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A Study of the Effectiveness of Neural Networks for Elemental Concentration from Libs Spectra

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A STUDY OF THE EFFECTIVENESS OF NEURAL NETWORKS FOR ELEMENTAL CONCENTRATION FROM LIBS SPECTRA

By

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Laser-induced breakdown spectroscopy (LIBS) is an advanced data analysis technique for spectral analysis based on the direct measurement of the spectrum of optical emission from a laser-induced plasma. Assignment of different atomic and ionic lines, which are signatures of a particular element, is the basis of a qualitative identifcation of the species present in plasma. The relative intensities of these atomic and ionic lines can be used for the quantitative determination of the corresponding elements present in different samples. Calibration curve based on absolute intensity is the statistical method of determining concentrations of elements in different samples. Since we need an exact knowledge of the sample composition to build the proper calibration curve, this method has some limitations in the case of samples of unknown composition. The current research is to investigate the usefulness of ANN for the determination of the element concentrations from spectral data.

From the study it is shown that neural networks predict elemental concentrations that are at least as good as the results obtained from traditional analysis. Also by automating the analysis process, we have achieved a vast saving in the time required for the data analysis.

DEDICATION

Amma & Naana, this is for you.

ACKNOWLEDGMENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

ANN Artifcial Neural Network

LIBS Laser Induced Breakdown Spectroscopy

PE Processing Element

Cr Chromium

Mg Magnesium

Mn Manganeese

Cu Copper

Rel. Accry Relative Accuracy

Rel. Prec. Relative Precision

CHAPTER I

INTRODUCTION

The Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University develops advanced data analysis techniques for spectral analysis for environmental concern. Laser-induced breakdown spectroscopy (LIBS) is one method of analysis by direct measurement of the spectrum of optical emission from a laser-induced plasma. Laser-induced breakdown spectroscopy (LIBS) analysis has been the subject of research over many years [35, 33]. This technique is attractive as a remote, real time, and non-destructive method of monitoring material composition. In this technique a high power laser radiation is focused on sample surface, which instantaneously evaporates a thin surface layer and initiates an avalanche ionization of the sample elements, giving rise to the so-called breakdown effect. Assignment of different atomic and ionic lines, which are signatures of a particular element, is the basis of a qualitative identifcation of the species present in plasma.

The relative intensities of these atomic and ionic lines can be used for the quantitative determination of the corresponding elements present in different samples. Use of calibration curve based on absolute intensity is a statistical method for determining concentrations of elements in different samples. Since we need an exact knowledge of the sample com-

position to build the proper calibration curve, this method has some limitations in the case of samples of unknown composition.

The current research is to investigate the usefulness of artifcial neural networks (ANN) for the determination of the element concentrations from spectral data. Recently ANN have been fnding use in many applications. Its classifcation and prediction capabilities are especially useful in spectral analysis. It has been used to identify modifed starches from infrared spectra [22], polymer from LIBS spectra [38], and to obtain quantitative composition of chlorinated hydrocarbons from Raman spectra [11]. By training neural network, it is possible to analyze LIBS data for species that constitute a sample, without calibration curve.

1.1 Hypotheses

The research hypotheses are

1. Elemental concentrations determined from spectral data using artifcial neural networks are at least as good as those obtained using traditional statistical calibration methods.
2. Operator assistance needed to acquire and analyze spectral data may be minimized through automation.

The hypotheses are supported through the development of artifcial neural network models for each element and analyzing the spectral data for each element. Data analysis process was automated to compare operator assistance for manual and automated analyses. The research results will provide spectroscopists with an alternate method of analyzing spectral data and enable them to determine concentrations of the elements of interest.

1.2 Organization

The organization of this thesis is as follows: Chapter 2 discusses related work in the application of artifcial neural networks for the analysis of spectral data. Chapter 3 presents the architecture, working and design of an artifcial neural network. Chapter 4 gives the experimental details while the results and analysis are given in Chapter 5. Chapter 6 concludes the thesis and suggests some directions for future research.

CHAPTER II

RELATED WORK

This chapter provides a brief discussion of the application of LIBS technique in different felds, a brief introduction to artifcial neural networks, its application in diverse areas and their advantages, and concludes with the details of neural network applications for analysing LIBS spectral data.

2.1 Laser Induced Breakdown Spectroscopy

The area of spectral analysis has grown considerably in the past decades. A multitude of methods are available like the Fourier Transform, AutoRegressive and Inductively Couped Plasma (ICP). These methods of spectral analysis provide poor resolution and exhibit spurious peaks when high-resolution is requried [23, 4]. Laser induced breakdown spectroscopy (LIBS) is an advanced diagnostic technique for spectral analysis. It is a novel, rapid and feld-deplo yable method of elemental analysis. Ever since its inception it has been the subject of research over many years. LIBS has been a promising tool to investigate the constituents of solids, liquids and gases [41, 40, 32]. This method of analysis is ideal for differentiation of metals based on their relative concentrations, and is applicable to both conducting and non-conducting samples. In the LIBS method, laser pulses

are focused on a material to form plasmas or sparks which are emitted from the excited atoms. This light is detected for the presence of elements on the basis of their unique spectral signatures. It is important in this analysis to determine the spectral region where the isolated emission lines corresponding to the species of interest lie [1]. LIBS can provide on-line elemental analysis during processing, quality assurance and quality control decisions. This enables real-time analyses of molten metals, as well as analyses of metals in otherwise inaccessible locations [34].

Advantages of LIBS over conventional elemental analysis methods are [8]: little to no sample preparation, rapid analysis (one measurement per laser pulse), simultaneous multi-element detection and simple with stand-off analysis capability.

LIBS technique is useful for a variety of applications ranging from environmental monitoring, material analysis (metals, plastics), forensics and biomedical studies, military and safety needs (such as explosive particles, chemical and biological warfare agents) and art restoration [1]. Several research groups were engaged to explore the possibility of using LIBS by comparing the LIBS signal obtained for a given element to a suitable calibration curve [35]. Calibration based on absolute intensity and line ratios were used by many researchers and have certain degree of success. For quantitative measurements, the calibration data should be collected with experimental condition as close to the measurements as possible. Galbacs et al. [12] has proposed a new calibration approach based on linear correction for binary alloy. This method can be considered as a reliable semi quantitative method for samples containing 2-4 components. Ciucci et al. [7], have recently developed

an algorithm for calibration-free LIBS analysis. However, it requries the existence of local thermal equilibrium in laser-induced plasma.

2.2 Artifcial Neural Networks

An artifcial neural network (ANN) is an information processing paradigm. ANN tries to solve problems by imitating the structure and function of human brain [10]. Ever since the establishment of this feld before the advent of computers, neural networks with their remarkable ability to derive meaning from complicated or imprecise data, were used to extract patterns and detect trends that are too complex to be noticed by either humans or computer techniques [24]. It is confgured for a specifc application through learning process. With their superior classifcation and prediction capabilities, ANN's have broad applicability to real world business problems. Some of the areas where neural networks are helpful are sales forecasting, industiral process control, customer research, data validation, risk management, target tracking and marketing [43]. Schoones [39] in his work has given an overview of the practical applications of artifcial neural networks and their potential application in signal processing. Neural networks were used to predict the testability and faults in software systems [20, 21]. ANNs have found their ways in the defense applications also. Pirate et al. [30] developed a neural network based system for the identifcation, localization and tracking of a moving target in a visual scene . The potential of artifcial neural networks (ANNs) for satellite image classifcation of land cover/land use, according to the hierarchical statistical nomenclature (CLUSTERS), were demonstrated

and tested [18]. The work also involves: analysis of the potential for automating image classifcation tasks using ANNs in terms of their level of details, the possible use of ANNs in quality control procedures during classifcation/interpretation, and the quality control on the results.

Artifcial neural networks have found their impact in spectral analysis. Keller et al. [19] discusses their application in analyzing nuclear spectral data. Benzing, Hopkins, and Whitaker [5] have shown how ANN has been used to analyze exhaust fame from space shuttle engine to identify trace elements. Puranik [31] reports how parameter monitoring with the help of embedded ANN may be used to control a thermal process. Jones, Irwin and Hippel [17] have been investigating the use of artifcial neural networks (ANNs) with principal components analysis (PCA) front-end compression as a means of quantifying stellar spectral classifcation. Ponz and Vieira [44] explored two automated classifcation methods to classify the stellar spectral data using neural networks. Neural Networks were also used to identify modifed starches from infrared spectra [22] and to obtain quantitative composition of chlorinated hydrocarbons from Raman spectra [11].

There has been little work towards the application of artifcial neural networks for the analysis of LIBS spectra. Samek, Telle, and Beddows [37] has shown that the combination of LIBS and pattern recognition algorithms provide a potentially useful tool for dentists for fast material identifcation problems, for example the precise control of the laser drilling/cleaning process. They are used in the polymer identifcation of the LIBS spectra [38]. Philip et al. [28] used artifcial neural networks to identify elements present

in exhaust gases from LIBS spectra. Philip et al. [29] discuss the use of neural networks in spectral analysis to verify the concentration of elements present in gaseous media. Inakollu et al. [16] has shown that application of neural networks for elemental concentration determination in molten alloys gives results at least the same as those from conventional calculations but many times the results are better than those from the conventional calculations.

Not much work has been done towards the automation of LIBS spectral analysis for elemental concentrations. Panda [27] has developed an intelligent system, ”Spectral Support System (SSS)”, to make the LIBS a real time measurement technique. This system uses different artifcial neural networks and predicts the concentrations of different elements in the exhaust gas and the glass produced by a plasma torch. This thesis is towards developing an automated software for the elemental analysis of LIBS spectral data for molten alloys.

CHAPTER III

ARTIFICIAL NEURAL NETWORKS

Neural Networks can simulate some intelligence activities of the human brain, such as sense and inspiration, as well as thinking of images. [3]

Researchers in many distinct disciplines like biology, mathematics, electronics, medicine, computing, psychology and physics work with artifcial neural networks (ANN). The basic idea is to use the knowledge of the nervous system and the human brain to design intelligent systems. They represent a computational paradigm, in which the solution to a problem is learned from a set of examples. It is thought to be an information-processing archetype similar to the densely interconnected, parallel architecture of the mammalian brain-processing unit [24]. They have the capability for comprehension, reasoning, perception, communication and learning [10]. This can make fast, intuitive and optimum answers after training. They evolve mathematical models by learning from input examples, and handle non-linear, noisy and imprecise data quite well.

Neural network models give ideal solutions to classifcation and prediction problems with high degree of precision and accuracy [13]. Their robust and highly parallel processing nature makes them capable of non-linear modelling. This chapter begins with various defnitions used to describe neural network in literature. In section 3.2, we will see the

different architectures and their working principle. The third section deals with the design of the neural network, the fourth section gives insights into the training and learning processes. This chapter ends with a listing of neural networks applications, their advantages and disadvantages.

3.1 Defnitions

In literature a wide variety of defnitions and explanations for the terms *Artifcial Neural Networks* can be found. There is no universally accepted defnition for an ANN. In this section, a few of the defnitions from different authors are provided.

According to [2] *".... a neural network is a system composed of many simple processing elements operating in parallel whose function is determined by network structure, connection strengths, and the processing performed at computing elements or nodes."*

According to Zurada [45] *"Artifcial neural systems or neural networks, are physical cellular systems which can acquire, store, and utilize experiential knowledge."*

According to Nigrin [26] *"A neural network is a circuit composed of a very large number of simple processing elements that are neurally based. Each element operates only on local information. Furthermore each element operates asynchronously; thus there is no overall system clock."*

According to Haykin [15] *"A neural network is a masively parallel distributed processor that has a natural propensity for storing experiential knowledge and making it available for use. It resembles the brain in two respects:*

1. *Knowledge is acquired by the network through a learning process.*
2. *Interneuron connection strengths known as synaptic weights are used to store the knowledge".*

Harvey defnes it as [14] *"A neural network is a dynamical system with one-way interconnections. It carries out processing by its response to inputs. The processing elements are nodes;the interconnects are directed links. Each processing element has a single output signal from which copies fan out."*

3.2 Architecture and Working of the Network

Artifcial neural network consists of a large number of simple processing elements (PEs) densely interconnected, analogous to neurons of human brain. The neural network is made up of several layers of processing elements connected together via unidirectional signal channels associated with weights, analogous to synapses. These processing elements work in unision to slove a problem. The knowledge of the network is represented by its weights [36]. Every useful artifcial neural net has a minimum of three layers: an input layer through which data is given to the network, an output layer that holds the response relative to the input and optional layer between the input and output layers called the hidden layer where learning takes place. The number of neurons in the input and output layers can be determined by the number of input and output variables in the physical system [42]. The number of hidden layers and the nunber of neurons in the hidden layers are arbitrary and can vary from zero to any fnite number.

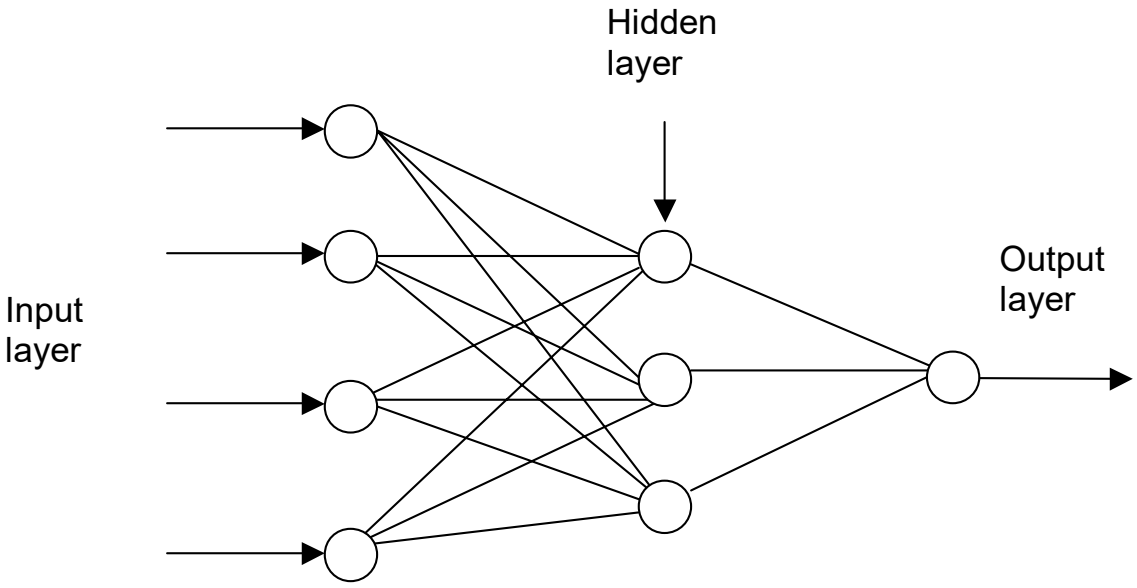

Figure 3.1 A simple neural network architecture

Figure 3.1 shows a simple network architecture with four inputs and one output. The circles in the fgure denote the PEs arranged in layers. A processing element (PE) can have many input paths and combines, usually by a simple summation, the values of these input paths. The network learns by adapting the weights of its connections according to surrounding environment. The behavior of the output unit depends on the activity of the hidden and input units. They are data driven devices. Neural networks are exceptionally effective for predicting events when the networks have large training data sets to pull on.

With the given inputs and the related outputs, the network learns how the inputs of each data set are associated to the output. The network then continuously refnes and organizes itself by adjusting the synaptic weights to ft the data, so that it produces relatively accurate response for a given input. Information processing of a single processing element is shown

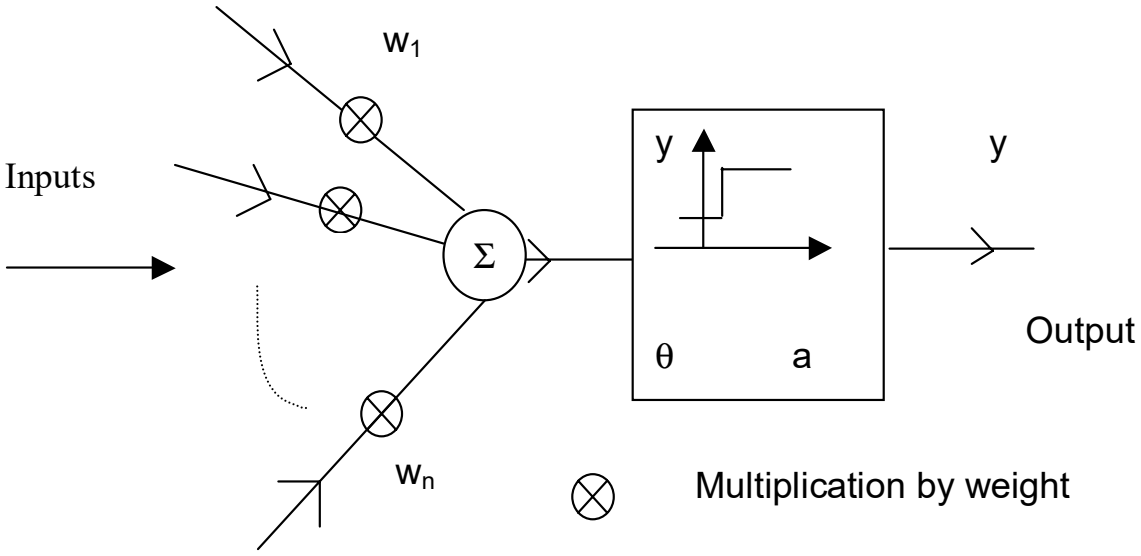

Figure 3.2 Information processing of a single processing element

in Figure 3.2 . Multiplying the input x_i by weight w_i can approximate the effect of a particular input unit. These weighted signals are added up to produce overall internal activation for the processing element. This activation level is passed through a transfer function, which produces an effective signal 'a'. If the activation is beyond a certain threshold, then the system gives the output response 'y'.

In Figure 3.2 there are n inputs with signals $x_1, x_2, ..., x_n$ and corresponding weights w_1, w $, ...,w_n$. The signals shown are Boolean valued with values '1' or '0' only. The system activation a is given by [10],

$$a = w_1x_1 + w \quad x_2 + ... + w_nx_n \tag{3.1}$$

With this system activation, the output y is given by,

$$y = 1 \qquad \text{if} \qquad \text{a} \leq \theta$$

$$= 0 \qquad \text{if} \qquad a \geq \theta \tag{3.2}$$

Generally there are two types of neural network architectures, Feed-forward networks and the Feedback networks [43, 10].

3.3 Learning Process

Every neural network possesses knowledge which is contained in the values of the connection weights. The knowledge stored in the network can be modifed by changing the values of the weights and applying specifc learning rule. The process of determining the weights by which the best match between the desired output and the ANN output is called *training process* [6]. In this training process all the weights are changed to minimize the error between desired output and the ANN output. This kind of networks which are able to change their weights are known as ”adaptive networks” [10]. Neural networks are trained to learn the real non-linear relationships between the inputs and outputs of the system under study. The only information needed to train the ANN is ample input/output data. No prior knowledge of the system is needed. Figure 3.3 gives the algorithm involved in the learning process.

A suitable means of data representation to the neural network is the most important characteristic which affects the performance of the network. Input data needs to be scaled in conjunction with the outputs. To get the desired outputs, the connection weight vectors must be small values (<1) [9]. Hence the inputs must be with in the same range. Thus, the input data are normalized such that they lie between 0 and 1. The output of the

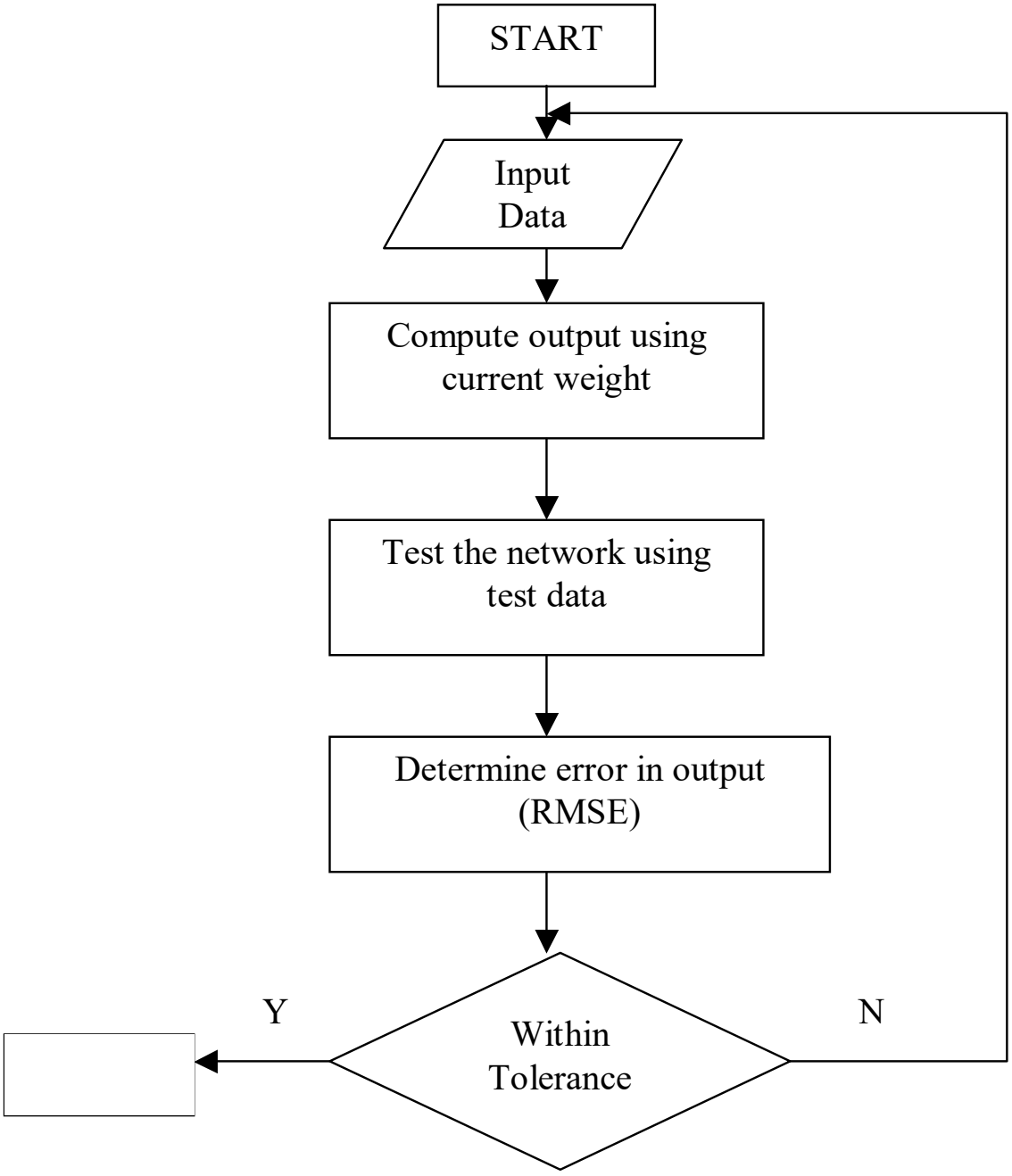

Figure 3.3 Flow chart of the learning process

neural nets is dependent on their weights. The learning paradigm of neural networks involves developing mathematical models to learn from the input data and extract important features, training the network with input/output data sets, in accordance with a training algorithm, iteratively adjusts the connection weights, which contributes to the knowledge necessary to solve related problems. Training will be most effective if the training data is spread throughout the input space. Learning algorithms are classifed into two types namely supervised and unsupervised [24].

3.3.1 Supervised learning

In supervised training, the network gets a set of labeled training data. By labeled, it means that the training data consists of many pairs of input/output patterns. The inputs are processed and the resultant output is compared against the desired output. The error is then propagated back through the system, enabling the system to adjust its weights in order to reduce the error. This process is repeated until the connection weights are refned to allow for the minimum error. Thus the network learns from the training data, in accordance with the learning rule and infers a relationship between the inputs and the corresponding outputs. With this knowledge of the relationship between input and output, a neural network can make predictions for unknown input data.

3.3.2 Unsupervised learning

A labeled data set is not provided for unsupervised learning. The training set consists of input training patterns only. The network learns to adapt based on the experiences collected through the previous training patterns. Unsupervised algorithms perform clustering of the data into similar groups based on the measured attributes or features serving as input [24].

The difference between the desired output and the network output is taken as the criteria for stopping the network training. Root-mean Sqaure Error method can be used for this purpose. However, over-trained network would result in overftting. Overtraining is a phenomenon occured when a network instead of learning trends in the presented data, memorizes peculiarities of the training data [9].

3.4 Validating Process

Validating Process is carried out to validate the network on new/unknown data sets, called the validation set. This is a process which is performed after training the network. A properly built and trained network will result in the output which is acceptable. The network which can yield the best performance on the validation samples would be the best accurate model. If the validation sample outputs are not acceptable then a new network is to be built undergoing the whole process of learning and testing. Figure 3.4 gives the algorithm involved in the validation process.

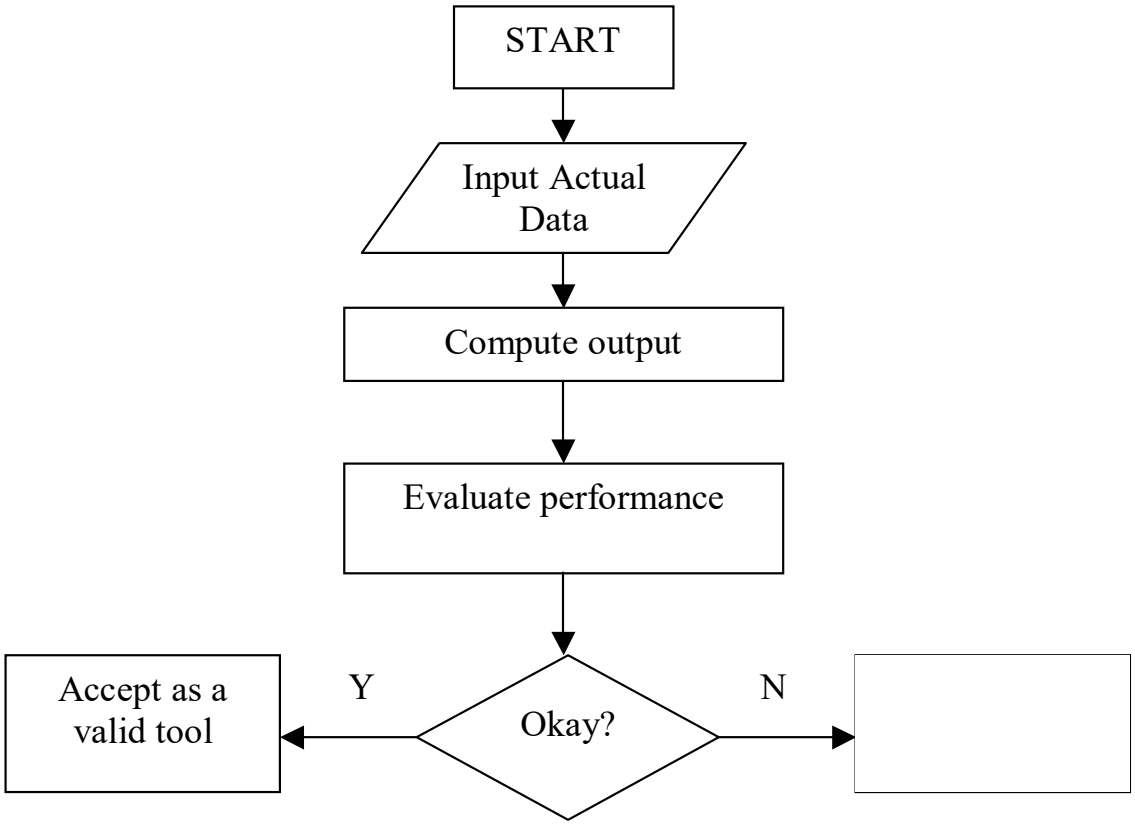

Figure 3.4 Flow chart of the validation process

3.5 Design of Neural Networks

The design issues are based on the application. The design decisions involve in the arrangement of processing elements in different layers, the number of hidden layers, the number of processing elements in the hidden layer, the learning algorithm, and the data set. Design of a neural network is an iterative process and goes on by trial and error method. In general, there are different kinds of neural network architectures available, such as Learning Vector Quantization (LVQ), Probabilistic Neural Network (PNN), Back Propagation (BP) and Self-Organizing Map (SOM) etc. Back Propagation is the most known architecture.

The weights connected to the output units are adjusted in order to reduce these errors. Finally, errors are propagated back to the connections from the input units. This process of backpropagaiton continues until the error is within the threshold value. Depending on the complexity of the problem the number of hidden layers vary, but theoretically no more than three hidden layers should be used. The number of hidden neurons is determined by trial and error until the network performs its best. As the number of hidden layer neuron increases, the network becomes overft resulting in imprecise and over predictions.

3.6 Applications of Neural Networks

Given the explanation of neural networks and how they work, in this section various applications of neural networks are mentioned. They have broad applicability in industry and to real world business problems. Some of the areas where neural networks are

very helpful are sales forecasting, industrial process control, customer research, data validation, risk management, target tracking and marketing [43]. They have also been used for bankruptcy prediction for credit card institutions. The most successful applications of neural networks are in categorization and pattern recognition. They are used to classify the object under investigation e.g. an illness, a pattern, a picture, as one of numerous possible categories. Neural networks are good tools for Data Association and Data Mining. They are used for data fltering e.g. take the noise out of a telephone signal [15].

CHAPTER IV

EXPERIMENTAL DESIGN

This chapter presents the experimental setup and the methodologies to validate the proposed hypotheses. Experiments were conducted at LIBS lab at the Diagnostic Intrumentation and Analysis Laboratory, Mississippi State University. The organization of this chapter is as follows: frst section provides the experimental details and the methodology towards the validation of the frst hypothesis, details of the neural network models and the data processing techniques used. Second section gives details about the automation of data analysis and provides prototype for the automation for spectral data analysis using artifcial neural networks. This prototype is used for validating the second hypothesis.

4.1 Comparison of the analysis techniques

This section provides the details of experimental setup and the methodologies used to support the frst hypothesis of this thesis which proposes that analysis of LIBS spectral data using neural networks is at least as good as traditional calibration analysis. LIBS instrument is used to record the spectra of the element of interest in the given sample. LIBS spectra of seven different samples were recorded.

4.1.1 LIBS data acquisition and analysis

Data Acquisition is the process of porting data in different formats from different instruments or devices to computer memory or storage devices. Once the data is acquired it is analyzed for the results. The stages of data acquisition and analysis are shown in Figure 4.1

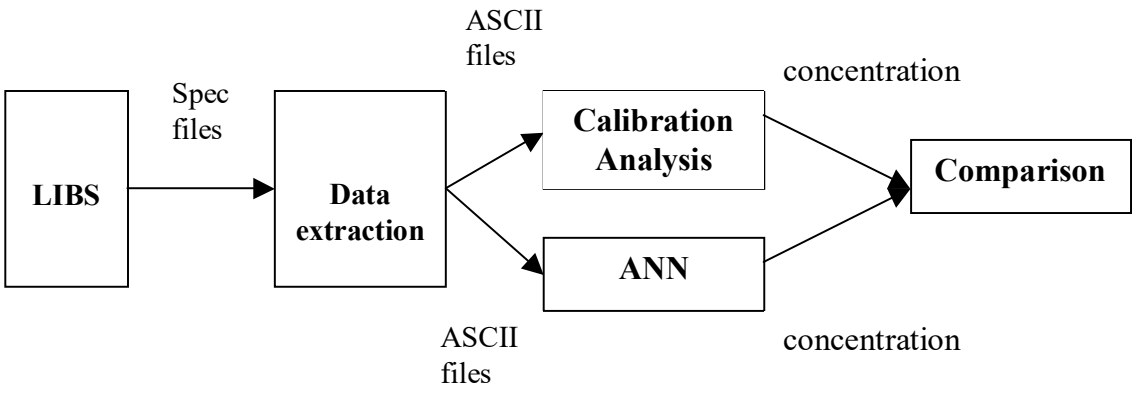

Figure 4.1 Stages of data analysis

Data acquisition for this thesis was done by fber optic LIBS system. Figure 4.2 shows the LIBS setup and the details of the experimental setup are described in [33]. In brief, a frequency-doubled Nd:YAG laser beam is coupled to the optical fber by using dichroic mirror and 10 cm focal length lens. The laser beam transmitted through the optical fber is collimated with a 10cm focal length lens and then focused on the sample with another plano convex lens f = 10 cm. The emission from the laser produced plasma at the focal point is collected by the same lenses and optic fber. The optical emission travelling through the backward direction with respect to the laser beam in the optical fber is fnally

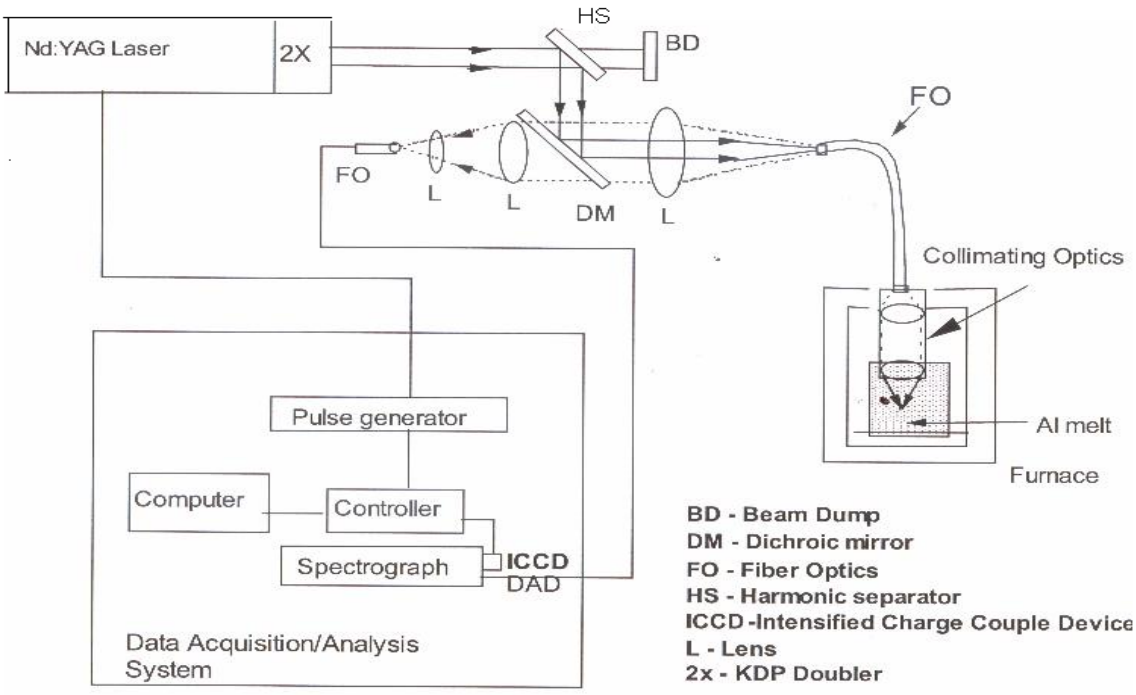

Figure 4.2 LIBS experimental set-up

focused on to an optical fber bundle with a 20-cm focal length lens. The fber bundle is round to slit type, which consists of 78 fbers of 100 μm diameter. The slit type end of the fber bundle delivers the emission to the entrance slit of a spectrometer equipped with a 2400 lines/mm grating blazed at 300 nm. An intensifed charge couple detector was used to detect the dispersed optical emission from the spectrograph. A computer with Win-Spec/32 software is used for data acquisition and analysis. Multiple laser shots (100 pulses) spectrum was stored in ”accumulation” mode.

Fifty spectra were stored in one fle for analysis to get average area/intensity value for the desired line. Figure 4.3 shows a sample spectrum, which is intensity vs wavelength. The region of interest is about the wavelength 404.154 nm for Manganeese. In calibration

curve analysis, the relative composition of various elements can be determined and the bulk elements in the sample can be identifed. The key to this type of analysis is to fnd a spectral region where there are isolated emission lines corresponding to the species of interest. Once the positions of these lines have been determined, regions of interest can be defned and the net peak area (equal to the difference between the total peak area and the background area) can be calculated. The quantitative spectral analysis involves relating the spectral line intensity of an element in the plasma to the concentration of that element in the target sample. All the Al alloy samples were also analyzed chemically to get the exact concentration of the elements in particular samples.

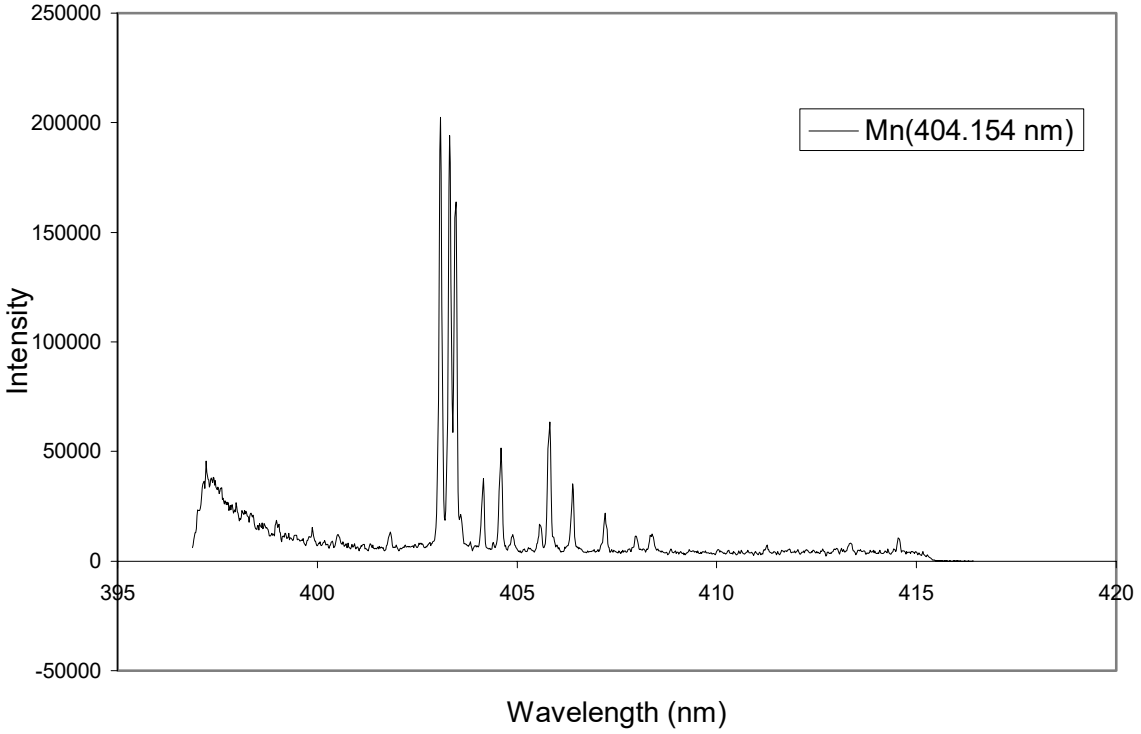

Figure 4.3 Typical LIBS spectrum

4.1.2 Neural network analysis

For this thesis, an automated neural network tool Predict from Neural Ware was used. Scott Fahlman of Carnegie Mellon University developed this constructive model [25]. The number of input neurons of the neural net is determined by the number of inputs to the system. The details of the input data selection is given in the next chapter. The output of the net is the concentration of the element and hence we have one output neuron.

4.1.2.1 Standardization

To get the desired outputs, connection weights of the neural net should be small values, which makes the inputs also to be within the same range [9]. To get this effect, the experimental results were normalized such that they lie between 0 and 1. This removes instability in the network output due to wide variations in the intensities of the peaks from different spectra. The formula used was

$$I_{stand} = \frac{I - I_{min}}{I_{max} - I_{min}} \tag{4.1}$$

where I_{stand} is the standard intensity

I_{min} is the minimum intensity

I_{max} is the maximum intensity

I is any intensity on the spectrum

4.1.2.2 Extraction

Each data fle consists of 200-350 spectra for any one concentration of an element. Each spectrum contains 27 kilobytes of data. Each value in the spectrum corresponds to the emission intensity at a specifc wavelength within the spectrum. The nature of raw data from Winspec and more details of the data fle are discussed in section 4.2.1.

Stability of output from a neural network model depends on its input data sets. The most common approach in selecting the data sets was to input an entire spectrum. Philip et al. [29] has shown that giving a complete spectrum to the neural network as input would increase the model complexity under training, and the presence of noise in the data makes the model ineffcient. Another choice was to select the data at regular intervals to form the input data set. But some valuable information from the data set can be missing and can affect the result of analysis. Other alternatives are centered on the peaks in the spectra. One of them is to use the peak intensities of characteristic lines. This single point approach does not make use of special properties of a line such as its width or shape. The other approach is to use intensity values along a line of interest to capture its properties. Since our interest was to fnd concentration of a particular element we concentrated on those peaks of the elements. The analyte lines of Chromium (359.349 nm), Magnesium (383.829 nm), Manganese (404.16 nm) and Copper (327.45 nm) were used for analysis of the elements in Al alloy samples. We have used intensities from +/-10 channels from the peak of the analyte lines as input to the ANN. These 21 values along with the experimental

conditions such as laser power, neutral density flter , forms the input vector of the network model.

Neural network model was trained with a learning set of 2000 - 2500 input vectors and tested with a data set of 1500- 2000 data points. Initially, a single network for all the concentrations of each element was developed. However, its outputs varied widely from the expected values. The reason for this could be that the network was over trained with particular sets of data and was not able to learn for general cases. Therefore, separate models were developed for each element based on their concentration values. Element concentrations more than 1 were labeled as high, and those less than 1 as low. This separation of the data sets produced results that agreed with actual values. The resultant elemental concentration is the average of all predicted values of the respective neural network model. Neural network model is validated using new data sets. Validation set consists of 50 data points. Results of the analysis are discussed in Chapter 5.

4.2 Prototype for Automation

This section provides the experimental setup and the methodology details used to test the second hypothesis, which states that operator assitance for the acquisition and analysis of spectral data can be minimized by automating the system. To test this hypothesis, interface software was developed to integrate all the steps from data acquisition to results. Currently data analysis using ANN is done off-line. Stages of the prototype for automation is shown in Figure 4.4. The prototype takes data from LIBS measurements and performs on-line

analysis. Each stage is discussed in detail in the following sections.

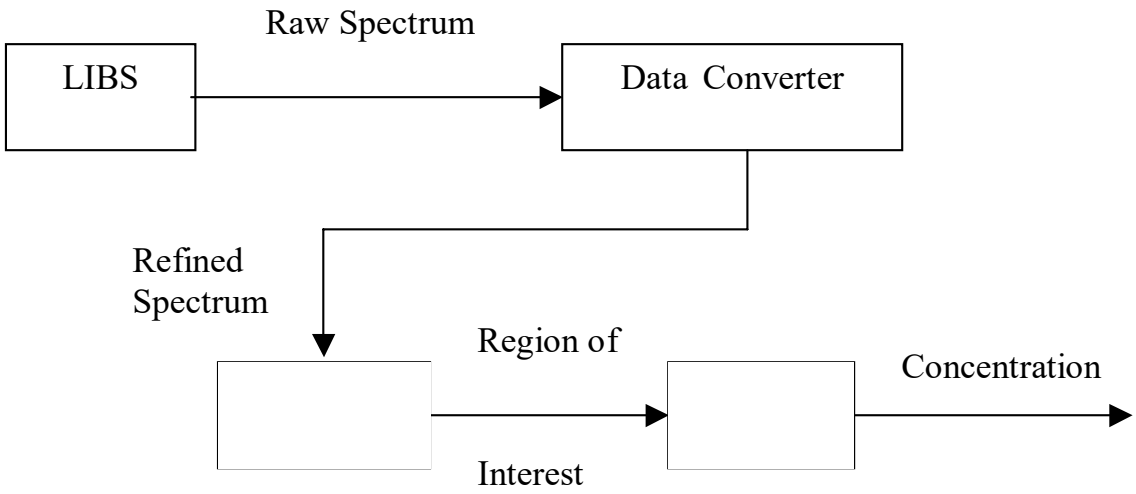

Figure 4.4 Prototype for automation

4.2.1 Data conversion

Spectral fles obtained from the LIBS experiment set-up are in binary format with .spe extension. All WinSpec fles (version 1.6) begin with 4100-byte header, followed by the raw signal data. Format of a spectral fle is shown in Figure 4.5. Each fle consists of 50 frames (spectra), with each frame containing 1024 data values. Spectral data is extracted from each fle and is written into text fles.

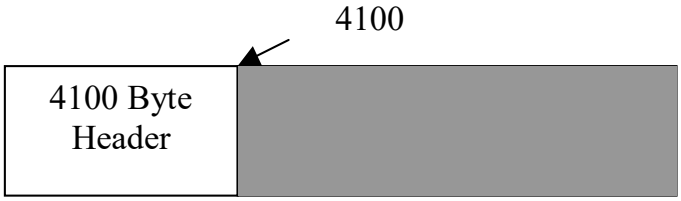

Figure 4.5 Spectrum fle format

During off-line analysis Winspec software was used to convert data from binary to ASCII manually. However, a software interface was developed for on-line conversion of raw data fles into ASCII fles. ASCII fle format is shown in Figure 4.6. This converted data fle forms the primary input for the artifcial neural network in the automated prototype. The frst column contains the wavelength and the second column contains corresponding intensity.

4.2.2 Data preprocessing

The ASCII fle is further preprocessed to improve learning effcienc y of the ANN and to get better results. Procedures like standardization and data extractions that were performed on the ASCII data fles are the same as discussed in 4.1.2.1 and 4.1.2.2. However, preprocessing was done right after data conversion automatically in the prototype.

304.99202	311
305.1246	393
305.202	411
....	….
.....	….
....	….
....	….
326.01652	-36
326.05801	-83

Figure 4.6 ASCII data fle format

4.2.3 Selection of executable artifcial neural network models

Neural networks developed for each specifc element and concentration, and a common network trained for all elements and concentrations, are included in the prototype. The prototype uses a two - step approach to select an appropriate neural network:

1. Determine the region of concentration (high/low) for a given data set using the common network.
2. Based on the region from step 1, select a specifc network for more accurate concentration.

To support different levels of user expertise, both manual and automatic modes of operation are provided in the prototype. According to the selection of the mode and the selection of element of interest, respective network selection is determined. In the auto mode steps 1 and 2 of the network selection process are performed automatically, without

user intervention. However, in the manual mode, after step 1 of the selection process, the system waits for the user to select a specifc network.

4.2.4 User Interface

User interaction with the system is described in this section. The main page of this GUI is shown in Figure 4.7. On selecting either Auto/Manual modes, the system displays one of the windows shown in Figure 4.8 and Figure 4.9. The user may select the element of interest and corresponding spectrum fle from this window.

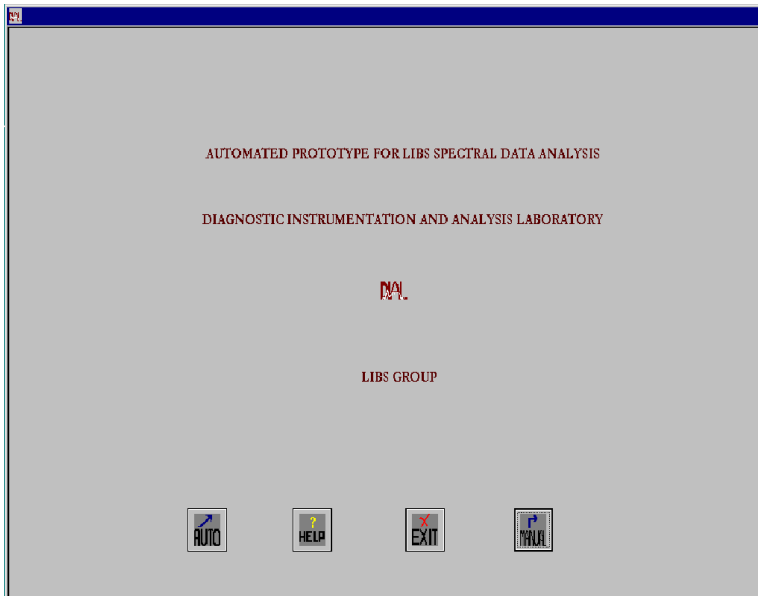

Figure 4.7 Main user interface

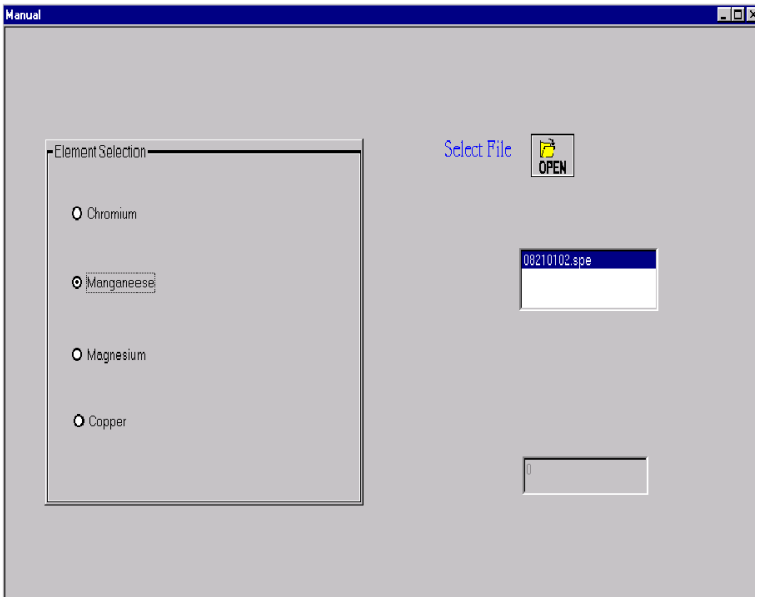

Figure 4.8 Auto mode

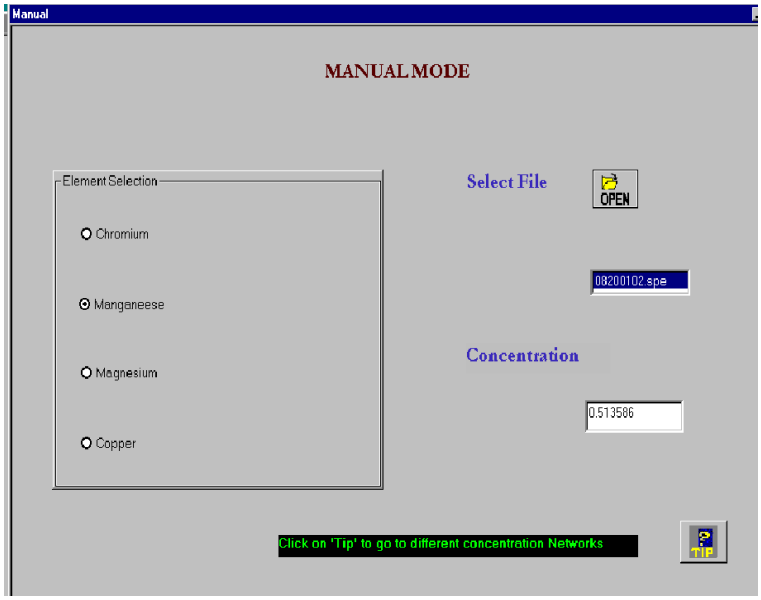

Figure 4.9 Manual mode

4.2.5 Experiments on Effort Analysis

Data fles for each element were analyzed manually. We have considered the elements Magnesium for 1.450 and 0.518 wt(%), Cr for 0.044 wt(%), Mn for 0.079 wt(%) and Cu for 1.222 wt(%). The manual mode of analysis consists of, converting the raw spectrum fle which is in binary format into ASCII format using the Winspec software. This conversion gives us 50 different fles. The next step is to put all the 50 fles into one excel sheet, extract the data sets in the given region of interest. These data sets forms the inputs to the neural network. Time taken for this manual analysis is measured using a stop watch. Factors that effect the manual analysis are discussed in Chapter 5. Files which are considered for manual analysis are analyzed automatically by the prototype. In the auto mode, after the selection of the element for analysis and the corresponding spectrum fle, all the above mentioned steps in manual process is carried out automatically. The experimental results are discussed in Chapter 5.

CHAPTER V

RESULTS AND ANALYSIS

This chapter analyses in detail the experimental results obtained from the steps discussed in Chapter 4. Section 5.1 provides details of the factors that are used for the analysis of the calibration results and the neural network predictions, in order to prove the frst hypothesis. Section 5.2 analyses the times taken for the manual operation and the auto operation for neural network predictions, to prove the second hypothesis.

5.1 Comparison of Data Analysis Techniques

LIBS spectra of different alloy elements were recorded. Analyte lines of Cr(359.349 nm), Mg (383.829 nm), Mn (404.16 nm) and Cu (327.45 nm) were used for the analysis of these elements in Al alloy samples. Data was analyzed using traditional calibration curve method and also using neural networks. We have used relative accuracy and precision as the criteria to compare the results obtained from the two. Relative accuracy and relative precision are defned in equations 5.1 and 5.2.

$$RelativeAccuracy = \frac{PredictedConcentration - ActualConcentration}{ActualConcentration} \tag{5.1}$$

$$RelativePrecision = \frac{StandardDeviation}{AveragePrediction} \tag{5.2}$$

The results of data analysis using the neural networks and the calibration method for Cr (359.349 nm) line are shown in Table 5.1.

Table 5.1 Comparison of neural predictions with the calibration curve analysis for Cr

Chemical	Neural Network			Calibration		
Analysis	Prediction	Rel.	Rel.	Prediction	Rel.	Rel.
(%)	(%)	Accry.(%)	Prec.(%)	(%)	Accry.(%)	Prec.(%)
0.0	0.009	—	24.784	0.094	—	26.878
0.040	0.037	7.500	16.153	0.062	54.075	16.583
0.042	0.043	2.381	4.651	0.042	0.043	16.4573
0.044	0.043	2.273	18.047	0.029	34.100	18.9606
0.060	0.059	1.667	3.559	0.029	50.813	22.251
0.173	0.175	1.156	12.881	0.236	36.636	17.445
0.275	0.280	1.818	8.065	0.268	2.473	14.172
0.473	0.466	1.479	0.566	0.316	33.102	19.705

Column 1 of the table contains concentrations from chemical analysis (actual concentrations) of the samples. Results from neural networks are given in columns 2 to 4 and the traditional calibration results are given in columns 5 to 7. The concentrations shown in the table are wt(%) concentrations. The table shows the average of neural networks output values, relative accuracy and relative precision of the predicted values along with the values from calculations using calibration curve. The performances of the two methods are more evident in the graph shown in Figure 5.1.

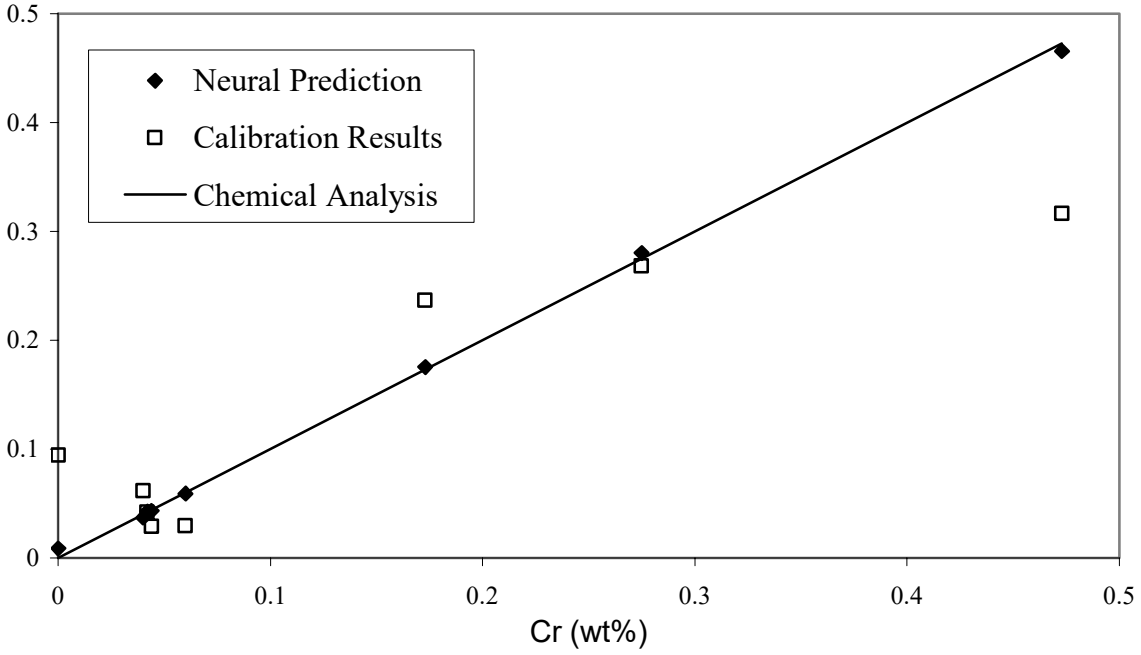

Figure 5.1 Variation of neural and calibration results from chemical analysis for Cr

The straight line represents the actual concentrations as determined by the chemical analysis. Overall, the values from the neural network are closer to the actual concentrations. Similar plots for Mg, Mn, and Cu are given in Figure 5.2 - Figure 5.4.

It is clear from the fgures that the results obtained from ANN are closer to the results obtained from the elemental analysis as compared with the calibration analysis. This observation shows that prediction of elemental concentration in unknown material by ANN is suitable even for a material having a range of elemental concentrations from 0-5%. It is evident from the tables and plots that overall neural network predictions of element concentrations are as good as or better than the values obtained through analytical methods. Neural networks predicted concentration values are closer to those determined through

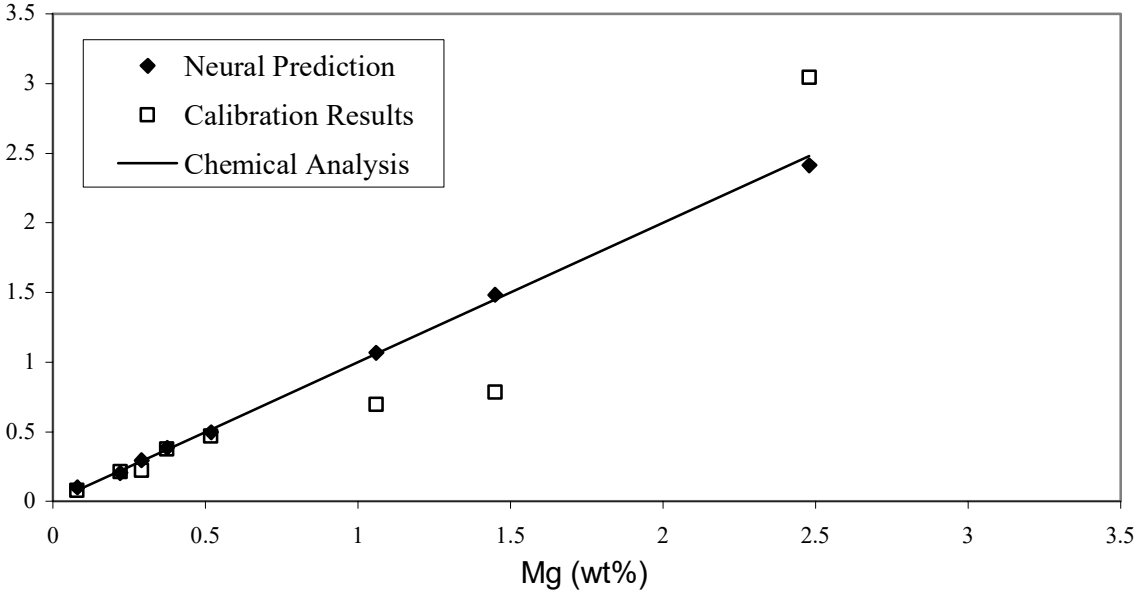

Figure 5.2 Variation of neural and calibration results from chemical analysis for Mg

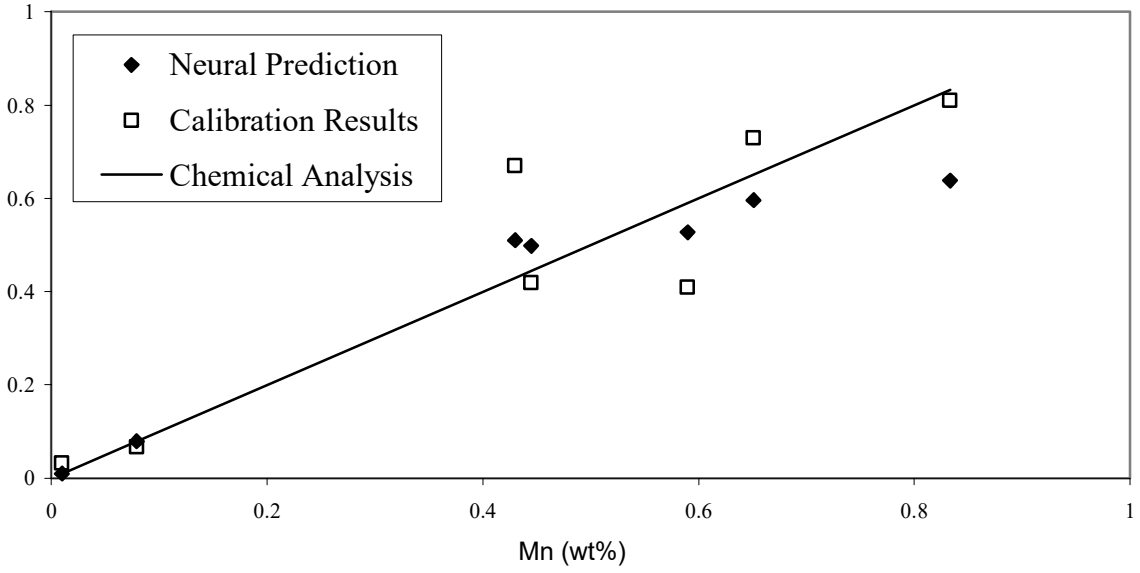

Figure 5.3 Variation of neural and calibration results from chemical analysis for Mn

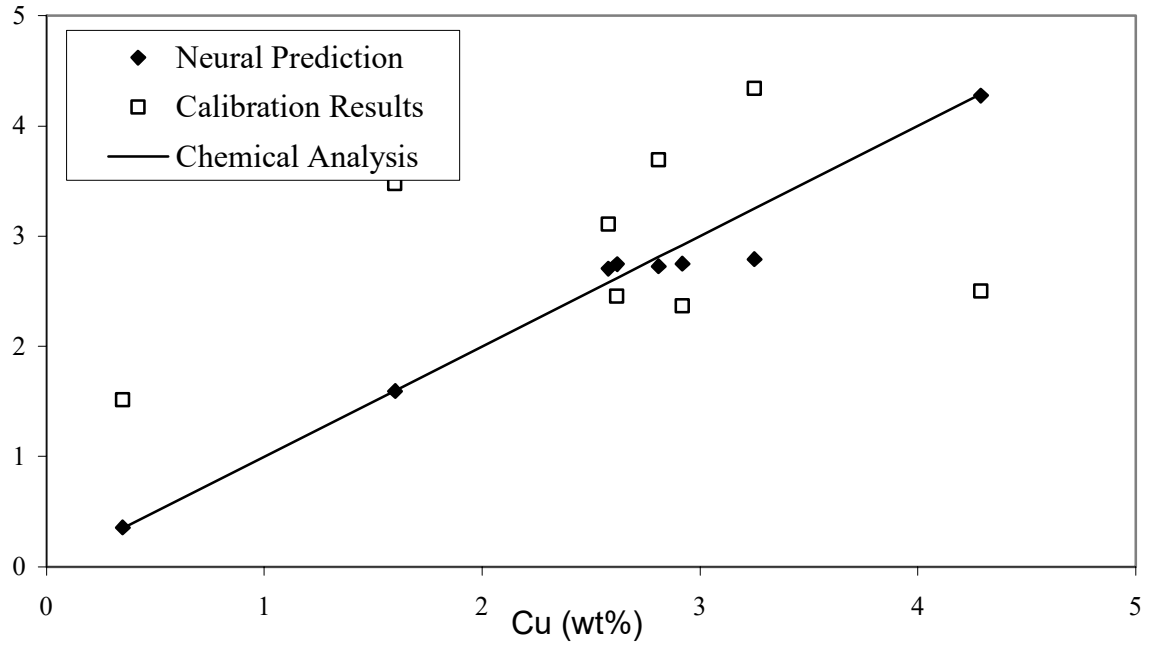

Figure 5.4 Variation of neural and calibration results from chemical analysis for Cu

chemical analysis than calibration method in 75% of the cases. This trend is consistent with the values for other elements also. From the absolute concentration plots in Figure 5.1 through Figure 5.4, one may notice that only two neural network predicted points deviates more than those estimated otherwise. All these indicate superior performance of artifcial neural networks in predicting elemental concentrations.

Since Neural Networks learn from examples, we need to create networks that can deal with general situations such as fuctuations in experimental conditions. Such a neural network model makes good predictions for different elements without the need to make a new network each time. A limiting factor in this case is the need to expose the network with

data distributed across the range of fuctuation of interest. However, this would eliminate the need to use separate calibration curves depending on the experimental conditions.

5.2 Effort Analysis

Spectral data analysis using ANN can be done off-line. The system is automated to perform on-line analysis of the spectral data. In this section we analyze the results obtained from both the versions. We compare both the process and prove that automation minimizes the time required for the data analysis using ANN.

The manual mode of analysis consists of converting the raw spectral fle which is in binary format into ASCII format using the Winspec software. This conversion produces 50 different fles. The next step is to put these 50 fles into one excel sheet to extract the data sets in the given region of interest. These data sets form the inputs to the neural network. When the above outlined process is done manually, this accounts for much of the time for the elemental analysis. To optimize this time in computation, we have automated the process. Once the user selects the fle, all the above steps of the manual process are carried out automatically. Table 5.2 gives the comparitive times in both the modes of operation.

It can be seen from the table that by automating the system, the system performance has been improved exceptionally. There are few factors which effect the manual mode of operation.

1. Human Work Time

   Much of the manual time can be attributed to the person incharge of the work.

Table 5.2 Comparison of automated and manual modes of operation

Element Concentration wt(%)	Manual Time(sec)	Automated Time(sec)	Time Saving(%)
Mg - 1.450	1887.60	12.00	99.34
Mg - 0.518	1401.60	15.00	98.93
Cr - 0.044	1200.00	6.00	99.50
Mn - 0.079	1956.51	18.00	99.10
Cu - 1.222	2106.00	21.00	99.00

- Usage of the Excel Software
  If a chemist trying to analyze the spectral data using neural networks is fairly new to the Excel software, then there is high possibility that he takes hours and hours trying to formatting the data using Excel sheets. The user should be profcient with few of the tricks in Excel which makes the software more time effcient.
- Mood of the User
  If the User, is in a really bad mood, then he fnds it hard to concentrate on data formatting and keeping track of the fles converted and included in the Excel sheet. This may reduce the data sets available for the neural network, thereby resulting in a prediction of the concentration which is not accurate and precise.

2. Urgency

   If the analyst does not feel the urgency to analyze the spectral data, then he/she may take their own time for the manual process of data conversion and formatting.

3. Noise Level in the fle

   If the noise level is high in a fle, then the ASCII conversion takes more time.

None of the user- involved factors will effect the system time with the automated version. The only factor which effects the time is the noise level in the fle. The program written to convert the binary fle into ASCII, takes few seconds to account for the noise. Rather than this there is no other factor which hampers the automated system. From the

Table 5.2, the maximum time the manual mode of operation takes is 2106.00 seconds and the minimum time is 1200.00 seconds. The maximum time accounts for the noise level in the fle and the leisure at which the user worked on the formatting and data conversion. By automating, the maximum time taken is 21.00 seconds and minimum being 6.00 seconds. The maximum % time saving was calculated using the formula:

$$\%TimeSaving = \frac{ManualTime - AutomatedTime}{ManualTime} * 100 \tag{5.3}$$

Table 5.2 shows that the % time saving ranges from 98.93 to 99.50. This vast difference in the system time can be seen in the bar chart given in Figure 5.5. X- axis has four sets of elements for different concentration values, and the Y-axis the time in seconds. One can see the vast variation in the time taken for both the automated and manual mode of operations. Hence the following analysis leads to the fact that the system time has been optimized due to the automation of the system; thereby validating the second hypothesis.

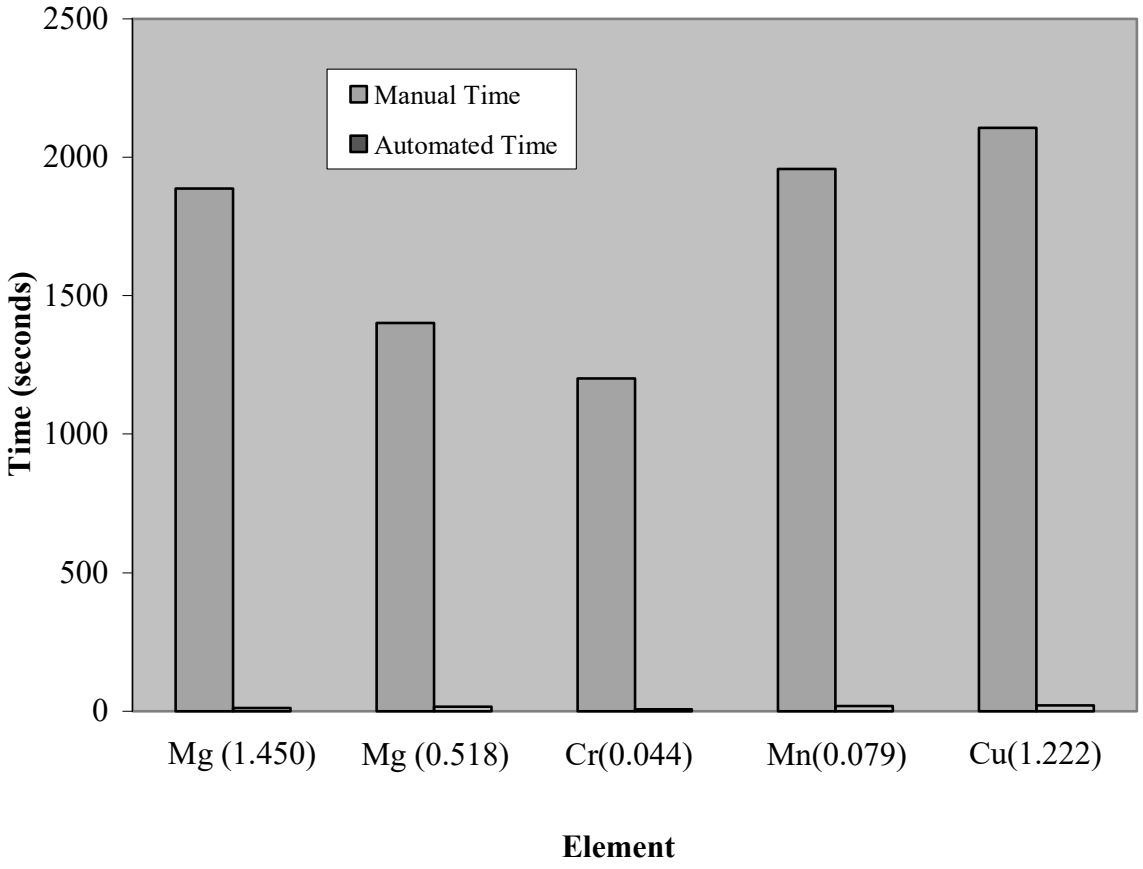

Figure 5.5 Chart showing the manual and automated Effort

CHAPTER VI

CONCLUSIONS AND FUTUREWORK

This concluding chapter synthesizes all the chapters in the body of this thesis. The stated hypotheses for this work are:

1. Elemental concentrations determined from spectral data using artifcial neural networks are atleast as good as those obtained using traditional statistical calibration methods.
2. Operator assisstance needed to acquire and analyze spectral data may be minimized through automation.

To prove the above stated hypotheses, experiments were conducted at the LIBS laboratory at the Diagnostic Intrumentation and Analysis Laboratory, Mississippi State University. LIBS instrument is used to record the spectra of the element of interest in the given sample. LIBS spectra of seven different samples were recorded. The analyte lines of Cr(359.349 nm), Mg (383.829 nm), Mn (404.16 nm) and Cu (327.45 nm) were used for the analysis of these elements in the Al alloy samples. Two data analysis techniques, traditional calibration method and neural network analysis were performed on the spectral data to determine the elemental concentration.

The results of data analysis using the neural networks and the calibration method for Cr (359.349 nm) line are shown in Table 5.1. Results of the analysis using ANN were compared against traditional analysis for relative accuracy and precision. The performances

of the two methods are more evident in the graphs shown in Figure 5.1 - Figure 5.4. It is evident from the table and plots that overall neural network predictions of element concentrations are as good as or better than the values obtained through analytical methods. Neural networks predicted concentration values are closer to those determined through chemical analysis than calibration method in 75% of the cases. From these results, we conclude that artifcial neural networks are capable of predicting values at least as good as the traditional method, validating the hypothesis.

Further, a prototype for automated analysis of LIBS data using artifcial neural networks was developed. The manual mode of analysis consists of, converting the raw spectrum fle which is in binary format into ASCII format using the Winspec software. This conversion produces 50 different fles. The next step is to put all the 50 fles into one Excel sheet, extract the data sets in the given region of interest and then input to the neural network. Time taken for the manual process steps accounts for much of the time for the elemental analysis. To optimize this time in computation, we have automated the process. Once the user selects the fle, the above mentioned manual process is carried out automatically. Table 5.2 gives the comparitive times in both the modes of operation. The maximum time the manual mode of operation takes is 2106.00 seconds and the minimum time is 1200.00 seconds. It is seen that the % time saving ranges from 98.93 to 99.50. It can be seen from the table that by automating the system, the system performance has been improved exceptionally. The prototype behaved as expected and optimized the system time compared to manual operation. Thus the proposed hypotheses that operator assisstance

needed to acquire and analyze spectral data may be minimized through automation, was validated.

6.1 Contribution

The research results will provide the spectroscopy community, a unique time-effcient method for analyzing the LIBS spectral data and if adapted by them, to determine the concentrations of the elements of interest.

6.2 For Further Research

In the current work, for each element in the given region different neural networks were developed based on the range of the element concentration. Element concentrations more than ’1’ were labeled as high, and those less than ’1’ as low. This is an arbitrary criteria selected. If the concentrations fall in the boundaries, then the average of the high concentration network prediction and the low concentration network prediction is taken as the fnal element concentration. But, in future we would like to come up with a more reasonable and analytical way of sorting the boundary values. Also, we would like to work with one neural networks for all ranges of elemental concentrations rather than having two different nets based on concentration ranges.

The current automated software uses simulation of real-time LIBS data acquisition. A future extension for this can be developing a client-server environment for online data

acquisition and analysis. This would allow a user at any location to access the experimental data measured at DIAL and do the analysis using neural network models.

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