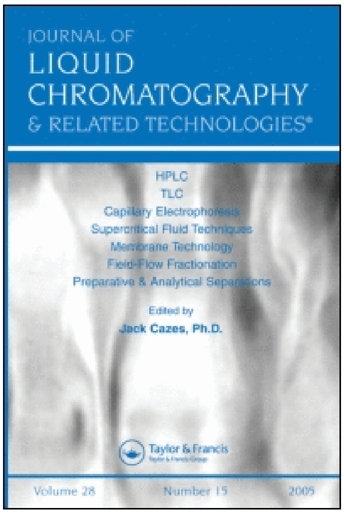

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Tomislav Bolanča[a]; Štefica Cerjan Stefanović[a]; Šime Ukić[a]; Marko Rogošić[a]
[a] University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

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Development of Temperature Dependent Retention Models in Ion Chromatography by the Cascade Forward and Back Propagation Artificial Neural Networks

Tomislav Bolanča, Štefica Cerjan Stefanović, Šime Ukić, and Marko Rogošić

University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

Abstract: The most important part of the complex ion chromatography method development process is retention modeling. It tries to integrate the demands for high quality ion chromatography with the demands for low consumption of chemicals, fast analysis, and the short time of method development. This work compares the properties of the cascade forward and back propagation artificial neural network in the development of temperature dependent retention models. The retention times of bromate, bromide, nitrite, iodide, and perchlorate were modeled in relation with temperature of separation process, concentration of hydroxide eluent competing ion, and eluent flow rate. Artificial neural networks were optimized in term of selecting the optimal training algorithm, optimal number of hidden layer neurons, activation function, and number of experiments needed for modeling procedure. The retention model based on cascade forward methodology exhibited superior predictive ability and, therefore, should be the method of first choice for the temperature dependent optimization in ion chromatography.

Keywords: Back propagation artificial neural network, Cascade forward artificial neural network, Ion chromatography, Retention model, Temperature of separation process

Correspondence: Tomislav Bolanča, University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 20, 10 000 Zagreb, Croatia. E-mail: Tomislav.Bolanca@fkit.hr

INTRODUCTION

Mathematical models based on artificial intelligence are proven to be helpful in the description and understanding of the behavior of ion chromatography systems and can speed up the method development. The developed methods are highly selective, provide good chromatographic resolution, and have shortened chromatographic runtimes.

The first issue in modeling of an ion chromatographic separation is to determine the relationship between the retention time and parameters controlling the retention, both in isocratic and/or gradient elution mode. The most important parameters are the concentrations of eluent competing ions. Several approaches have been used in isocratic elution retention modeling. These are: 1) the stoichiometric approach,[1–9] 2) the electrostatic interaction theory,[10,11] and 3) the empirical approach by the artificial neural networks.[12,13] The comparison between theoretical and empirical retention models in ion chromatography was extensively investigated showing that empirical retention models based on the artificial neural networks exhibit better predictive ability.[14–19] The problem of retention modeling becomes even more complex when gradient elution is examined. If gradient elution is predicted on the basis of isocratic elution information, then the predictive ability is compromised by the applied isocratic elution model.[20–23] Therefore, it is extremely important to develop the isocratic elution retention model with as high a predictive ability as possible.

Recently, the temperature as a separation parameter has attracted the growing attention. It has been demonstrated that the variation of column temperature may affect the separation between monovalent and divalent cations on a Dionex CS12A stationary phase.[24] The separation of halides has been altered by increasing the temperature from 25 to 60°C.[25] These observations created the need for extensive investigation of temperature dependent retention models. The artificial neural networks seem to be the reasonable choice, because of their high speed and accuracy in modeling multiparameter, nonlinear relationships between input and output variables.

The most commonly used neural network model is the back propagation network,[12,17–19] which is a multilayer feed forward network. The disadvantage of multilayer feed forward networks using error back propagation lies in the fact that the optimal number of hidden layers and units varies from task to task and, therefore, must be determined experimentally. If too many hidden units are used, the network will learn irrelevant details in the training set and, once trained, will not generalize well. Conversely, overly simple networks will fail to describe the real features of the system properly. One approach to automatically determine the optimum network size is to start with a minimum size network and then to add hidden units and connections gradually. This is the principle of the so called cascade forward artificial neural networks, which increase the number of hidden layers dynamically during the learning phase.[26]

The aim of this work is the development of retention models in ion chromatography by using two approaches: cascade forward and back propagation artificial neural networks. The retention of bromate, bromide, nitrite, iodide, and perchlorate were modeled in relation with the separation temperature, concentration of hydroxide competing ion, and eluent flow rate. The number of hidden layer neurons, activation function, and different training algorithms (gradient descent with momentum and adaptive learning rate, scaled conjugate gradient, Levenberg-Marquardt and Levenberg-Marquardt with Bayesian regularization) were optimized in terms of obtaining precise and accurate retention models with respect of minimization of unnecessary experimentation. The performance characteristics of developed artificial neural networks retention models were validated with external experimental data sets.

Theory

The standard multilayer perceptron algorithm can train any network as long as its weights, net input, and transfer functions have derivative functions. The weights can be adjusted according to gradient descent:

$$\Delta w = \eta \frac{\partial E}{\partial w} \tag{1}$$

where η is the learning rate, Δw is the weight change, and E is the sum of the squares of errors. The problem arises if a standard gradient descent method gets trapped into local minima, hence variations were suggested, i.e., gradient descent with momentum and learning rate according to:

$$\Delta w_n = \alpha \Delta w x_{n-1} + \eta(1 - \alpha)\frac{\partial E}{\partial w} \tag{2}$$

where α is the smoothing factor for applying the momentum and η is the learning rate.

The cascade forward algorithm was developed by Fahlman and Lebiere.[26] The procedure begins with a minimal network that has some inputs and one or more output nodes as indicated by input/output considerations, but no hidden nodes. The gradient descent algorithm, for example, may be used to train the network. The hidden neurons are added to the network one by one, thereby obtaining a multilayer structure. Each new hidden neuron receives a synaptic connection from each of the input nodes and also from each preexisting hidden neuron. When a new hidden neuron is added, the synaptic weights on the input side of that neuron are frozen; only the synaptic weights on the output side are trained repeatedly. Learning in cascade forward artificial neural network takes place as repeating two phase steps. The first involves the embedded standard learning algorithm, which in our case is back propagation. The learning algorithm begins with no hidden units. The direct input output connections are trained as far as possible over the entire training set. When no significant error reduction has occurred after a certain number of training cycles (controlled maximum number of epochs set by the user), the entire training set is presented to the network one last time to measure the error. If the network's performance is satisfactory, the procedure is halted; if not, there must be some residual error that needs to be reduced further. This is achieved by adding a new hidden unit to the network, using the unit creation algorithm.

The second phase involves the creation of a "candidate" unit. The candidate unit is connected with all input units and all existing hidden units. This leads to the cascading architecture, as each new unit is connected to all preceding units. There are no connections from these candidate units to the output units. The links leading to each candidate unit are trained with the selected standard learning algorithm (back propagation) to maximize the correlation between the residual error of the network and the activation of the candidate units. The goal of this adjustment is to maximize S, the sum over all output units o of the magnitude of the correlation between V, the candidate unit's value, and E_o, the residual output error observed at unit o. S is defined as:

$$S = \Sigma_o |\Sigma_p (V_p - \overline{V})(E_{p,o} - \overline{E_o})| \tag{3}$$

where o is the network output at which the error is measured and p is the training pattern. The quantities $\overline{V}$ and $\overline{E}_o$ are the values of V and E_o averaged over all patterns. In order to maximize S, $\partial S/\partial w_i$, the partial derivative of S with respect to each of the candidate unit's incoming weights, w_i is computed.

$$\frac{\partial S}{\partial w_i} = \Sigma \sigma_o (E_{p,o} - \overline{E_o}) f_p I_{i,p} \tag{4}$$

where σ_o is the sign of the correlation between the candidate's value and output o, f'_p is the derivative for pattern p of the candidate unit's activation function with respect to the sum of its inputs, and $I_{i,p}$ is the input the candidate unit receives from unit i for pattern p. After computing $\partial S/\partial w_\mathrm{i}$ for each incoming connection, gradient ascent is performed to maximize S. Once again only a single layer of weights are trained.

When S stops improving, the new candidate is installed as a unit in the active network, input weights are frozen, and the cycle is continued as described above. Because of the absolute value in the formula for S, a candidate unit cares only about the magnitude of its correlation with the error at a given output, and not about the sign of the correlation. As a rule, if a hidden unit correlates positively with the error at a given unit, it will develop a negative connection weight to that unit, attempting to cancel some of the error; if the correlation is negative, the output weight will be positive. Since a unit's weights to different outputs may be of mixed sign, a unit can sometimes serve two purposes by developing a positive correlation with the error at one output and a negative correlation with the error at another.

Training is stopped if the correlation ceases to improve or a predefined number of cycles are exceeded. The final step of the second phase is the inclusion, as a hidden unit, of the candidate unit. This involves freezing all incoming weights (no further modifications will be made) and creating randomly initialized connections from the selected unit to the output units. This new hidden unit represents, as a consequence of its frozen input connections, a permanent feature detector. The weights from this new unit and the output units will undergo training. Because the outgoing connections of this new unit are subject to modification, its relevance to the final behavior of the trained network is not fixed. These two phases are repeated until either the training pattern has been learned to a predefined level of acceptance or a preset maximum number of hidden units have been added, whichever occurs first.

EXPERIMENTAL

Instrumentation

A Dionex DX600 chromatography system (Sunnyvale, CA, USA) was used in all experiments, equipped with a quaternary gradient pump (GS50), chromatography module (LC30), and detector module (ED50A). The separation and suppressor columns used were Dionex IonPac AG16 (4 × 50 mm) guard column, IonPac AS16 (4 × 250 mm) separation column, and ASRS – ULTRA II – 4 mm suppressor, the latest working in recycle mode. The sample loop volume used was 25 μL. The system was computer controlled by the Chromeleon 6.70, Build 1820 software. The temperature of separation was set at 30.0°C, 35.0°C, 40.0°C and 45.0°C; the concentration of eluent competing ion was set at 10.00, 33.00, 56.00, and 80.00 mmol/L; the eluent flow rate was set at 0.70, 0.80, 0.90, and 1.00 mL/min. The full factorial experimental design was used providing A total of 64 experimental data points.

Reagents and Solutions

Standard solutions of bromate, bromide, nitrite, iodide, and perchlorate (1.0000 g/L) were prepared from the air dried (at 105°C) salts of individual anions of p.a. grade (Merck, Darmstadt, Germany). Appropriate amounts of individual salts were weighed into volumetric flasks (100 mL) and dissolved with Milli-Q water. Mixed stock standard solutions of all the mentioned anions (100.00 mg/L) was prepared by measuring the appropriate volumes of standard solutions into 100 mL volumetric flasks; these were filled to the mark with Milli-Q water. Working mixed standard solutions of anions (10.00 mg/L) were prepared by measuring the appropriate volume of the mixed stock standard solution into 100 mL volumetric flasks, again filled with Milli-Q water. Working eluent solutions were prepared by the appropriate on line dilution of KOH from a standard Dionex cartridge with Milli-Q water. In all cases, 18 $M\Omega cm^{-1}$ water (Millipore, Bedford, MA, USA) was used for dilution.

Neural Networks

The two neural networks studied in this paper were the cascade forward and back propagation artificial neural network. The input layer consisted of three neurons representing temperature of separation process, concentration of OH^- in eluent, and eluent flow rate. The output layer consisted of five neurons representing the retention of particular anions (bromate, bromide, nitrite, iodide, and perchlorate). The training algorithm, activation function connecting input and hidden layer, number of neurons in hidden layer, and number of experimental data points used for training calculations had to be optimized. The linear activation function connecting hidden and output layer was used in all cases. The training algorithms tested were gradient descent with momentum and adaptive learning rate, scaled conjugate gradient, Levenberg-Marquardt, and Levenberg-Marquardt with Bayesian regularization. Two activation functions were used: sigmoid and hyperbolic tangent. The number of neurons in the hidden layer was varied from 3 to 12 (in the case of the cascade forward network this was the maximum allowed number, in the case of the back propagated network this was the fixed number). The number of experimental data points in the training set was varied from 4 to 20; the experimental data was used for validation purposes.

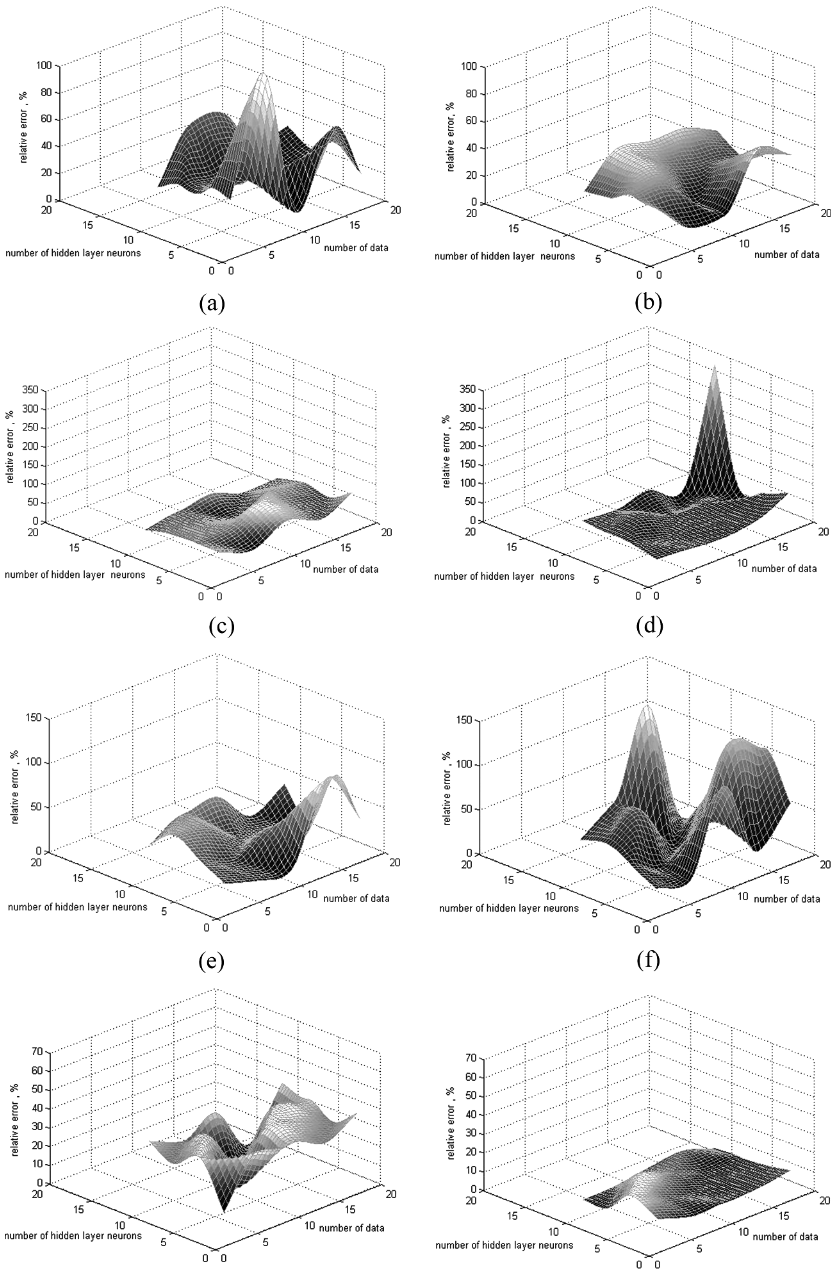
It is preferable that every experimental data point has an equal influence on the neural network model, if training and testing sets are aimed to be the representative groups of data of the whole design area. For this reason, the random function was applied for selection of experimental data points used for training, testing, and validation sets of data. The input experimental data were scaled to obtain their mean values and standard deviations of 0 and 1, respectively. This was necessary because most neural networks could accept input values in any range, but they were sensitive to inputs in a far smaller range.

To test the predictive performance of the developed artificial neural network retention model, an independent validation set was used followed by statistical evaluation. All calculations were performed in MATLAB 7.0.0. (MatWorks, Sherborn, USA) environment.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the results of optimization of artificial neural network retention models. One can observe that the cascade forward artificial neural network optimization produces results with significantly different error hyperplanes than those obtained by using the back propagated artificial neural network. The error hyperplanes obtained by using the cascade forward artificial neural networks show more emphasized minimums and maximums. The reason for that lies in the fact that cascade forward artificial neural networks add and train one neuron at the time, resulting with an additional factor helping the overall global search for the minimum on the error hyperplane. More developed error hyperplanes offers several advantages. The first one is a more accurate training process due to a lower possibility for getting trapped in the local minimum. Furthermore, the training process is faster due to higher gradients in the hyperplane. The overall numbers of local minima are lower than those observed by using back propagated artificial neural networks. This indicates the cascade forward artificial neural network is a more suitable retention modeling methodology in ion chromatography.

Within the chosen artificial neural network methodology, both the training algorithm and the activation function show the greatest influence on the results of the overall neural network optimization process. Figures 1 and 2 show that the Levenberg-Marquardt training algorithm with Bayesian regularization produces models with the lowest relative error of all the tested algorithms in all domains of the optimized parameters (activation function, number of hidden layer neurons, and number of experimental data points used for the training procedure). This leads to the significant increase of predictive ability of the final artificial neural network retention model and could enable lowering of the number of experimental data points used for the training procedure without severe impact on the performance characteristics of the model. The Bayesian regularization procedure allows for the possibility of overlapping the training and validation data sets. This advantage may lower significantly the experimental time and effort by reducing the overall size of data sets.


relative error , %
number of hidden layer neurons
number of data
0
20
40
60
80
100
50
150
200
250
300
350
10
30
70
5
15

(a) (b)

(c) (d)

(e) (f)

(g) (h)

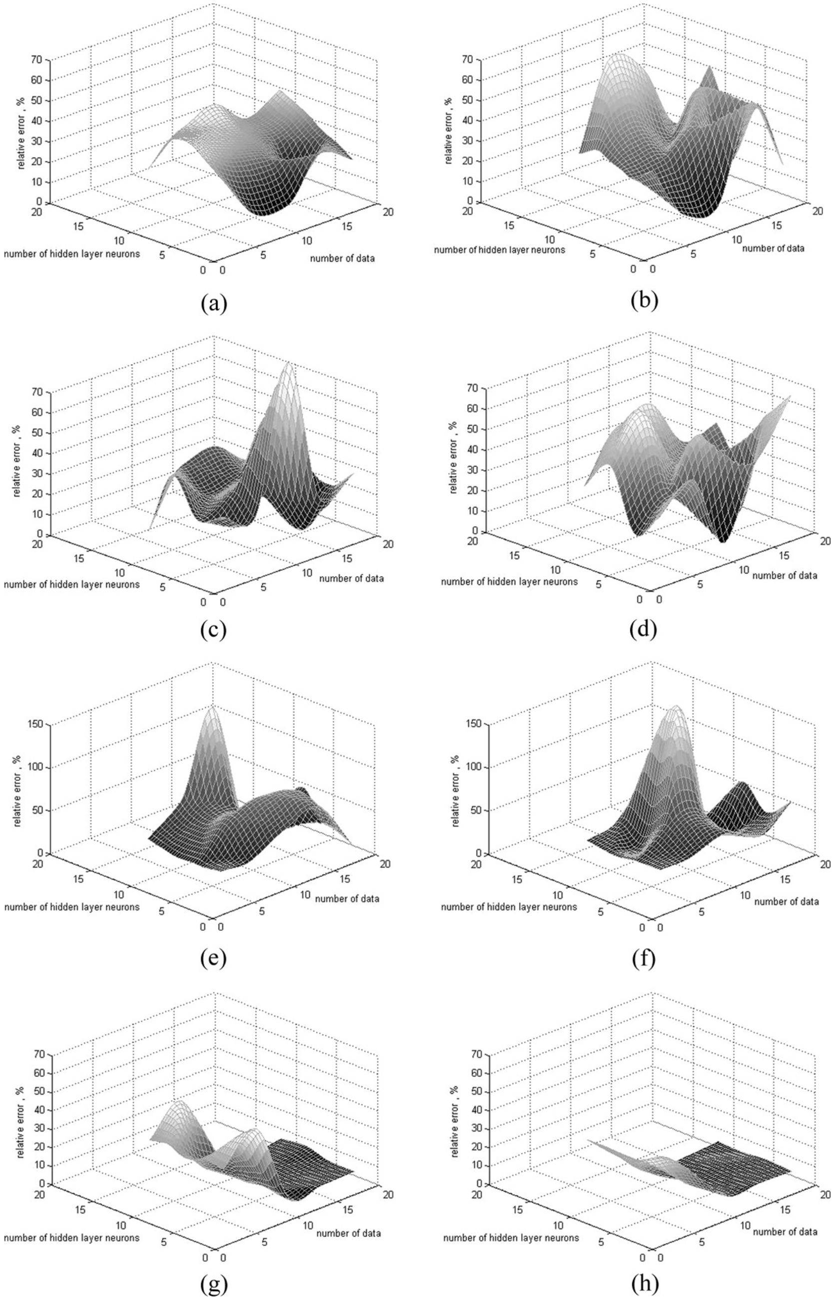
Furthermore, Figures 1 and 2 show that the hyperbolic tangent activation function provides lower relative errors than the sigmoid one, for all the training algorithms. This result, in conjunction with the previous discussion about the selection of the training algorithm, indicates the Levenberg-Marquardt training algorithm with Bayesian regularization and hyperbolic tangent activation function, is the optimal combination for retention modeling in ion chromatography.

Figures 1 and 2 also indicate the optimization of the number of hidden layer neurons and number of experimental data points needed for the training set. It is preferable to reduce the number of experimental data points used for training in order to shorten the experimental procedure. Figures 1 and 2 show that the number of experimental data points used for training procedure can be reduced to 16 without severe influence on the predictive ability of the retention model. The optimal allowed number of neurons in the hidden layer in the case of the selected optimal conditions (cascade forward artificial neural network, Levenberg-Marquardt training algorithm with Bayesian regularization, hyperbolic tangent activation function, and 16 experimental data points for training set) is 9.

The prediction power of the optimal artificial neural network retention models was tested with an external experimental data set and the results are shown in Table 1. The zero value for the intercept and unity value for the slope are expected to be found within the boundaries of the 95% confidence interval, which is the case for all of the investigated anions. The correlation coefficients are found in a very narrow area, between 0.9977 for nitrite and 0.9940 for perchlorate. That proves the very good agreement between the measured and predicted retention, and shows that there is no systematic error in the optimized artificial neural network retention model. The model can, therefore, be used for the method development in numerous applications in ion chromatography. The model is capable to predict the separation and analysis time simultaneously, in relation with the separation temperature,

◀

Figure 1. Influence of the number of hidden layer neurons and number of experimental data points on the relative error of the cascade forward artificial neural network retention model. (a) Gradient descent with adaptive learning rate; sigmoid activation; (b) Gradient descent with adaptive learning rate; hyperbolic tangent activation; (c) scaled conjugate gradient; sigmoid activation; (d) scaled conjugate gradient; hyperbolic tangent activation; (e) Levenberg-Marquardt; sigmoid activation; (f) Levenberg-Marquardt; hyperbolic tangent activation; (g) Levenberg-Marquardt algorithm with Bayesian regularization; sigmoid activation; (h) Levenberg-Marquardt algorithm with Bayesian regularization; hyperbolic tangent activation.


relative error , %
number of hidden layer neurons
number of data
0
10
20
30
40
50
60
70
100
150
0
5
10
15
20

(a) (b) (c) (d) (e) (f) (g) (h)

Table 1. The performance characteristics of the optimal artificial neural network retention model. Predicted against measured retention

Ions	Bromate	Bromide	Nitrite	Iodide	Perchlorate
R^2	0.9968	0.9959	0.9977	0.9957	0.9940
Slope					
Value	0.9711	0.9324	0.9188	0.9081	0.9851
Lower 95%	0.8039	0.7978	0.8142	0.8052	0.8698
Upper 95%	1.1384	1.0662	1.0233	1.0109	1.0971
Intercept					
Value	0.0472	0.1148	0.0882	0.0303	0.4993
Lower 95%	−0.0399	−0.0439	−0.1602	−0.1060	−0.1109
Upper 95%	0.1345	0.2253	0.1605	0.5004	0.8878

concentration of eluent competing ion, and eluent flow rate, without performing unnecessary experimentation.

CONCLUSION

This work describes the development of temperature dependent retention models in ion chromatography by using cascade feed forward as well as back propagated artificial neural networks. The retention of bromate, bromide, nitrite, iodide, and perchlorate were modeled in relation with the temperature of separation, concentration of eluent competing ion, and eluent flow rate. It is shown that the cascade forward artificial neural network structure offers several advantages over the standard back propagation algorithm. The developed model, by its faster training and additional accuracy properties, reduces the analysis time and experimental effort, and provides valuable savings. It is shown that the developed retention model has superior predictive ability (coefficient of correlation

◀

Figure 2. Influence of the number of hidden layer neurons and number of experimental data points on the relative error of the back propagated artificial neural network retention model. (a) Gradient descent with adaptive learning rate; sigmoid activation; (b) Gradient descent with adaptive learning rate; hyperbolic tangent activation; (c) scaled conjugate gradient; sigmoid activation; (d) scaled conjugate gradient; hyperbolic tangent activation; (e) Levenberg-Marquardt; sigmoid activation; (f) Levenberg-Marquardt; hyperbolic tangent activation; (g) Levenberg-Marquardt algorithm with Bayesian regularization; sigmoid activation; (h) Levenberg-Marquardt algorithm with Bayesian regularization; hyperbolic tangent activation.

ranged between 0.9977 for nitrite and 0.9940 for perchlorate) and is not affected by the systematic error (95% confidence intervals include values zero and one for the intercept and slope, respectively). That indicates that the developed cascade forward artificial neural network retention model can be beneficial for the development of temperature dependent methods in ion chromatography.

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