at 10 µg/L concentration level.
‡ Alkyl halides were at 500 µg/L concentration level, and alkyl benzenes at 50 µg/L concentration level.

Table IV. The Concentration of Alkyl Halides and Alkyl Benzenes in Real Water Samples

Analyte	Tap water 1	Tap water 2	Tap water 3	River water	Lake water
Dichloromethane	–*	–	–	–	–
Chloroform	–	9.8	–	7.4	11.6
1,2-Dichloroethane	–	–	–	–	–
Benzene	–	–	–	3.9	–
Toluene	–	–	–	7.1	7.4
Ethylbenzene	1.6	–	–	-	5.5
p-Xylene	–	–	–	–	–
m-Xylene	–	–	–	1.4	0.8
o-Xylene	–	–	–	–	4.5

* Not detected.

Analysis of real samples

The present method was then applied to the determination of the real samples including tap water, river water, and lake water. The concentrations of analytes in the real water samples were determined by their linear equations. The results exhibited in Table IV indicate that the contents of alkyl halides and alkyl benzenes in three samples of tap water are strictly below the guideline values listed in WHO Guidelines for Drinking-Water Quality (11). The experiments reveal that the river water was somewhat polluted.

Conclusion

It was the first time SRA was used to process multiple chromatographic peaks simultaneously. The method provided good quantitative relationship for each analyte between concentration and intensity and offered lower LODs, as well. The developed method also obtained a satisfactory application in the analysis of real water samples. The successful application of SRA in this paper indicates that the algorithm should be an effective tool to improve the detection capability of the instrument and should be a promising approach to trace analysis of multiple analytes.

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