Classification of Venezuelan spirituous beverages by means of discriminant analysis and artificial neural networks based on their Zn, Cu and Fe concentrations

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Abstract

Copper, zinc and iron concentrations were determined in "aguardiente de Cocuy de Penca" (Cocuy de Penca firewater), a spirituous beverage very popular in the North-Western region of Venezuela, by flame atomic absorption spectrometry (FAAS). These elements were selected for their presence can be traced to the (illegal) manufacturing process of the aforementioned beverages. Linear and quadratic discriminant analysis (QDA), and artificial neural networks (ANNs) trained with the backpropagation algorithm were employed for estimating if such beverages can be distinguished based on the concentrations of these elements in the final product, and whether it is possible to assess the geographic location of the manufacturers (Lara or Falcón states) and the presence or absence of sugar in the end product. A linear discriminant analysis (LDA) performed poorly, overall estimation and prediction rates being 51.7% and 50.0%, respectively. A QDA showed a slightly better overall performance, yet unsatisfactory (estimation: 79.2%, prediction: 72.5%). Various ANNs, comprising a linear function (L) in the input layer, a sigmoid function (S) in the hidden layer(s) and a hyperbolic tangent function (T) in the output layer, were evaluated. Of the networks studied, the (3L:5S:7S:4T) gave the highest estimation (overall: 96.5%) and prediction rates (overall: 97.0%), demonstrating the superb performance of ANNs for classification purposes.
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1. Introduction

The assessment of trace elements in products for human consumption (food and beverages) is of utmost importance for a number of reasons. Firstly, it is well known that they may be harmful, and even lethal, above certain concentration levels [1]. Therefore, very stringent regulations have been issued in order to insure and preserve the consumer's well being. Secondly, and from the marketing point of view, some elements may determine, but also negatively affect the organoleptic characteristics and overall quality of a given product. The latter goes in detriment of the manufacturer; thus, great care must be placed on quality control protocols so as to maintain the quality of the product and its niche in the market. Finally, and interestingly enough, certain chemical components can serve as markers for identification of the product's geographic origin and authenticity. This plays an important role in preventing illegal products to pass off as the authentic ones, not only fooling the consumer, but then again, affecting the manufacturer as well.

The observations stated in the preceding paragraph are particularly evident when it comes to worldwide popular beverages such as beer, wine, coffee, etc. Effectively, a great deal of methods has been developed for the determination of trace, minor and major elements in such beverages [2–7]. Assessment of these sample's origins has been mostly conducted through the application of chemometric techniques, namely, partial least-squares regression (PLSR) [8], principal components analysis (PCA) [9–13], linear discriminant analysis (LDA) [11,14,15], k-nearest neighbor (KNN) [10,11], etc.

Cocuy is a spirituous beverage, similar to the worldwide famous tequila, which is very popular in the North-Western region of Venezuela. It is made by distillation of the plant *Agave cocuy*, aged for 3 years, with a maximum addition of cane alcohol of 70% v/v. The "aguardiente de Cocuy de Penca" (Cocuy de Penca firewater) is, on the contrary, an illegal beverage produced in clandestine distilleries hidden in the forest away from local authorities. Evidently, production of this beverage is not under any quality control supervision by the regional government. As such, it is supposed that concentration of some metals may be above acceptable levels. Capote et al. determined the concentration of Cu, Fe and Zn in homemade Cocuy beverages by total-reflection X-ray fluorescence spectrometry (TXRFS) and flame atomic absorption spectrometry (FAAS) [4]. These authors found that, while iron and zinc levels were below the maximum permissible levels in rum and whiskey (there are no current Venezuelan legislation concerning metals concentrations in alcoholic beverages such as Cocuy), copper levels where well above them. The latter derives from the fact that copper coils are employed in the manufacturing process, thus part of the element is leached into the final product. Paredes determined lead by FAAS in Cocuy samples ($N = 28$) using an on-line pre-concentration system [16]. This author found concentration levels ranging from 12.6 to 370.0 $\mu g \, l^{-1}$ Pb, with an average of $78.9 \pm 98.5 \, \mu g \, l^{-1}$ Pb. For comparison purposes, 7% of the samples had lead concentrations exceeding maximum permissible levels set for wine in Europe (300 $\mu g \, l^{-1}$), 11% were above those in Canada (200 $\mu g \, l^{-1}$) and 25% violated the corresponding limit (100 $\mu g \, l^{-1}$) in the US.

The aim of the present work was the development of a strategy for evaluating whether zinc, copper and iron could be used to classify these illegally-manufactured Cocuy firewaters according to the geographic location of the manufacturers, distributed along the Venezuelan states of Lara and Falcón, and the presence or absence of sugar in the final products. The selection of such elements was based on a previous work [4]. As these elements are directly related to the utilization of copper coils, they may provide information on the manufacturing process, and may be useful in establishing a quality-control policy in the making of such beverage. Artificial neural networks (ANNs) will be used for such a goal, due to their well-recognized capacity for pattern recognition [17–20]. LDA and quadratic discriminant analysis (QDA) will be performed for comparison purposes. The latter were selected on the basis that, like ANNs trained with the backpropagation algorithm, they also work on a supervised-training fashion.

2. Theory

ANNs derive their names from their similarity to their biological counterparts. They are pseudo-parallel processing systems capable of "adaptable learning", meaning that they can do so without the formalisms and restrictions of computer programming languages. The fundamental constituents of the ANNs are called nodes or neurons. Fig. 1a shows a basic representation of one of such units. Each node performs a series of simple calculations. Firstly, the input signals (X_i) are processed in the "body" of the neuron according to:

$$Net_i = \sum_i w_i X_i \qquad (1)$$

where w_i, the weights, are an analogy of the biological synapses. Net_i may take large positive or negative values; therefore, it is further modified in a second step. Various transfer functions (Γ) have been proposed for this purpose, each of them accomplishing different transformations. The unipolar sigmoid (Eq. (2)) and the hyperbolic tangent are among these functions:

$$\Gamma_i = f(Net_i) = Out_i = \frac{1}{1 + \exp[-(Net_i + \theta)]} \qquad (2)$$

They are both monotonous, non-linear functions which restrict the output of the neuron to between 0 and 1, or −1 and 1, respectively. The term θ is known as the bias, and it represents a threshold value above which the neuron is said to "fire", or emit a signal. This kind of transfer function is what makes ANNs particularly suitable for modeling non-linear systems. The value Out_i is thus propagated to the neurons on to the following layers.
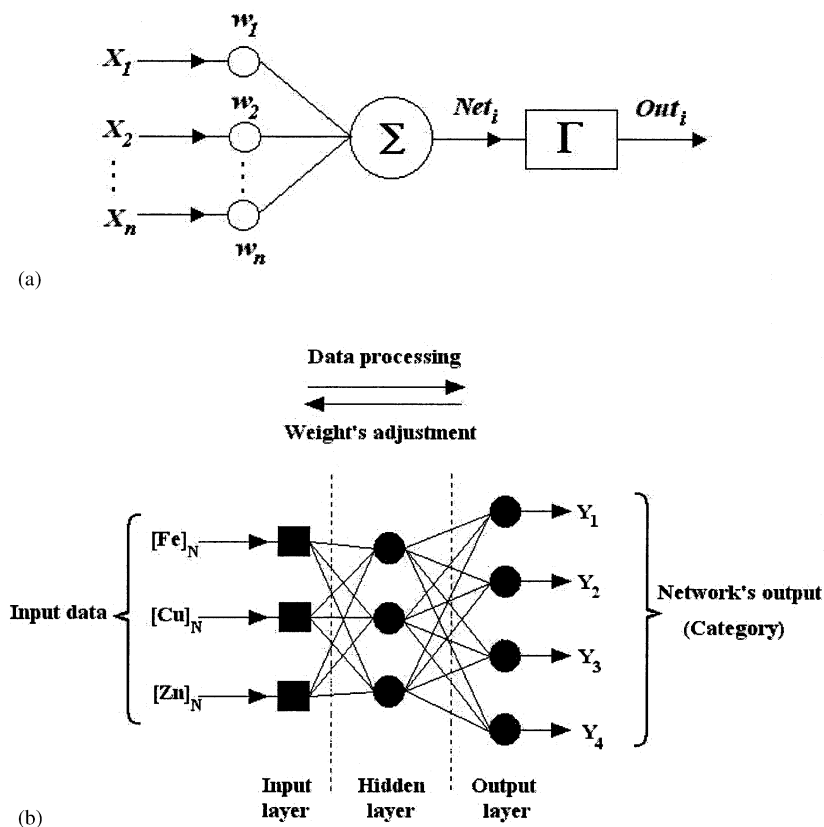

Fig. 1. Diagram of (a) an artificial neuron; and, (b) an ANN with two (active) layers (see text for details).

While a neuron is clearly an important part of an ANN, is the linking among them—the ''networking''—which gives ANNs their outstanding performance [21]. Fig. 1b shows a diagram of a fully connected, ANN with two active layers. Each black symbol represents an individual neuron performing the operations described previously. The input layer serves to distribute the data and does not perform any calculation. The hidden layers are known as such for they neither receive nor transmit data directly from or to the user. Finally, there is the output layer, which provides the results of the network calculations. In this case, data ''flows'' exclusively from the input to the output layer. On the other hand, and for the particular type of ANN employed in this work, the adjustments of the weights are performed on the opposite direction. This ''backpropagation'' process means that the weights of the output layer are modified first, followed by those on the layer immediately preceding it, and so on [21,22]. ''Learning'' consists of adjusting the weights so that the error, that is the difference between the neuron (or the network's) output and the expected value, is minimized (supervised learning). With this regard, the mean squared error (MSE) may be utilized [23]:

$$MSE = \left[\frac{\sum_i (d_i - o_i)^2}{n} \right] \tag{3}$$

in which d_i and o_i represent the desired and the actual network output values, respectively, and n the number of input-output pairs (patterns) used to training the network.

3. Materials and methods

3.1. Equipment and software

A Perkin–Elmer atomic absorption spectrometer, model 460, was used for all the determinations. Perkin–Elmer hollow cathode lamps for Zn, Cu and Fe were used according to the manufacturer recommendations [24]. The Statistical Package for SOCIAL SCIENCES 7.0 (SPS Inc.) and MINITAB 13.1 (Minitab Inc.) were used for statistical analyses. ANNs were developed using PROPAGATOR 1.0 (ARD Corporation) for Windows [23]. The software generates a list of weights after training is concluded. Those weights, together with the appropriate transfer functions, were processed by EXCEL XP (Microsoft Corp.), running under WINDOWS ME (Microsoft Corp.), to yield the network's numerical output.

3.2. Reagents and samples

Titrisol® (Merck) stock solutions (1000 mg l^{-1}) were used for preparation of working standards. Ethyl alcohol (98% v/v, Riedel de Haen) and a 40% ethyl alcohol solution from a local producer were used for matrix matching.

Samples ($N = 40$) from different producers from Lara and Falcón states (Venezuela) were collected in glass bottles and stored at 4 °C until analysis. Bottles were washed with nitric acid, and rinsed with distilled, de-ionized water prior to sample collection. Table 1 resumes the coding used to identify the samples, the number of samples collected from each region, the nature (with or without sugar) and geographic origin.

3.3. Determination of zinc, copper and iron by FAAS

The determination of Cu and Fe concentrations in Cocuy samples was carried out following the recommendations of the manufacturer [25]. The method was also effectively implemented for the determination of zinc [4]. Quantitation was made against a matrix-matched calibration curve. When necessary, the samples were diluted with 40% alcohol in order to bring the concentration of a given analyte within the corresponding linear dynamic range. Concentration values for each sample were estimated as the average of at least three consecutive measurements.

3.4. Discriminant analysis

Linear and quadratic discriminant analyses were performed using Zn, Cu and Fe standardized

Table 1
Classification and characteristics of the Cocuy samples

Code/category	Number of samples	Nature	Origin	Network's output code
SP	12	Pure	Municipio Sucre (Falcón)	−1 1 1 1
SS	10	With sugar	Municipio Sucre (Falcón)	1 −1 1 1
UP	12	Pure	Municipio Urdaneta (Lara)	1 1 −1 1
US	6	With sugar	Municipio Urdaneta (Lara)	1 1 1 −1

concentrations as input data, and the samples' categories as outputs. Standardization was conducted according to the following equation:

$$[X_{ij}]_s = \frac{X_{ij} - \langle x_j \rangle}{s_j} \tag{4}$$

where $[X_{ij}]_s$ and X_{ij} correspond to the ith standardized and raw concentration of the jth element, $\langle X_j \rangle$ and s_j are the average concentration and standard deviation of the jth element. Data was split in two groups: i) 75% of the data was randomly selected in order to develop the discriminant functions; and, ii) the remaining 25% (prediction group) was used to validate the model.

3.5. Development of artificial neural networks

In the present work, the code (3:n:m:4) is used to describe the topology of the neural networks; where n and m represent the number of nodes in the hidden layers. For sake of simplicity, the transfer functions of the network's layers are not included in the code, as they were fixed for all topologies evaluated.

Preliminary assays revealed that low MSEs were attained when a learning rate of 0.01 and a momentum factor of 0.5 were used. In order to avoid a local minimum during training, the adjustment of the network weights for a given topology was conducted at least three times. In each case, the initial weights were randomly started (−1.0 to 1.0). Table 2 shows the parameters and characteristics of the ANNs under evaluation. Normalized data, according to Eq. (5), was used as inputs.

$$[X_{ij}]_s = \frac{X_{ij}}{X_{(\max,j)}} \tag{5}$$

Table 2
Parameters and characteristics of the ANNs under evaluation

Parameter	Characteristics
Input layer	Number of nodes: 3
	(Zn, Cu and Fe normalized concentrations)
	Transfer function: lineal (L)
Hidden layers	Number of layers: variable (1–2)
	Number of neurons: variable (1–7)
	Transfer function: sigmoid (S)
Output layer	Number of neurons: 4 (Category)
	Transfer function: hyperbolic tangent (HT)
Learning rate	0.01
Momentum	0.5
Training cycles	Variable (10^4–10^5)

where $[X_{ij}]_N$ and X_{ij} are the ith normalized and raw concentrations for the jth element, respectively, and $X_{(\max,j)}$ the maximum concentration for the jth element. A group constituted by 75% of the data was used for training the ANNs; whereas the remaining 25% was employed for validation. A sigmoid transfer function was implemented in the hidden layers, and a hyperbolic tangent was employed in the output layer. A code comprising a combination of −1 and +1 was used for definition of the corresponding categories (see Table 1).

4. Results and discussions

4.1. Determination of Zn, Cu and Fe in Cocuy samples by FAAS

Zinc, copper and iron were selected on the basis of a previous work [4]. A more detailed elemental characterization of these samples would have

required a more complex methodology [16] or, certainly, more sensitive techniques, which was beyond the scope of this first approach. Work is being currently conducted in this direction, and will be the subject of a future publication. Although other elements could be employed that may relate the product with soil characteristics, thus with the geographic origin of the raw material, Zn, Cu and Fe may be useful in establishing a relationship between the illegal products and their manufacturing process. It is believed that, at first, this may be helpful in the establishment of quality-control policies.

Table 3 summarizes the concentrations of Zn, Cu and Fe found in Cocuy samples from different manufacturers from Falcón and Lara states. Particular attention must be paid to the elevated concentration of copper, which is evidently the result of the leaching of the element from the distillation coil. Although copper is an essential element, its ingestion above certain levels may pose a likely threat to human health [26]. The results presented here confirm previous findings by Capote et al. [4].

A look at the concentration ranges presented in Table 3 reveals an ample variability, not only between the two states (Falcón and Lara), but within states as well. Copper and zinc concentrations represent a clear evidence of the latter, their concentrations varying by as much as $1-2$ orders of magnitude. Such variability is clear evidence of the lack of quality control measures regulating the manufacturing of such beverages. The latter will exact an important influence in the classification of such samples, as will be seen in the ensuing sections.

4.2. Classification of Cocuy samples: discriminant analysis

Discriminant analysis (DA) is a chemometric technique whereby a set of functions (latent variables), which are combinations of the original (predictor) variables, are developed. The resulting model seeks to cluster observations by maximizing the between-group variance [27]. The dimensionality of the space can be reduced from a higher p-dimensional space (number of initial descriptors) to a smaller n-dimensional space (number of resulting discriminant functions) by this means. The latter has the benefit of permitting the visualization of the latent variables in 2 or 3 dimensions for graphical classification. Two variations of DA can be differentiated, depending on whether the latent variables are linear (LDA) or quadratic (QDA) combinations of the predictor variables. Irrespective of the model, correct application of the DA technique relies on the predicting variables having a multinormal distribution [27]. A preliminary study of the raw data revealed that frequency distributions showed high asymmetry. Therefore, it was necessary to perform a transformation of such variables which would help in smoothing their distributions so as to comply with the requirements of the technique. The variables were thus standardized according to the Eq. (4) (see Section 3.4).

A LDA was first performed on the standardized data set. Fig. 2 shows a scatter plot of the Cocuy samples by means of the first two linear discriminant functions. Copper and iron have the highest values in both discriminant functions, thus they contribute the most to the separation of the

Table 3
Zn, Cu and Fe average concentrations and ranges found in Venezuelan spirituous beverages (Cocuy) from Lara and Falcón states

Category	Concentration (mg l^{-1})[a]		
	Zn	Cu	Fe
SP	0.12 ± 0.05 (0.03–0.17)	28.03 ± 27.99 (6.12–85.69)	0.32 ± 0.07 (0.27–0.51)
SS	0.97 ± 0.04 (0.89–1.00)	31.36 ± 0.67 (30.64–33.13)	0.26 ± 0.06 (0.18–0.36)
UP	0.23 ± 0.21 (0.02–0.65)	14.63 ± 14.69 (4.49–58.46)	0.36 ± 0.13 (0.20–0.55)
US	0.13 ± 0.02 (0.03–0.38)	15.58 ± 0.07 (7.82–26.12)	0.33 ± 0.01 (0.12–0.59)

[a] Values correspond to the average $\pm$ S.D. Concentration ranges are shown in parenthesis.
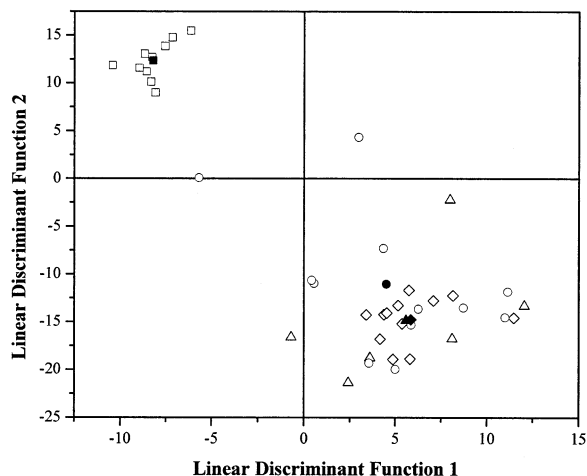
Fig. 2. Linear discriminant plot for Cocuy samples: ($\diamondsuit$) SP; ($\square$) SS; ($\bigcirc$) UP; and, ($\triangle$) US. Black symbols correspond to the groups' centroids.

groups. It is clear that, with the exception of one group (Category SS), all other groups present similar characteristics leading to the superposition of the corresponding categories. This is particularly evident in the closeness of the groups' centroids located in the lower right quadrant of the plot. The latter is attributed to the fact that, with the exception of group SS, the normalized concentrations of zinc, copper and iron are very similar among groups. The corresponding (normalized) concentrations in group SS are higher and statistically different to those of the remaining groups, which clearly contributes to its better separation by the first two discriminant functions. The high overlap between the groups is reflected in the low estimation and prediction percentages

summarized in Table 4. The overall classification accuracy is approximately 50%, which is evidently unsatisfactory.

Based on the fact that the high dispersion of the raw data is certainly responsible for the inability of the LDA model to provide adequate groups' separation, it was deemed appropriate to attempt the classification by means of a non-linear model. The statistical packages used along this work have a quadratic function which was used for this purpose. Quite surprisingly, it did not seem possible to plot the numerical outputs as in the case of LDA. Nonetheless, the results (see Table 4) indicate an improved performance of the corresponding model. Again, Category SS can be clearly separated from the rest of the groups, as inferred from the 100% classification accuracy. For the remaining groups, estimation and prediction accuracies $\geq 50\%$ could be attained, with an overall estimate of ca. 80% and 72%, respectively.

The results discussed in the preceding paragraphs pinpoint to the groups been clearly non-linearly separable. The function though, must be more complex than a simple second-order polynomial, as evidenced by the still unacceptable estimation/prediction accuracy of the QDA model. Such a function, or combination of functions, cannot be determined a priori, thus impeding the application of classical mathematical models, and calling for a more effective alternative. ANNs are well recognized for the ability to model highly non-linear model, without the need of knowing which function could actually perform the separation [22]. The ensuing section is devoted to the

Table 4
Estimation and prediction accuracy of the LDA and QDA, and the (3:5:7:4) neural network on the determination of the category and geographic provenance of Cocuy samples

Category	LDA		QDA		ANN (3:5:7:4)	
	Estimation (%)	Prediction (%)	Estimation (%)	Prediction (%)	Estimation (%)	Prediction (%)
SP	33.3	27.8	83.3	72.2	88.5	100.0
SS	100.0	100.0	100.0	100.0	100.0	100.0
UP	33.3	33.3	55.6	50.0	100.0	83.3
US	44.4	44.4	83.3	72.2	100.0	100.0
Overall	51.7	50.0	79.2	72.5	96.5	97.0

evaluation of this alternative for the classification of the Cocuy samples.

4.3. Classification of Cocuy samples: artificial neural networks

Unlike many chemometric tools, data do not have to comply with any specific distribution, e.g. multivariate normal distribution, to be processed by ANNs. However, in order to prevent the networks from a priori giving more relevance to some elements based on the magnitude of their concentrations, as would be the case for copper, normalized data was used instead of the raw data. Standardized data was also evaluated for this purpose, but it was found that normalization led to ANNs showing a better classification performance, as will be shown later on.

The selection of the ANNs for classification of Cocuy samples was conducted considering the reduction in the mean square error (MSE) for various networks' topologies. Fig. 3 shows the trend in the MSE for the (3:5:7:4) ANN, which was considered the best on this basis. Clearly, the MSE experiences a monotonic reduction as the network is trained eventually reaching a plateau. Such a tendency is an indication of overtraining, i.e. the network has adjusted the weights so as to

match the training set, thus reducing its predicting capabilities. Training the network was thus stopped after 4000 cycles, in order to avoid the aforementioned problem.

Table 4 shows the performance of such ANN for estimating the provenance and nature of Cocuy samples. The superiority of this approach for determining the origin and nature of such samples is clear. The latter is certainly attributable to the fact that not only are the observations not linearly separable, but also because a more complex non-linear function is needed for a correct clustering. By adjusting the weights, ANNs are capable of developing extremely complex functions, which could be nearly impossible to emulate by most mathematical methods. The longest development time of ANNs may be considered a disadvantage when compared with the immediateness with which most chemometric tools are implemented. However, once trained they are able to predict the category to which the samples belong almost instantaneously, thus compensating such a drawback.

5. Conclusions

LDA, QDA, and ANNs were evaluated for classification of Cocuy de Penca firewater samples based on their Zn, Fe and Cu concentrations. ANNs clearly outperformed LDA and QDA, showing an excellent overall predicting capability (97% vs. 50% and 72%, respectively). The high dispersion of the data, resulting from the lack of quality control measures in the manufacturing of such beverages, exacts a detrimental effect on the classification powers of these chemometric tools. This represents a clear example of the capabilities of ANNs for developing complex mathematical models for classification purposes, without the inherent limitations of many chemometric techniques. Further work is being conducted so as to improve the classification of the various samples taking into account other trace elements that may provide additional information on the geographic origin of these beverages.
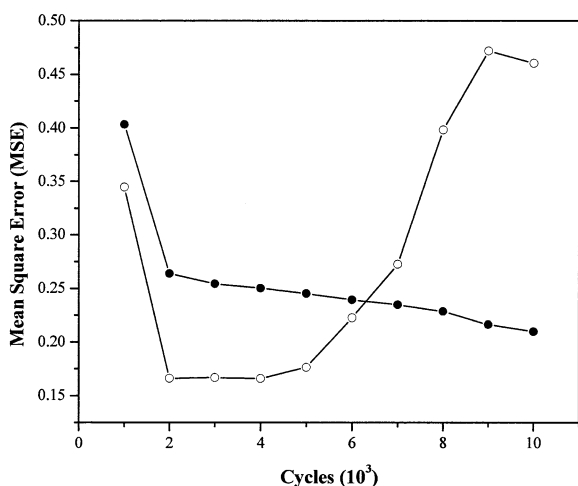

Fig. 3. Training (●) and validation (○) MSE for a (3:5:7:4) ANN.

Acknowledgements

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