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Increasing the working calibration range by means of artificial neural networks for the determination of cadmium by graphite furnace atomic absorption spectrometry

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Abstract

Feed-forward artificial neural networks (ANNs), trained with the generalized delta rule, were evaluated for modeling the non-linear behavior of calibration curves and increasing the working range for the determination of cadmium by graphite furnace atomic absorption spectrometry (GFAAS). Selection of this analyte was made on the basis of its short linear range (up to 4.0 $\mu g\,l^{-1}$). Two-layer neural networks, comprising one node in the input layer (linear transfer function); a variable number of neurons in the hidden layer (sigmoid transfer functions), and a single neuron (linear transfer function) in the output layer were assessed for such a purpose. The (1:2:1) neural network was selected on the basis of its capacity to adequately model the working calibration curve in the range of study (0–22.0 $\mu g\,l^{-1}$ Cd). The latter resulted in a nearly six fold increase in the working range. Cadmium was determined in the certified reference material "Trace Elements in Drinking Water" (High Purity Standards, Lot No. 490915) at four concentration levels (2.0, 4.0, 8.0 and 12.0 $\mu g\,l^{-1}$ Cd), which were experimentally within and above the linear dynamic range (LDR). No significant differences ($P < 0.05$) were found between the expected concentrations and the results obtained by means of the neural network. The proposed method was compared with the conventional "dilution" approach, and with fitting the working calibration curve by means of a second-order polynomial. Modeling by means of an ANN represents an alternative calibration technique, for its use helps in reducing sample manipulation (due to the extension of the working calibration range), and may provide higher accuracy of the determinations in the non-linear portion of the curve (as a result of the better fitness of the model).

Keywords: Cadmium; Calibration curves; Graphite furnace atomic absorption spectrometry (GFAAS); Artificial neural networks (ANNs); Backpropagation

1. Introduction

Electrothermal atomic absorption spectrometry (ETAAS) is well recognized to be among the most powerful techniques for analysis at trace levels. This technique is characterized by its high sensitivity, considerable robustness towards matrix interferences, low sample consumption, excellent performance for the analysis of solid, liquid and gaseous samples, etc. However, ETAAS is not without disadvantages, being the short linear dynamic ranges (LDRs) among them [1]. For comparison purposes, while the LDR for this technique extents only for about one to two decades, inductively coupled plasma, either with optical emission or mass detection, or total reflection X-ray fluorescence spectrometry can achieve LDRs spanning 4–6 orders of magnitude [2,3]. Working outside the linear range may render inaccurate results [4]. Therefore, the analyst is often forced to dilute a given sample in order to bring the analyte concentration within the linear range. Besides being time-consuming, the latter poses the intrin-

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sic risk of contaminating the sample during the dilution process.

Several methods have been proposed with various degrees of success, in an attempt to salvage the above inconvenience. Among the various approaches are worth mentioning: the use of peak area instead of peak height [5], high-pressure atomizers [6,7], quantitation at non-resonant absorption lines [8,9], non-stop gas condition during atomization [8], atomization off the platform or the atomizer wall [8,9], mathematical corrections of the cause of deviations from linearity [10–12], and less often modeling of the calibration curve with polynomial expressions [4,13,14].

Artificial neural networks (ANNs) are known for their capacity to model non-linear systems [15–18]. Therefore, on a first approximation, they could be used for modeling the behavior of calibration curves in atomic absorption spectrometry. Even though ANNs have received significant attention for spectrophotometric applications [19–22], their use in atomic spectrometry is relatively scarce [23–25].

The purpose of the present work was to evaluate the applicability of ANNs for modeling non-linear calibration curves in graphite furnace atomic absorption spectrometry (GFAAS), aiming at extending the working range. Cadmium was chosen as the analyte of study due to its short LDR. A certified reference material, "trace metals in drinking water" (High Purity Standards), was used to check the accuracy and precision of the method. For comparison purposes, the determination of cadmium in such a material was also performed through the conventional dilution procedure and by fitting the entire calibration curve with a second-order polynomial.

2. Theory

ANNs are pseudo-parallel processing systems capable of "adaptable learning," meaning that they can implement tasks without the formalisms and restrictions of computer programming languages [26]. The fundamental constituents of the ANNs are called neurons. Fig. 1a shows a basic representation of one of such units. Each neuron performs a series of simple calculations. First, the input signals (X_i) are processed in the "body" of the neuron according to:

$$Z_i = \sum_i w_i X_i \tag{1}$$

where w_i, the weights, represent the "artificial synapses". This value is further modified in a second step by means of a transfer function (Γ). The unipolar sigmoid (Eq. (2)) is one of the most popularly used functions:

$$Y_i = \frac{1}{1 + \exp(-(Z_i + \theta))} \tag{2}$$

This is a monotonous, non-linear function, which restricts the output of the neuron (Y_i) between 0 and 1. 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.

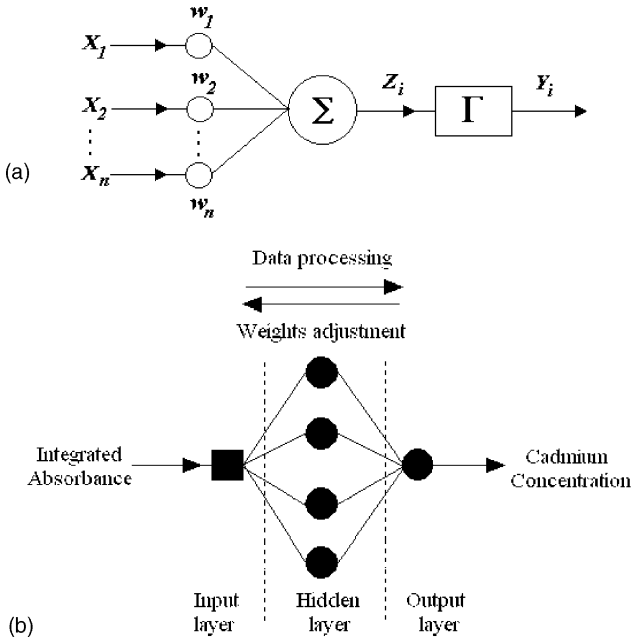

Fig. 1. Diagram of: (a) an individual neuron; and (b) an ANN with two (active) layers.

Transfer functions such as the one shown above are what make ANNs particularly suitable for modeling non-linear systems. The value Y_i is thus propagated to the neurons on to the following layers. "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). On this regards, the mean squared error (MSE) may be utilized [27]:

$$\text{MSE} = \frac{\sum_i (d_i - o_i)^2}{n} \tag{3}$$

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.

The ANNs evaluated in this work are fully connected arrangements such as the one depicted in Fig. 1b. Each black circle represents an individual neuron performing the operations described previously. The input layer serves to distribute the data and does not perform any calculation; thus the units are represented as black squares, and they are referred to as "nodes" instead. Neither is this layer taken into account when describing the topology of a given network. On this regards, the diagram in Fig. 1b shows a two-layer ANN. The hidden layer is known as such for it neither receives nor transmits data directly from or to the user. Finally there is the output layer, which provides the results of the networks calculation. Data "flows" exclusively from the input to the output layer, and thus this particular topology is usually referred to as "feed-forward ANN". On the other hand, the adjustment of the weights is performed on the opposite direction, i.e. it is "backpropagated". This means that the weights of the output layer are modified

first, followed by those on the layer immediately preceding it, and so on, until the weights of the input layer are finally adjusted [26,28]. The process is iteratively repeated until the error reaches a pre-determined level, or after a certain number of learning/validation cycles, also selected by the analyst, have been completed.

3. Experimental

3.1. Equipment, accessories and software

A Perkin–Elmer atomic absorption spectrometer, model 2100, provided with an electrothermal atomization system model HGA-700, an autosampler system model AS-70, and a deuterium lamp background correction system, was used. Pyrolytically-coated graphite atomizers (Perkin–Elmer) with totally-pyrolytic graphite platforms (Perkin–Elmer) were employed after proper conditioning [29]. A monoelemental, cadmium hollow-cathode lamp (Varian), operated at 6 mA, was used at the 228.8 nm Cd line. All other conditions were as recommended by the manufacturer of the spectrometer.

The neural networks were developed using PROPAGATOR 1.0 (ARD Corporation) for Windows 3.X [27]. The software generates a list of weights after training is concluded. Those weights, together with the appropriate transfer functions, can be processed by different computational tools to yield the network's numerical output when presented with the corresponding input values. EXCEL 2002 (Microsoft Corp.) was employed for this purpose in a Windows Me (Microsoft Corp.) environment. Statistical evaluations, as well as linear and second-order polynomial fittings, were conducted with MINITAB Statistical Software v. 13.1. (Minitab Inc.).

3.2. Reagents and materials

Cd metal powder (Merck, pro analysi) was employed for preparation of the analyte's stock solution. Ten percent (10% w/v) palladium nitrate solution (Aldrich), and magnesium nitrate hexahydrate (Carlo Erba) were used as chemical modifiers. Nitric acid (Alfa Aesar, metal basis, 99.999% purity) served for dilution and stabilization of solutions. Distilled, de-ionized water (Millipore, 18 MΩ cm^{-1}) was utilized for preparation of sample and standard solutions.

The "trace metals in drinking water" certified reference material (High Purity Standards, Lot No. 490915) was employed to verify the accuracy of the methodology hereby proposed. Such reference material has a certified concentration of cadmium of 12.0 μg l^{-1} (±0.5%) [30].

4. Procedure

4.1. Preparation of working solutions

Cadmium standards were prepared from a laboratory-made stock solution (1000 mg l^{-1} Cd in 1.0% HNO_3) by proper dilutions with a 0.2% v/v HNO_3 solution. Fifteen standards were prepared having the following concentrations: 0 (blank), 0.5, 1.0, 2.0, 4.0, 5.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0 and 22.0 μg l^{-1} Cd. A 6000 mg l^{-1} magnesium nitrate solution was prepared by weighing an exact amount (1.037 g) of $Mg(NO_3)_2{\cdot}6H_2O$ and diluting to 100 ml with 0.2% v/v HNO_3. A mixed 500 mg l^{-1} Pd + 300 mg l^{-1} $Mg(NO_3)_2$ chemical modifier was prepared directly in an autosampler vial by proper dilution of the corresponding solutions. This concentration of modifier was chosen based on preliminary assays, in order to correct for a recurrent distortion of the analyte's peak profile observed during the analysis of the reference material.

The reference material was prepared by serial dilution to yield cadmium concentrations at four levels, namely, 2.0, 4.0, 8.0 and 12.0 μg l^{-1} Cd. These were selected to be inside and outside the linear calibration range.

Table 1
Atomization program for the determination of Cd by GFAAS[a]

Step	Temperature (°C)	Ramp (s)	Hold (s)
Dry	200	20	5
Pyrolysis	800	5	15
Cool down I	50	1	5
Cool down II[b]	50	1	5
Atomization[b]	1400	0	3 (read)
Clean	2500	1	3
Cool down	20	1	8

[a] Injection temperature: 100 °C; injection speed: 40%.
[b] Gas stop mode: 300 ml min^{-1} Ar flow in all other stages.

4.2. Determination of cadmium by GFAAS

Table 1 summarizes the optimized atomization program employed for the determination of Cd. Ten microliters of the standards/samples and ten microliters of the mixed Pd + $Mg(NO_3)_2$ modifier were injected sequentially into a pre-heated (100 °C) graphite furnace electrothermal atomizer. A single, high-temperature drying step was used in order to reduce the span of the atomization program. A double-staged, pre-atomization cool down step was introduced in order to promote the formation of the atomic cloud in a more favorable thermodynamic environment [31,32]. All temperatures correspond to nominal values given by the software controlling the spectrometer. Five replicates (integrated absorbance values) for each standard/sample were taken.

The determination of Cd in the standard reference material was conducted three fold: (i) dilution of the sample and quantitation of the analyte's concentration using the linear portion of the calibration graph (0–4.0 μg l^{-1} Cd); (ii) modeling the entire working calibration curve (0–22.0 μg l^{-1} Cd) with a second-order polynomial; and, (iii) modeling the calibration curve in the same range as before, by means of an ANN.

4.3. Artificial neural networks

Two-layer ANNs with one node in the input layer (linear transfer function), a variable number of neurons in a single hidden layer (sigmoid transfer function), and a single neuron in the output layer (linear transfer function), were evaluated. The different ANNs were trained/validated for a variable number of cycles (10^4–10^5). The program employed in the development of the ANNs uses the generalized delta rule for weights' correction [27].

Preliminary assays revealed that low MSE where obtained using a learning rate of 0.04 and a momentum factor of 0.4, as well as with normalized cadmium concentrations instead of the raw ones for outputs. A group of patterns (45 integrated absorbance–concentration pairs) covering the entire working range were randomly selected and used for training the ANNs. A set of 30 patterns (validation set) was employed to prevent the networks from becoming overtrained. The adjustment of the network weights for a given topology was conducted at least three times, in order to avoid the networks to be stuck in a local minimum during training. In each case, the initial weights were randomly started (−1.0 to 1.0). The selected topology was that whose MSE best approached the average training MSE. The code (1:*n*:1) is used throughout to describe the topology of the neural networks (*n* representing the number of neurons in the hidden layer).

Testing the chosen ANN was conducted two fold. First, by evaluating the quality of a linear regression analysis of cadmium concentrations predicted by the network versus the actual concentrations in the working solutions. The goodness-of-fit of the model generated by the ANN was also assessed through the estimation of the root mean square of the percentage deviations (RMSPD) [13,33]:

$$\mathrm{RMSPD} = \left(\frac{1}{N} \sum_{i=1}^{N} \left(\frac{C^i_{\mathrm{Pred}} - C^i_{\mathrm{Real}}}{C^i_{\mathrm{Real}}} \times 100 \right)^2 \right)^{1/2} \quad (4)$$

where C^i_{Pred} and C^i_{Real} corresponds to the *i*th predicted and actual concentrations, respectively, and *N* is the number of points used in the calibration (excluding the blank). Second, employing the model thus generated for the determination of cadmium in the reference material at the concentration levels described in the preceding section.

5. Results and discussion

5.1. Cadmium calibration curve in GFAAS

Fig. 2 clearly shows the non-linear behavior of the integrated absorbance signal for cadmium with increasing concentrations in the range of 0–22.0 $\mu g\,l^{-1}$. Above this value the curve reached a quasi-plateau, and so those *X*–*Y* pairs were discarded from the studies that followed. Precision in the above concentration range was better than 2.5 %R.S.D., except at 0.5 $\mu g\,ml^{-1}$ Cd (ca. 4 %R.S.D.), which is still analytically acceptable. The data points were fit with the second-order polynomial described by $A_i = -0.0013[\mathrm{Cd}]^2 + 0.0761[\mathrm{Cd}] - 0.0002$ ($r'^2 = 0.9988$). The goodness-of-fit was assessed in the first place through the adjusted coefficient of determination (r'^2) [34]. This

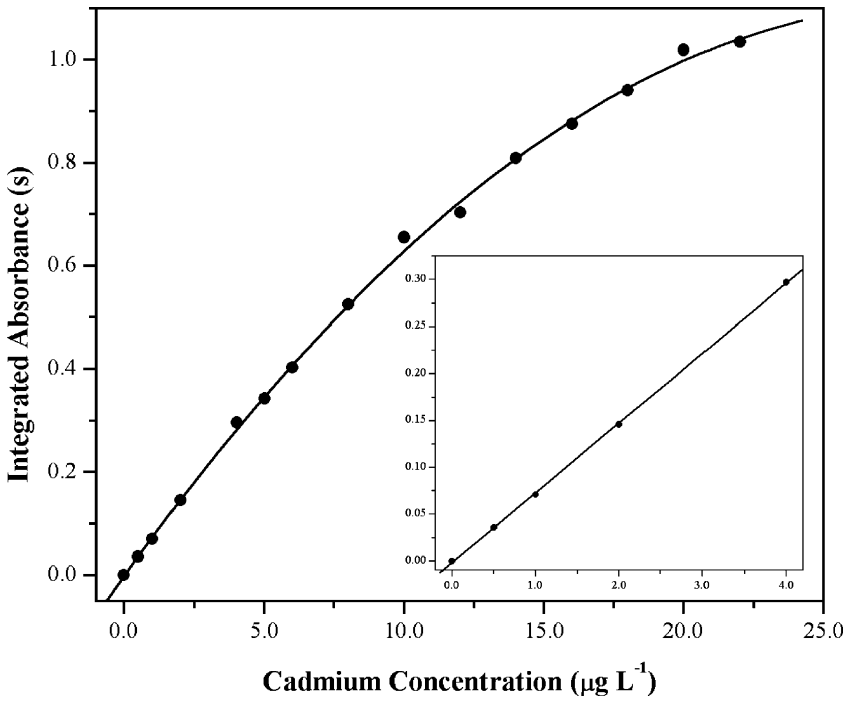

Fig. 2. Integrated absorbance as a function of Cd concentration. The line represents a second-order polynomial fit. Inset shows cadmium's LDR (see text for details).

parameter takes into account the variation in the degrees of freedom experienced by the residuals with the inclusion of further terms in a polynomial expression. Therefore, it provides a statistically more accurate reflection of the polynomial fitness than the coefficient of determination employed otherwise [35].

The linear range is significantly short, spanning up to 4.0 $\mu g\,l^{-1}$ Cd (see inset in Fig. 2). The regression equation best describing the variation of the integrated absorbance with concentration was found to be $A_i = 0.0745[\mathrm{Cd}] - 0.0019$ ($r^2 = 0.9998$). Inclusion of an additional X–Y pair already deteriorated the adequacy of the linear model ($r^2 = 0.9967$). Such a short LDR entails that samples with concentrations higher than the upper limit would require dilution, with all the disadvantages already mentioned. An alternative could be to extend the working range by modeling the entire (non-linear) calibration curve with ANNs.

5.2. Modeling the calibration curve by artificial neural networks

Vander Heyden et al. [24] developed a Kohonen neural network approach for diagnosing the adequacy of the calibration curves in AAS. Such an approach would determine whether a calibration graph contains outliers, may give rise to imprecision in the determinations, or deviates from linearity. In our case, we decided to evaluate another kind of ANNs, viz. feed-forward ANNs trained with the generalized delta rule, for modeling the non-linear calibration and increasing the working range for the determination of cadmium by GFAAS.

Several ANNs were evaluated for modeling the calibration curve depicted in Fig. 2. Variables to be optimized were the number neurons in the hidden layer and the training/validation cycles. The initial criterion for selection of the most adequate ANN was the achievement of the minimum MSE in a relatively small number of cycles.

Fig. 3 shows the trend in the training and validation MSEs for a (1:2:1) ANN. Only such values are presented for sake of simplicity, since increasing the number of hidden nodes did not yield a better performance. Also, using more complex networks would have unnecessarily complicated the data processing step, and were not further considered. The training MSE reached a quasi-plateau after ca. 4×10^4 cycles, whereas the validation one did so after 8×10^4 cycles. No significant variation in the MSE was observed beyond 10^5 cycles, and thus training/validation was stopped at this point. The training/validation time took only 15–27 s in a Pentium III processor; therefore, the development of the networks in this case was a relatively rapid process.

While a reduction of the MSE is an important aspect to be considered for selecting the most adequate topology, it is as relevant evaluating the generalization capacity with data not used during the training process. On this sense, a group of integrated absorbance data from the calibration set was input to the selected ANN, and the corresponding concentrations were estimated. A linear regression model of predicted versus expected cadmium concentrations was developed. The regression equation for the (1:2:1) network was $[\mathrm{Cd}]_{\mathrm{Pred}} = 1.002[\mathrm{Cd}]_{\mathrm{Real}} + 0.056$ ($r^2 = 0.999$). A statistical test, Student's t-test showed that the intercept and the slope of such equations did not differ significantly ($P = 0.05$)

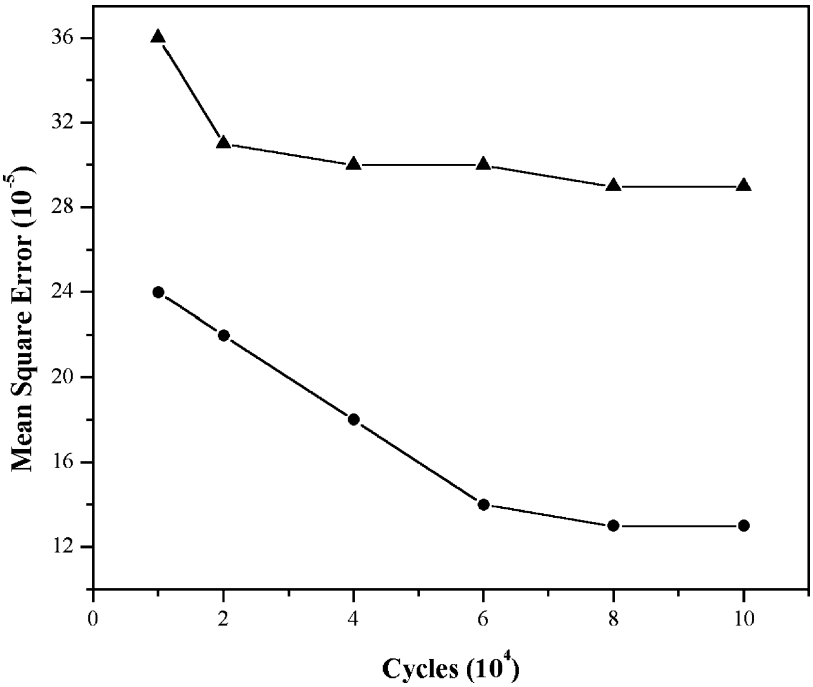

Fig. 3. Training (▲) and validation (●) mean square error for the (1:2:1) neural network.

Table 2
Determination of Cd in "trace metals in drinking water" certified reference material by GFAAS using different calibration approaches

Concentration ($\mu g\,l^{-1}$)	Method[a]		
	Dilution	Second-order polynomial	ANN (1:2:1)
2.0	2.09 ± 0.03 (1.4)	2.10 ± 0.03 (1.4)	2.03 ± 0.03 (1.4)
4.0	4.00 ± 0.04 (1.0)	4.19 ± 0.04 (1.0)	4.08 ± 0.04 (1.1)
8.0	–	8.05 ± 0.11 (1.4)	7.90 ± 0.12(1.5)
12.0	–	12.35 ± 0.08* (0.6)	12.30 ± 0.08 (0.6)

[a] Values correspond to the average ± standard deviation ($N = 5$). Relative standard deviation (%R.S.D.) is given in parenthesis.
* Significant differences ($P = 0.05$).

from 0 and 1, respectively [34], indicating the adequacy of the model in a first approximation. The RMSPDs (Eq. (4)) was also estimated in order to assess the goodness-of-fit of the model generated by such a network. The low RMSPD (4.3%) is a clear indication of the capability of the neural network for modeling the calibration curve in the entire range of study.

5.3. Determination of Cd by GFAAS in a certified reference material

As the concentration of the analyte ($12.0\,\mu g\,l^{-1}$) in the reference material is clearly outside the linear range, a dilution of such a solution would have been certainly considered the first approach for the determination of cadmium. The results obtained in such a way are presented in Table 2. A statistical evaluation of Student's *t*-test [34] revealed no significant differences ($P = 0.05$) between the expected and estimated concentrations. Again, this method presents certain disadvantages, and alternative methods should be sought in order to overcome them.

A polynomial fitting of a non-linear curve is a relatively fast and simple method that can be easily implemented by any dedicated computer program. According to L'vov et al. [10], these methods should not be considered for calibration purposes, since the coefficients adjusting the polynomial lack physical meaning. Even though this observation (coefficients' lack of meaning) is clearly accurate, we estimate that an adequate fitting, as well as the ease and speed of such a method should make of this an interesting calibration alternative.

The determination of cadmium in the reference material was carried out using the second-order polynomial fit discussed in Section 5.1 (see Table 2). The statistical analysis indicates no significant differences ($P = 0.05$) for all but the highest concentration. Attempts to increase the accuracy of the determination at such a level, for instance by modeling solely the non-linear portion of the curve ($5.0–22.0\,\mu g\,l^{-1}$), did not render better results. Therefore, and in spite of the apparently goodness-of-fit of the second-order polynomial (high r'^2), this method was found partially inadequate for the case of study. Other authors have long reported on problems associated with the accuracy of the determinations in the non-linear portion of the calibration curves [4], yet second-order polynomials have still been successfully used [35]. Finally, the determination of cadmium in the reference material was conducted by means of the model generated by the ANN. Contrarily to the previous case, no statistical differences ($P = 0.05$) were found between the expected concentrations and those obtained by the proposed method at all levels (see Table 2).

The results presented here indicate that the working calibration range can be extended by means of an ANN, without sacrificing either accuracy or precision. For the specific case of cadmium, a nearly six fold increase could be achieved. The high sensitivity of the measurements is still preserved at the linear portion of the calibration graphs. The latter permits the determination of cadmium at both low (linear portion) and moderately-high (non-linear portion) concentrations with the same calibration curve. This is not possible with some methods which resort to decreasing the sensitivity of the measurements for increasing the LDR, thus allowing only the determination of elements at high concentrations [8,9]. Another advantage of modeling by ANNs is, in general, the fact that no a priori knowledge of the system is required ("soft" modeling), as it is when modeling by conventional mathematical methods ("hard" modeling).

It is important to highlight that, just like the coefficients of the second-order polynomial, the neuron's weights do not have any physical meaning. Furthermore, while an ANN can model almost any system, it is not possible to translate such a model into a mathematical expression, particularly for large networks. This is in fact one of the major criticisms to ANNs, i.e. their "black box" character. However, we reiterate that such models could be used for practical purposes, e.g. for routine analysis, as long as they provide results that could be proved to be accurate, while having an acceptable degree of precision. Modeling calibration curves by means of ANNs could be an alternative in multielemental (simultaneous) GFAAS, wherein selection of the dilution factor for the determination of various analytes in a single sample is more critical than in other multielemental techniques, e.g. ICP–OES, TXRFS, etc. due to the intrinsically shorter linear range.

6. Conclusions

An ANN was successfully used for modeling the calibration graph and increasing the working range for cadmium in

GFAAS. An interesting aspect is that, contrary to some instrumental methods hitherto developed, the ANN approach allows retaining the high sensitivity of the measurements at the linear portion of the curve. This aspect may be of importance in those cases where the analyte concentration varies in such a way that high sensitivity is still required for some samples, yet dilution may be needed for some others. Modeling by ANNs may represent an alternative in multielemental (simultaneous) GFAAS, as a means of coping with the shorter linear range of the technique and the compromise dilution conditions required for multielemental analysis in a single sample.

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References

[1] L. de Galan, J. Anal. At. Spectrom. 2 (1987) 89.
[2] R.B. Boss, K.J. Fredeen, General characteristics of ICP–OES, in: Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, Perkin–Elmer Corp., USA, 1999, pp. 2-12 (Chapter 2).
[3] R.P. Petterson, TXRF, in: Design of a Total-Reflection X-ray Fluorescence Spectrometer and Application to Periphyton Communities, Ph.D. Thesis, Chalmers University of Technology and Götenborg University, Sweden, 1997, pp. 8–11 (Chapter 3).
[4] J.M. Marchante Gayón, A. Sanz-Medel, C. Fellows, P. Rock, J. Anal. At. Spectrom. 7 (1992) 1079.
[5] R.E. Sturgeon, C.L. Chakrabarti, P.C. Bertels, Anal. Chem. 47 (1975) 1250–1257.
[6] R.E. Sturgeon, C.L. Chakrabarti, P.C. Bertels, Spectrochim. Acta Part B 32 (1977) 257.
[7] C.M. Smith, J.M. Harnly, J. Anal. At. Spectrom. 10 (1995) 187.
[8] M.A. Belarra, M. Resano, J.R. Castillo, Spectrochim. Acta Part B 51 (1996) 697.
[9] J.B. Borda da Silva, M.B. Oss Giacomelli, I. Gonçalves de Souza, Anal. Chim. Acta 401 (1999) 307.
[10] B.V. L'vov, L.K. Polzik, N.V. Kocharova, Spectrochim. Acta Part B 47 (1992) 889.
[11] E.G. Su, A.I. Yuzefovsky, R.G. Michel, J.T. McCaffrey, W. Slavin, Spectrochim. Acta Part B 49 (1994) 367.
[12] A.I. Yuzefovsky, R.F. Lonardo, J.X. Zhou, R.G. Michel, Appl. Spectrosc. 51 (1997) 738.
[13] S.R. Bysouth, J.F. Tyson, J. Anal. At. Spectrom. 1 (1986) 85.
[14] H.C. Wagenaar, L. de Galan, Spectrochim. Acta Part B 30 (1975) 361.
[15] J.R. Long, V.G. Gregoriu, P.J. Gemperline, Anal. Chem. 62 (1990) 1791.
[16] Z. Li, Z. Cheng, L. Xu, T. Li, Anal. Chem. 65 (1993) 393.
[17] T.B. Black, S.D. Brown, Anal. Chem. 65 (1993) 3081.
[18] L. Hadjiiski, P. Geladi, P. Hopke, Chemom. Intell. Lab. Syst. 49 (1999) 91.
[19] Y. Ni, C. Liu, Anal. Chim. Acta 396 (1996) 221.
[20] A. Safavi, G. Absalan, S. Maesum, Anal. Chim. Acta 432 (2001) 229.
[21] G. Absalan, A. Safavi, S. Maesum, Talanta 55 (2001) 1227.
[22] Y. Zhou, A. Yan, H. Xu, K. Wang, X. Chen, Z. Hu, Analyst 125 (2000) 2376.
[23] C. Schierle, M. Otto, Fresenius J. Anal. Chem. 344 (1992) 190.
[24] Y. Vander Heyden, P. Vankeerberghen, M. Novic, J. Zupan, D.L. Massart, Talanta 51 (2000) 455.
[25] R. Zhang, X. Chen, S. Chen, Z. Hu, Fenxi Huaxue 24 (1996) 724.
[26] J. Zupan, J, Gasteiger, Neural Networks in Chemistry and Drug Design, second ed., Wiley-VCH, Germany, 1999.
[27] Propagator, Neural Network Development Software, Version 1.0 for Windows, ARD Corp., USA, 1993.
[28] B.J. Wythoff, Chemom. Intell. Lab. Syst. 18 (1993) 115.
[29] HGA-700 Graphite Furnace Operator's Manual, Perkin–Elmer Corp., Part No. B017-4145, 1990.
[30] HPS Certified Reference Material "Trace Metals in Drinking Water", Certificate of Analysis, High Purity Standards, Charleston, SC, USA.
[31] E.A. Hernández Caraballo, J.R. Domínguez, J. Alvarado, At. Spectrosc. 21 (2000) 132.
[32] E.A. Hernández Caraballo, J.R. Domínguez, J. Alvarado, At. Spectrosc. 22 (2001) 295.
[33] N.J. Miller-Ihli, T.C. O'Haver, J.M. Harnly, Spectrochim. Acta Part B 39 (1984) 1603.
[34] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fourth ed., Prentice Hall, UK, 2000.
[35] M.G.R. Vale, M.M. Silva, B. Welz, R. Nowka, J. Anal. At. Spectrom. 17 (2002) 38.