Kinetic Determination of Organic Vapor Mixtures with Single Piezoelectric Quartz Crystal Sensor Using Artificial Neural Networks and Partial Least Squares

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A single piezoelectric quartz crystal coated with one kind of crown ether was applied to the simultaneous determination of acid and amine vapor mixtures. From the adsorption and desorption curves of analytes, which had somewhat differences in shape, frequency shifts from ten time windows were taken as inputs for two chemometric methods, partial least squares (PLS) and artificial neural networks (ANN). The results showed that the prediction was better for artificial neural networks in both sample sets.

Recently the piezoelectric crystal sensor has received much attention as a fast, convenient and sensitive analytical tool, which has been used for detection of both vapors and liquids.[1-3] For multicomponent analysis in gaseous phases, the use of piezoelectric crystal array has been proposed.[4-6] Our laboratory has also detected some organic vapor mixtures with an array of nine piezoelectric crystal sensor coated with different crown ether derivatives.[7] In the process of measurement, we discovered that the adsorption and desorption model for some analytes had some differences. So in this paper, we only used one single piezoelectric crystal sensor coated with crown ether to quantitatively detect organic vapor mixtures. Two groups of analytes each contained two components were detected with two chemometric techniques, PLS and ANN. The frequency shifts from ten time windows were taken as inputs for PLS and ANN. This method has not been reported previously, which makes the detection device more convenient and practical. We have also tested this method successfully to simultaneously determine the concentration of sulfuric dioxide and the relative humidity.[8]

The apparatus shown in Figure 1. consisted of an piezoelectric quartz crystal (AT-cut, 9-MHz) with silver electrodes (No. 707 Factory, Beijing, China) was used in a Transistor-Transistor-Logic oscillator of our design. The frequency change was monitored by an N3165 frequency counter (Lodestar Electronics Corp., Taiwan) and the power was supplied by a PL2002A d. c. voltage regulator (Weituo Electronics LTD., Shenzhen, China). The Back-Propagation network program of ANN in data analysis was written in Turbo C language by ourselves, the PLS program was offered by the Central Laboratory in our school. All data analysis were treated by an PC-DX486 computer.

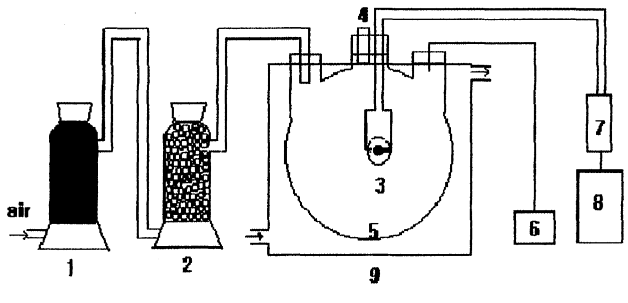
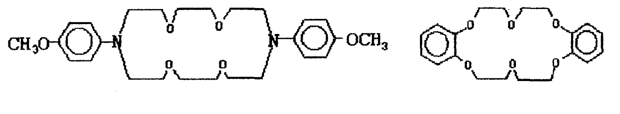


Figure 1. Diagram of the experimental system.
1. active carbon, 2. silica gel, 3. piezoelectric crystal
4. sample injection port, 5. 1L glass flask, 6. vacuum pump,
7. oscillator, 8. frequency counter, 9. water jacket.



(1) (2)

Figure 2. Molecular structure of crown ether used as coating material.

The coating material, crown ethers, was synthesized by Polymer Chemistry Institute in our school. Their molecular structure is in Figure 2. The first one was used to detect the first sample set consisting of formic acid and acrylic acid, and the second one was used to detect the second sample set consisting of n-butylamine and aniline. Both sides of the each crystal were coated with crown ether via the dropping method using a microsyringe.

The piezoelectric quartz was mounted in an 1.4L flask which was thermostated at 30±0.5 ℃. The stable oscillation frequency f_0 was recorded. Then we decreased the stress in detection cell with an vacuum pump until it arrived about 5 mm-Hg, the stable frequency f_1 was again recorded. After injection a certain amount of mixture of analytes using a microsyringe, i. e. formic acid and acrylic acid or n-butylamine and aniline, the initial reaction time was registered immediately. Five minutes after injection, the air was introduced in and the stress in the detection cell became normal. Let the system equilibrate for another five minutes, then purged the detection cell with dried and purified air at 3 $Lmin^{-1}$ till the frequency of the sensor restored to its fundamental value. From the initial reaction time, the frequency values at different time $f(t)$ (per 10 sec) were recorded. Frequency shifts $f_0 - f(t)$ from ten time windows, which could reflect the characteristics of the samples' adsorption and desorption process, were taken as inputs for PLS and ANN. Each sample was detected in triplicate in order to obtain an estimation of the precision of the sensor response.

A two-layer back-propagation network was used in our experiment which that has ten inputs (frequency shifts of different time windows) in the input layer, an arbitrary number of artificial neurons in the hidden layer (6) and two artificial neurons in the output layer (organic vapors). In our study, we have used a sigmoid activation function so the neural output o_i is given by

$$O_i = 1/[1+exp(-y_i)] \qquad (1)$$

and

$$y_i = \sum_{i=1}^{n} w_i x_i \qquad (2)$$

Where w_i is the weight and x_i is the input. In our experiment, learning rate in the network training was set as 0.1, the momentum coefficient, 0.6.

It can be seen from Figures 3, 4 that there were some differences in the outlines of the adsorption and desorption curves for the analytes because of the difference of interaction between the analytes and the coating material, crown ethers. The calibration lines between frequency shifts vs. the concentrations of the analytes have been checked for the four analytes in two sample sets (not shown here). The frequency shifts at different time are basically proportional to the concentrations of the analytes but not strictly. The interaction between the analytes and the crown ethers was explained in detail elsewhere.[7]

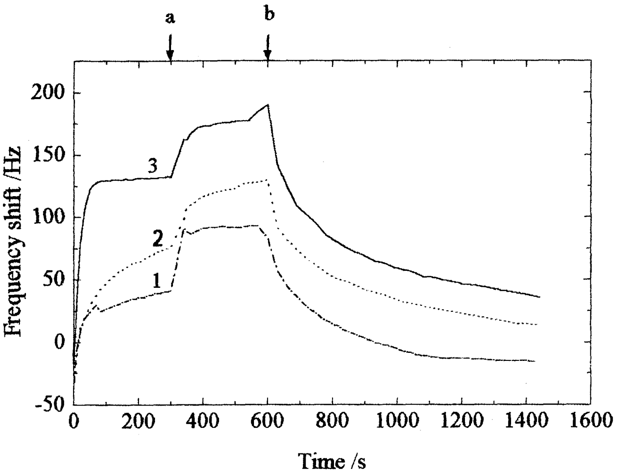


Figure 3. Frequency shift patterns for formic acid and acrylic acid. 1: formic acid (0.87 mgL^{-1}); 2: acrylic acid (1.6 mgL^{-1}); 3: sum of formic acid (0.87 mgL^{-1}) and acrylic acid (1.6 mgL^{-1}). a: The air was introduced in and the stress in the detection cell became normal. b: The dectection cell was purged with dried and purified air.

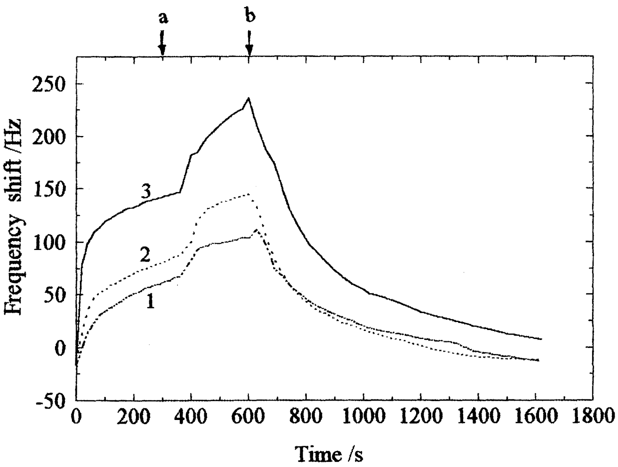


Figure 4. Frequency shift patterns for n-butylamine and aniline 1: n-butylamine (0.5 mgL^{-1}); 2: aniline (0.714 mgL^{-1}); 3: sum of n-butylamine (0.5 mgL^{-1}) and aniline (0.714 mgL^{-1}). a: The air was introduced in and the stress in the detection cell became normal. b: The dectection cell was purged with dried and purified air.

Table 1. Multivariate prediction results for formic acid and acrylic acid mixture

	actual concn, mg/L		PLS predicted concn, mg/L		rel error, %		ANN predicted concn, mg/L		rel error, %	
	A	B	A	B	A	B	A	B	A	B
1	2.61	2.40	3.10	2.42	18.7	0.67	2.56	2.16	2.15	9.67
2	3.05	3.20	4.11	5.44	34.9	70.0	2.85	3.03	6.70	5.40
3	1.74	2.40	1.93	1.85	10.7	23.0	1.59	2.34	8.35	0.95
4	2.18	2.80	1.45	3.28	33.6	17.1	2.11	2.65	3.14	5.42
av.					24.5	27.7			5.08	5.36

note : A: formic acid, B: acrylic acid

Table 2. Multivariate Prediction Results for n-butylamine and aniline mixture

	actual concn, mg/L		PLS predicted concn, mg/L		rel error, %		ANN predicted concn, mg/L		rel error, %	
	C	D	C	D	C	D	C	D	C	D
1	1.00	1.14	0.48	1.01	52.0	11.2	0.99	1.11	1.41	2.85
2	0.90	1.57	1.01	2.31	35.6	31.2	0.87	1.56	3.47	0.35
3	1.10	1.29	0.70	1.93	36.4	50.0	1.06	1.22	3.94	5.67
4	0.80	1.43	0.64	1.36	19.4	5.00	0.79	1.40	1.41	2.03
av.					35.4	24.4			2.56	2.72

note: C: n-butylamine, D: aniline.

In each group, eight mixtures of analytes of various concentrations were prepared as a calibration set according to factor-design, four other mixtures of analytes were prepared as test set and measured under the same experimental conditions. The predicted concentration results are given in Table 1 and Table 2. For the both sample sets predictions for ANN were better than those for PLS in all cases. The increase in prediction capacity for ANN is due to its advantageous ability to treat nonlinear problem, since while analyzing vapor mixtures, several components simultaneously interacted with the coating, crown ether, which may lead to complex nonlinear relationship between the responses of the sensor and the concentrations of the vapors. In contrast, PLS is good at dealing with linear problem, but it gave larger relative errors of prediction for the nonlinear problem.

The single crystal method put forward in this paper can be extended to other analytes and detection systems as long as there are some differences in the kinetic process. It is hopeful to become an practical method for multicomponent analysis.

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