Optimization and Empirical Modeling of HG-ICP-AES Analytical Technique through Artificial Neural Networks

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An artificial neural network technique has been applied to the optimization of a hydride generation-inductively coupled plasma-atomic emission spectrometry (HG-ICP-AES) coupling for the determination of Ge at trace levels. The back propagation of errors net architecture was used. Experimental parameters and their relationship have been studied, obtaining a surface response of the system. The results and optimization aspects achieved with the neural network approach have been compared to the "one variable at time" and SIMPLEX methods.

INTRODUCTION

The analysis of elements in different kind of matrices is a permanent challenge in analytical chemistry because it requires quantifying very low concentrations (ppb or ppt levels). Different methodologies have also been designed for purposes as follows: to maximize the sample throughput, to reduce the detection limits at trace and ultratrace levels, to save reagents consumption and wastes, etc.

Modern instruments are capable of generating a great number of data, and a careful analysis is necessary to be done in order to reduce its number without loss of any valuable information.

The coupling HG-ICP-AES has the advantage of conveying the sample directly in the gaseous form, thus avoiding problems associated with nebulization. However, this hyphenated system introduces additional variables that make the complete system much more difficult to handle. For instance, flow rate and concentration of reagents, length of the reaction coils, or the flow rate of carrier gas need to be optimized in order to achieve maximum signal intensity with reasonable standard deviation and reproducibility of measurements. Unfortunately, the understanding of the behavior of the variables and their correlation is difficult because there are not mathematical models developed for these systems up to now.

Perhaps the most common method still used for optimization of variables is the "one variable at time" (OVAT).[1−4] It is essentially an univariate procedure, and it consists on selecting at the beginning one variable to make changes while the other ones remain constant. This variable is fixed at the maximum response. A second variable is then selected, and the process is repeated until all parameters have been optimized. In many cases, this method approaches to the goal of maximizing the response but without achieving the optimum value.[5] One of the reasons of the unsuccessful results is that this method does not take into account the interactions between variables.[5,6] Furthermore, this method demands a great number of experiments time-consuming process. Some other chemometrics methods can be used for this purpose, and SIMPLEX, for instance, has been previously applied in a successful manner.[6−8] The work of Parker et al. deserves special mention; the authors checked four methods, factorial design, regression and canonical analysis, and SIMPLEX, to optimize the determination of As and Se through HG-ICP-AES.[6]

Artificial neural networks (ANNs) applications to chemistry have been increased in the past few years through the publication of many articles and textbooks.[9−13] Chemometrics,[14] and particularly classification,[15−17] resolution of interferents,[18,19] optimization modeling,[20,21] and multivariate calibration[22] are some of the analytical chemistry applications that ANNs can carry out efficiently. One of the advantages of ANNs in the optimization and modeling performance is their ability to trace the behavior of the variables without the hypothesis about the model function being necessary.[9] While optimization is achieved, an approach to the understanding of the behavior of variables and its correlation can be reached by plotting any two or three variables together.

The aim of this work is the optimization of a HG-ICP-AES technique through ANNs and the achieving of an empirical model in order to facilitate the understanding and handling of the system.

EXPERIMENTAL SECTION

Instrumentation. The determination of Ge at trace levels was achieved by coupling a hydride generator reactor to an ICP-AES detector, as shown in the block diagram of Figure 1. The experimental setup and the components used in this study were the same as previously described.[1] The instrumental operation conditions is summarized in Table 1.

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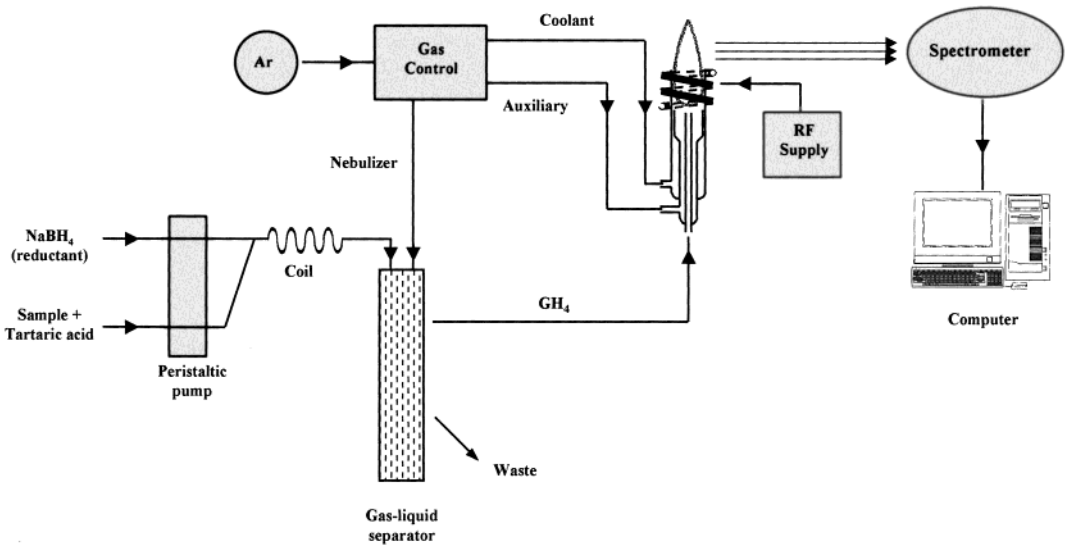

Figure 1. Block diagram of the HG-ICP-AES coupling.

Table 1. Initial Operating Conditions for the HG-ICP-AES Coupling

plasma		hydride generation	
forward rf power	1.1 kW	samples and reagents flow rate	2.5 mL min^{1}
frequency of rf generator	40 MHz	sample acidity (tartaric acid)	50 mM
coolant (outer) gas flow rate	15 L min^{-1}	$NaBH_4$ concentration	0.25% (m/v)
auxiliary (intermediate) gas flow rate	2 L min^{-1}	coil volume	750 μL
sample (aerosol) flow rate	0.7 L min^{-1}	tube size for sample and reductant	1.1 mm (i.d.)
wavelength	209.426 nm		
integration time	20 s		
viewing height above load coil	15 mm		

Table 2. Initial Trials for the Sequence of the SIMPLEX Method

$NaBH_4$ concn (%) $\Delta = 0.05$	tartaric concn (mM) $\Delta = 10$	RT (min) $\Delta = 0.1$	Ar f. rate (L·min^{-1}) $\Delta = 0.1$
0.075	100	0.3	0.55
0.025	100	0.2	0.55
0.075	100	0.2	0.65
0.075	90	0.2	0.55
0.025	90	0.3	0.65

Table 3. Optimized Operating Conditions for the HG-ICP-AES Coupling by Different Methods

parameter	OVAT	SIMPLEX	ANN
[$NaBH_4$] (% m/V)	0.25	(0.291) 0.234	0.28
[tartaric acid] (mM)	50	(91) 91	45
residence time (min)	0.300	(0.17) 0.28	0.145
Ar flow rate (L min^{-1})	0.7	(0.46) 0.52	0.3
signal intensity (arbitrary units)	68	(87) 78	119
trials for simplex	−	(14) 17	−

Reagents. To prepare all reagents and standard solutions deionized water (Barnstead, Dubuque, IA) was used. A commercially available 1000 mg L^{-1} Ge standard solution (Merck, Darmstadt, Germany) was used as stock solution. Dilute working solutions were prepared daily by serial dilutions of this stock solution. For the hydride generation reaction, tartaric acid was used. All tartaric acid solutions were prepared by dissolving appropriate amounts of the reagent in deionized water.

A 3% (m/v) sodium tetrahydroborate solution was prepared by dissolving 3 g of $NaBH_4$ powder (Baker, Phillipsburg, NJ) in 100 mL of 1% (m/v) NaOH (Merck) water solution and filtering through Whatman N 42 filter paper to eliminate turbidity.

Welding argon from AGA (Buenos Aires, Argentina) was found to be sufficiently pure for Ge determination.

Procedure. Germanium standard solutions were prepared in tartaric acid and continuously pumped through one channel of the peristaltic pump. The reductant was pumped through the second channel, and both solutions merged into an Y piece. The resulting mixture was injected into the hydride generator in a continuous flow. The GeH_4 (germane) was separated from the solution by a U-tube separator and swept by argon into the bottom of the quartz torch (the spray chamber was disconnected). When blank assays were analyzed, no Ge signal was observed.

Previous Optimization Approaches. Physical and chemical parameters were adjusted by applying OVAT approach using solutions containing 0.4 mg L^{-1} of Ge, unless notice is otherwise given.

The optimization process using the OVAT approach was fully described in a previous paper,[1] and the maximum values obtained are summarized in Table 3.

THEORETICAL ASPECTS OF THE ANN TECHNIQUE

The purpose of this work is to maximize the signal intensity of the instrument for the HG-ICP-AES technique. This output depends on the value of the operational parameters of the instrumentation. To optimize the hydride generation and plasma operating parameters, a matrix of data was assembled with five variables: signal intensity (the output variable) and the concentrations of $NaBH_4$ and tartaric acid solutions, sample Ar flow rate, and the residence time (RT) into the reaction coil (the input variables). The residence

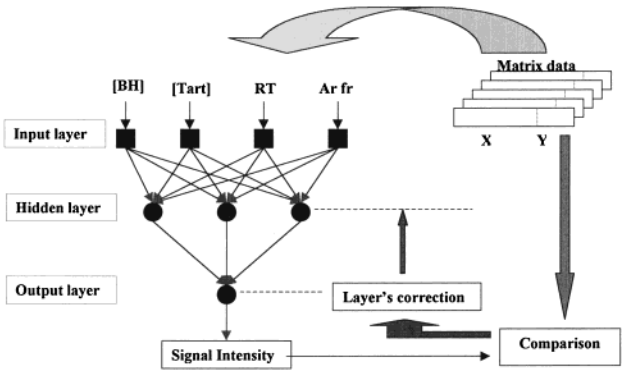

Figure 2. The net architecture and the input information for the training stage. *X* is the input variable part of each vector of the data matrix. The output variable part is *Y*.

time is the relationship between two experimental parameters, the volume of the reaction coil (Vrc) and the solution flow rate (Φ):

$$RT = Vrc \cdot \Phi^{-1} \quad (1)$$

The reduction of the number of variables is an important step, previous to optimization and modeling of a system. When two variables show high correlation, as in eq 1, the value of one of them can predict the value of the other one. That means that once the value of one variable has been determined, the other one does not yield much additional information. This is the case for coil length and solution flow rate.

The experiments were carried out at room temperature. All the variables were normalized at a range of 0 to 1. From the bunch of data that had been previously obtained from the OVAT approximation, we selected 31 experiments. A vector containing the above five variables represents each experiment. Due to the fact that 31 examples of input and output data are known beforehand, we are able now to use a supervised learning method.

For the purpose of solving this sort of problems, the "back propagation of errors" (BPE) ANN looks like the most convenient type of net, which was also successfully used for the optimization of another techniques.[20,21]

The 31 vectors constitute the data matrix for the training stage of the net. The range of each variable was selected taking into account the experimental limits (maximum and minimum) of the operational conditions.

There are not uniform criteria to select the correct number of samples for the training of the net. It is well-known that a low number of samples will cause an overfitting during the training stage. Some authors consider that the number of net weights should be at least slightly smaller than the number of samples (experiments).[9] Other authors consider that the number of samples should be greater than 30.[22] We found that, in general, the number of samples depends on the particular problem to solve, but there are strong reasons for preserving the first criteria.

The BPE net has architecture of multilayer of neurons (Figure 2). Usually the assembling involves three layers: one for input, another called hidden layer, and a final output layer. They are enough to solve a lot of problems. The number of neurons of the input layer is determined by the number of input variables, and in the same way, the number of neurons of the output layer is determined by the number of output variables. The complete architecture, that means, the number of hidden layers and the number of neurons in each one, is usually determined by trial and error.

The learning rate, η, and the momentum, μ, are parameters of the "learning algorithm", and they must be empirically adjusted in order to optimize the efficiency of the calculus.

The convergence is achieved after several epochs (usually thousands), and the net approaches progressively to the expected values within a reasonable error deviation. This error is checked through a "cost function". In our case the cost function is the square root of the sum of the quadratic differences between the net outputs and data intensities, that is

$$RMSE = \sqrt{1/n \cdot \sum_{i=1}^{n} (y_i - Out_i)^2} \quad (2)$$

"n" being the number of vector inputs or "objects". This error also depends on η and μ parameters.

Different architectures with four input neurons and one output neuron have been tested. Finally, we select a $4 \times 3 \times 1$ net due to the fact that it has the smallest output error. In our case the best approach to our system was achieved with an error RMSE = 7.5% after 4000 epochs, having η and μ constant values of 0.4 and 0.7, respectively.

When the number of epochs increases, after a fast initial diminution of RMSE, its value approaches asymptotically to zero. However, after an initial descent, the error for prediction increases with the number of epochs. Then, the training should be stopped taking into account both errors.[9,22]

The complete description of the calculation and programming of the BPE network is beyond the scope of this article. The readers who want to go further into BPE programming are addressed to references.[9−11]

After the net has been trained and its accuracy is considered acceptable, the simulation of a multitude of experiences is possible by inputting the required input variable values. Therefore, the study of the behavior and the relationships among them can be made possible. For all simulated experiments, the input variables are into the range values as those of the training stage. There are not extrapolated simulated experiments.

RESULTS AND DISCUSSION

The reaction conditions for GeH_4 formation is the first aspect to study. The relation among solution concentrations of $NaBH_4$ and tartaric acid and signal intensity is shown in Figure 3. It was found with the OVAT method that the signal intensity passes through a maximum when it is plotted against the tartaric acid concentration. This maximum can be observed in the continuous line in Figure 3. Furthermore, the concentration of $NaBH_4$ is much higher than the tartaric one; however, the $NaBH_4$ concentration controls the signal intensity only for the lowest tartaric concentrations and it practically has no influence on the higher ones. The conclusion found with the OVAT method, about that the signal increases when $NaBH_4$ concentration rises, is not valid in the latter case.

The analysis of another relation, among the RT, Ar flow rates, and output signal intensity is shown in Figure 4. The

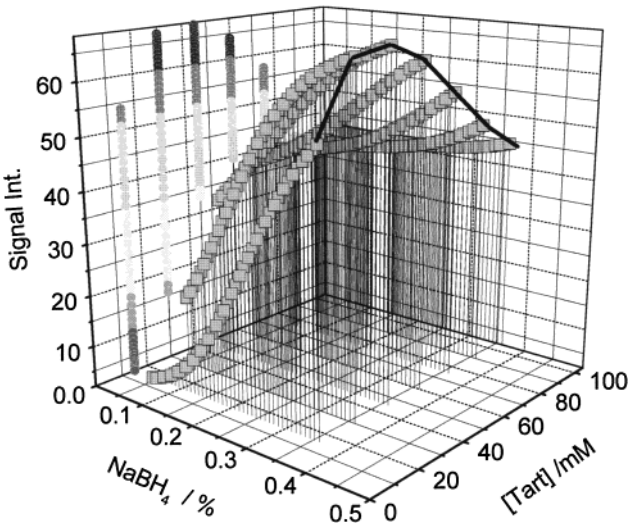

Figure 3. The relationship among the reagent concentrations and the output signal. Fixed factors: RT = 0.25 min; Ar flow rate = 0.625 L·min^{-1}. The full line shows a similar profile found by the OVAT method. See that this profile shape changes with $NaBH_4$ concentration.

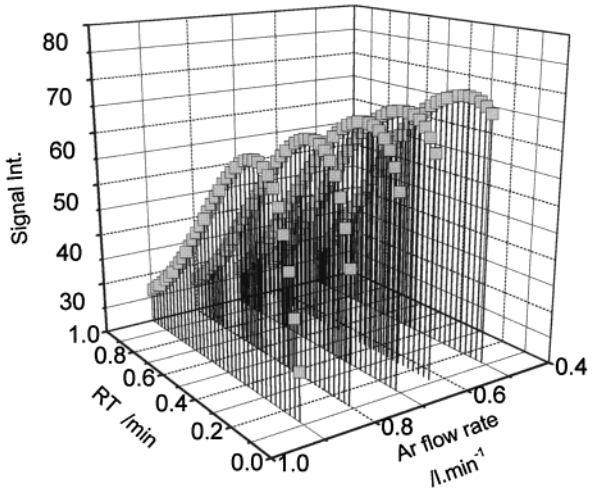

Figure 4. The variables related to the reaction and carrying times and their influence on the output signal. Fixed factors: $NaBH_4$ concentration = 0.34%, Tartaric acid concentration = 45 mM. Each Ar flow rate curve shows a top output signal, these maximums point out the ORT points.

RT is related to the kinetic of the formation reaction of GeH_4, and the Ar flow is related to the carrying on the reaction product to the plasma torch. As shown in said figure, there is an optimal RT for each Ar flow rate. An inspection of this figure shows that these maximums are spatially aligned. Effectively, a plot of Ar flow rate vs the maximums (optimums) of the retention time shows that a strong correlation exists between these two variables. The regression parameters for a $y = a + b \cdot x$ plot are the following: $y =$ Ar flow rate, $x =$ RT(optimus), $a = -0.13$ (Sda 0.08), $b = 3.6$ (Sdb 0.3), Sd = 0.0287 ($N = 5$), correlation coefficient $r = 0.987$.

This correlation means that in order to maximize the signal these two variables must be changed correlatively and not independently one from the other. We call optimum residence time (ORT) to the RT value where the maximum signal output occurs for a particular Ar flow rate.

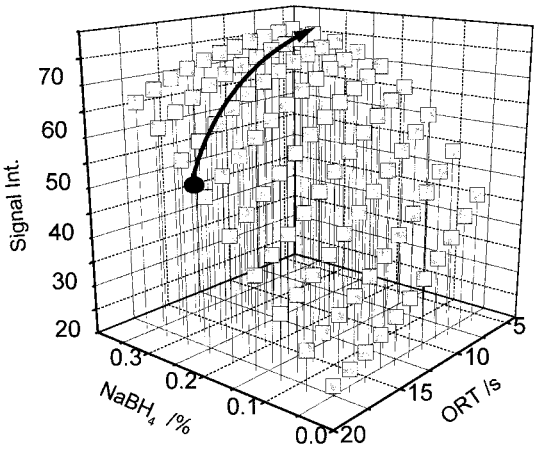

Figure 5. The response surface of the system. The tartaric acid concentration has been fixed previously to 45 mM, the Ar flow rate is changed in accordance with ORT correlation.

Now, we can build another relationship among ORT, concentration of $NaBH_4$, and the signal intensity. It is plotted in Figure 5. In this figure it is easy to see that the maximum response will be obtained in the upper part of the surface. In the same surface we can locate the position found by the OVAT method. This point is properly located for $NaBH_4$ concentration, but it is placed in the opposite side as regards to the ORT. When working at low ORT values it should give an increment of the signal. Looking at this figure, it could be interpreted that even shorter ORT or higher $NaBH_4$ concentrations than those selected for ANN optimization could have a beneficial effect. However, there are instrumental limitations that cannot be overstepped. If the $NaBH_4$ concentration is increased, the generation of H_2 is higher, and its excess finally extinguishes the plasma. On the other hand, to get shorter ORT the increase of the reagent flow rates is necessary. As a result of the pressure inside the piping increasing, the tubing connections begin to leak.

The SIMPLEX method is another competitive tool for optimization tasks. It operates in a sequential mode. You need to perform an experiment each time an approaching step is reached. In this work, a version of MULTISIMPLEX software has been used. For the first five initial experiments, each variable is changed at fixed steps. The initial values of the sequence and the step size for each variable are shown in Table 2.

Table 3 summarizes the optimized values obtained experimentally by three different methods: OVAT, SIMPLEX, and ANN. This table shows that, as a result of the ANN optimization, the signal output is increased 75%. SIMPLEX optimization approaches to only 30% of increment after 14 new sequential experiments. With the same approaching conditions, up to 17 experiments, the signal does not improve anymore. By using another narrower step condition for the variables (Δ in Table 2), a more efficient approach to the maximum response could be expected with SIMPLEX. The approaching to the optimum conditions with this new set of experiments will be slower than the previous one, because of the smaller value of Δ. Unfortunately, previous workers using SIMPLEX for similar systems have not informed the number of experiments they needed.[6,8]

As shown in Figure 5, the optimum system response is located at a flatter zone than those found by OVAT method.

Hilligsoe and Hansen have also described this flat zone close to the optimum conditions.[8] Then, the signal should be more reproducible on that area.

To check the prediction of a better reproducibility at the working point selected by the ANN method a new set of experiments were carried out. Fifteen repetitive measurements were made for each one at the conditions established by the OVAT and ANN methods. In the first case the relative standard deviation was 3.3% and for the second one was 2.5%.

CONCLUSIONS

The optimization and empirical modeling of the operative conditions of a HG-ICP-AES method for the determination of Ge at trace levels have been done. Empirical modeling helps to understand HG-ICP-AES technique. It was previously mentioned that Parker et al. have made a modeling for a similar system applied to As and Se determinations. For this purpose, they used regression and canonical analysis by applying a second-order polynomial approach. As it is shown in Figure 3, a second-order polynomial could be not enough to fit the system. We take advantage in that ANNs is a nonparametric, nonlinear regression estimator; that is, it is not based on a "a priori" assumption of the specific model form.

The linear relationship between Ar flow rate and ORT should be investigated in order to know whether it is just a behavior of GeH_4 generation and gas carrying or it is a general one for this kind of systems. To check these possibilities, we are currently investigating a similar modeling for SbH_3.

The HG-ICP-AES system requires to be considered as a multivariate experiment.[8] For this reason, when interactions between variables are present, theoretically this point can never be reached through an univariating method. Then, OVAT approaches deficiently to the optimum conditions, achieving a false optimum.

SIMPLEX is an appropriate method for a multivariate optimization. But, due to the fact that SIMPLEX is a sequential method, a risk exists in discarding a complete set of useless experiments during the optimization process. Furthermore, SIMPLEX does not give us any information about the relationship between variables, as it is of poor efficiency for modeling.

Modeling is carried out together with the optimization process while working with ANNs, as it also happens with parametric methods. Although it is semiempirical, due to the fact that no mathematical function is obtained, ANNs allows us to handle the system in different conditions. For instance, considering the kinetics of the GeH_4 formation and the signal intensity, Figure 3 shows two different operative conditions. At low tartaric acid concentration, $NaBH_4$ strongly controls the signal intensity. But, for high tartaric acid concentration the signal becomes almost independent of $NaBH_4$ variations. This behavior of the system is due to the fact that the pH strongly influences the efficiency of the hydride generation. This result agrees with those reported by Andreae et al. for the GeH_4 generation.[23] Figure 3 is 3D plot of a nonbuffered system, where pH is controlled for the relative concentrations of tartaric acid and $NaBH_4$.

For this optimization and modeling, we selected a set of experiments obtained from a great number of data used previously for the OVAT method. This is not the case for routine work. An estimation of the minimum number of experiments can be made taking into account the number of variables for inputs and outputs and the architecture of the net. To avoid overfitting, the condition about the number of samples, which should be greater than the number of weights, should be kept. For this work, the number of samples doubles the number of weights.

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