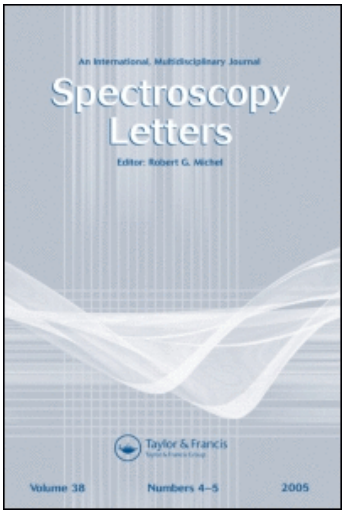

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Simultaneous Determination of Multicomponents in Air Toxic Organic Compounds Using Artificial Neural Networks in Ftir Spectroscopy

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SIMULTANEOUS DETERMINATION OF MULTICOMPONENTS IN AIR TOXIC ORGANIC COMPOUNDS USING ARTIFICIAL NEURAL NETWORKS IN FTIR SPECTROSCOPY*

Keywords: Multicomponents Analysis; Organic Compounds Analysis; Artificial Neural Networks; FTIR

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Abstract

The application of Artificial Neural Networks (ANNs) for nonlinear multivariate calibration using simulated FTIR data was demonstrated in this paper. Neural networks consisting of three layers of nodes were trained by using the back-propagation learning rule. Since parameters affect the performance of the network greatly, simulated data were used to train the network in order to get a satisfactory combination of all parameters. The mixtures of four air toxic organic compounds whose FTIR spectra are overlapped were chosen to evaluate the calibration and prediction ability of the network. The relative standard error (RSD%), the percent standard error of prediction samples (%SEP) and the percent standard error of calibration samples (%SEC) are used for evaluating the ability of the neural network.

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I. INTRODUCTION

Artificial neural networks (ANNs)[1,2] have gained much focus and popularity in recent years due to their ability to " learn " during a training process where they are presented with a sequence of stimuli(inputs) and a set of expected responses (outputs). Several works[3,4] have been done using artificial neural networks in multicomponent quantitative analysis.

The use of ANNs in FTIR spectroscopy is a new calibration method which is shown to be effective as well as Partial Least Squares Method (PLS)[5-7],Kalman Filter Method (KFM)[8], Classical Least Squares Method (CLS)[9].

In this paper, we demonstrate how artificial neural networks can be used to model spectra of mixtures to produce quantitative estimates of the concentrations of the compounds in the mixtures when there are serious overlapping between the spectral bands of the compounds. A set of parameters is obtained through the training process.

II. THEORY

A node is the fundamental element of an artificial neural network. Nodes of different layers are connected by series of weights between them. Then each nodes has a series of weighted inputs and the sum of the weighted inputs are transformed with a linear or nonlinear transfer function.

A three-layer feed-forward network which has an input layer, a hidden layer and an output layer were constructed in this paper. The input signals are absorbance values obtained from the spectrum region from 850 to 654 cm^{-1} at 4 cm^{-1} spectral resolution. The values are mean-centered before they are inputted the system. A sigmoid function as well as a linear function is used in the hidden layer to compare their effect on the network.

$$f(x) = 1/(1+e^{-x/?x})$$

The number of hidden nodes is adjustable. Changing the number of hidden nodes equals to changing the complexity of the neural network. The outputs from each hidden node are sent to each node in the output layer, the output of each output node is compared with the expected output. In this application, the concentration values were scaled to lie in the range from 0.2 to 0.8 by adding an offset and multiplying by a constant.

During the back-propagation learning process, the weights are adjusted by using a series of absorbance values and their corresponding expected output concentrations. When the output function is a linear one, the output layer error at node p is expressed by following:

$$\delta_{pk} = t_{pk} - o_{pk}$$

where δ_{pk} is the error between the target value t_{pk} and the actual output value o_{pk} at output node p. When a sigmoid output function is used, the output error is expressed as:

$$\delta_{pk} = (t_{pk} - o_{pk})\, o_{pk}\, (1 - o_{pk})$$

The hidden layer error at node j is associated with the weights w_{kj} between node k in the output layer and the node j in the hidden layer.

$$\delta_{pj} = o_{pj}\, (1 - o_{pj}) \sum \delta_{pk} w_{kj}$$

In the training process the errors from the output and hidden layers are back-propagated through the network by making adjustment to the weights of two connected layers.

$$\Delta w_{ji}(n) = \eta\, \delta_{pj}\, o_{pi} + \alpha\, \Delta w_{ji}(n-1)$$

where Δw_{ji} is the change of the weight between node j in the hidden layer and node i in the input layer. The change is determined by the learning rate η and the momentum α. n and $n-1$ are the present and previous numbers of iteration respectively. As the same, the change in the weight between node p in the output layer and node j in the hidden layer is

$$\Delta w_{pj} = \eta\, \delta_{pk}\, o_{pi}\, \alpha\, \Delta w_{pj}(n-1)$$

At the beginning of the processing the weights are initialized with random values.

The greater the parameter η, the faster the neural network converges. However, when the learning rate is set too high, the neural network is unstable and vibrates violently. It is necessary to add the momentum α to ease the vibration. An appropriate value of learning rate η should be found too. The satisfactory constants η and α are obtained after doing a series of tests using different combinations of these two parameters.

Then the "unknown" concentrations of components in the mixture samples and the percent standard error of prediction sample can be estimated. The result is satisfactory.

III. EXPERIMENT

3.1 The choice of four air toxic organic compounds in a mixture

The air toxic organic compounds chosen in this study are O-Xylene, m-Xylene, p-Xylene and Ethylbenzene. They have the following distinctive characteristics : 1) Their spectral feature are nearly indistinguishable, and as they have close boiling points, it is nearly

impossible to separate each component to measure their concentration. The characteristic absorption bands and the boiling points of the five organic compounds are listed in Table 1. The FTIR spectra of these components at the concentration of 100ppm and their mixture where the concentrations of each component are 100ppm can be seen from Fig.1 from which situations of strong overlap among the four organic compounds can be seen.

3.2 Calibration and prediction samples

Of the fifty simulated data sets, forty are used as calibration samples and ten are prediction samples. The concentration of each component in the calibration and prediction sample are varied from 10 to 100 ppm. The concentrations of components for each prediction sample are listed in Table 2.

3.3 The choice of the absorption bands for the measured wavenumbers

The spectral region in 850~654 cm^{-1} is used for the multivariate calibration. The spectral limits are selected in order to cut off most of the contribution from carbon dioxide (2400~2230 and 735~613cm^{-1}) and water vapor (4000~3170 and 2140~1230cm^{-1}). The interval of the measured wavenumbers is 4cm^{-1}.

IV. RESULTS AND DISCUSSION

4.1 Influence of parameters

Parameters Influence the performance of the artificial neural network greatly. In order to find a set of satisfactory parameters, a lot of work has been done.

4.1.1 Number for hidden nodes

The proper number of hidden nodes is determined by training the neural network with different number of hidden nodes ranging from one to ten and comparing the %SEP(average standard error of prediction)of o-Xylene. Fig.2 shows a plot of %SEP of o-Xylene when changing the number of hidden nodes. A minimum of in mean %SEP occurred when four nodes were used in the hidden layer which can be seen from Fig.2 and we can see that networks with fewer than four nodes in the hidden layer are not simplex enough to model the prediction concentration, while networks with more than four nodes are unnecessarily complex and then too much noise occurs.

4.1.2 Learning rate

A learning rate of 0.15 was found to work well with the spectroscopic data sets. This value helped to maintain the network stability during training process. If the learning rate was set too high, the network became unstable, accordingly the %SEP would be high.

4.1.3 Momentum α

In order to find a proper combination of the learning rate η and the momentum value α, we used various momentum α with the learning rate of 0.15. It was found that as the

Table 1. The characteristic absorption bands and boiling point of the four organic compounds

Compounds	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
bp[a] (°C)	142	138-139	138	136
Spectral bands[b]	3168-2800	3158-2825	3173-2839	3160-2850
(cm^{-1})	820-660	820-650	852-650	850-660

Note : a) Boiling point.

b) The characteristic absorption bands.

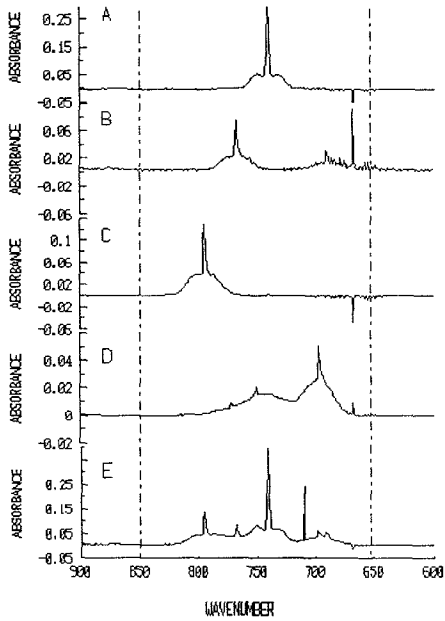

Fig.1. The spectra of the four organic compounds and their mixture.

A. o-Xylene; B. m-Xylene; C. p-Xylene;

D. Ethylbenzene; E. Their mixture.

Table 2. The composite of the prediction samples ppm

No.	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
1	65.00	50.00	25.00	25.00
2	50.00	65.00	25.00	50.00
3	30.00	25.00	65.00	50.00
4	25.00	25.00	25.00	65.00
5	65.00	65.00	65.00	65.00
6	75.00	30.00	15.00	40.00
7	30.00	75.00	40.00	40.00
8	25.00	50.00	70.00	100.00
9	40.00	35.00	85.00	60.00
10	80.00	80.00	80.00	80.00

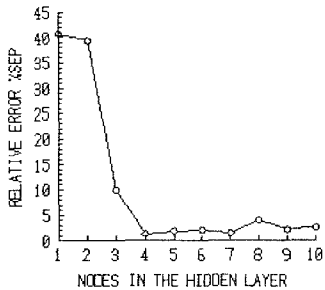

Fig.2. Plot of %SEP of o-Xylene, versus the number of nodes in the hidden layer. η=0.15, α =0.0, iteration number was 5000.

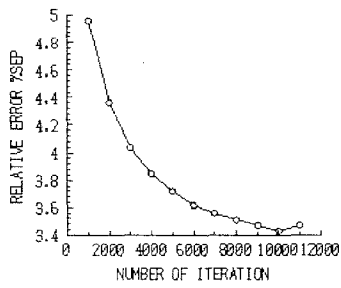

Fig.3. Plot of %SEP of Ethylbenzene, versus the number of iteration. η =0.15, α=0.0, number of nodes in the layer was 4.

Table 3. The results for the prediction samples at the spectral bands of 850-654cm^{-1}

No.	o-Xylene			m-Xylene			p-Xylene			Ethylbenzene		
	$C_{real.}$	$C_{meas.}$	RSD %	$C_{real.}$	$C_{meas.}$	RSD %	$C_{real.}$	$C_{meas.}$	RSD %	$C_{real.}$	$C_{meas.}$	RSD%
1	65.00	65.84	1.29	50.00	48.79	2.42	25.00	24.66	1.38	25.00	25.24	0.97
2	50.00	50.64	1.27	65.00	65.57	0.87	25.00	23.94	4.24	50.00	50.03	0.06
3	30.00	29.57	1.42	25.00	24.38	2.50	65.00	66.04	0.60	50.00	49.76	0.48
4	25.00	24.73	1.07	25.00	24.90	0.40	25.00	25.08	0.30	65.00	65.09	0.15
5	65.00	64.84	0.25	65.00	64.90	0.16	65.00	65.49	0.75	65.00	65.07	0.11
6	75.00	76.12	1.49	30.00	30.58	1.94	15.00	13.83	7.80	40.00	40.77	1.94
7	30.00	30.24	0.80	75.00	75.33	0.44	40.00	39.52	1.20	40.00	39.58	1.04
8	25.00	24.24	3.03	50.00	51.55	3.10	70.00	68.85	1.64	100.00	94.05	5.95
9	40.00	40.46	1.15	35.00	34.54	1.32	85.00	84.77	0.27	60.00	60.24	0.40
10	80.00	77.43	3.21	80.00	78.93	1.34	80.00	80.74	0.93	80.00	78.39	2.01
%SEP			2.07			1.60			1.58			3.43

Note : The conditions are as follows:

1)η=0.15, α=0.00, n=10000 ;

2) hidden nodes: 4 ;

3) Linear output function. Note: The number was beyond 10000 as seen from Fig.3, so we chose the iteration number 10000 to calculate the concentrations of the prediction samples.

learning rate was low, there was no apparent advantage of using the momentum term α. Therefore, the momentum term used in this study is set as zero.

4.1.4 Number of learning iteration n

Increasing the number of iteration can result in a better performance of the network, but there is only a little improvement when the iteration

4.2 The prediction results obtained in the spectral band of 850–654cm^{-1}

As the above parameters are determined, we use ten simulated groups of "unknown" samples listed in Table 3 to check the performance of the network. In Table 3 the relative standard deviation (RSD%) for each prediction sample was small. The %SEP for o-Xylene, m-Xylene, p-Xylene and Ethylbenzene in all the prediction samples were 2.07, 1.60, 1.58 and 3.43 %, respectively.

V. CONCLUSION

The concentration analysis of four-component mixture with ANNs used in FTIR spectroscopy has been introduced. Parameters affect the stability and capability of an artificial neural network greatly when it is used for multicomponent quantitative analysis. A better result is obtained when the measured spectral band in 850-654 cm^{-1} is selected. This result shows that in spite of its tedious training process, Artificial Neural Networks can be thought a powerful tool for the simultaneous analysis of the concentrations of even a complex mixture containing similar compounds with strongly overlapped absorption bands one another.

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