

**Determination of chromic acid and sodium dichromate
in a concentrated electrolytic solution with the aid of
Artificial Neural Networks**

by

Mr. Alfred Hlabana Seepe

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of

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Department of Chemistry
University of Pretoria
Pretoria

Supervisor: Professor Ignacy Cukrowski

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Declaration

I declare that this dissertation is my own work. It is being submitted for the partial fulfilment of the degree of Master of Science in the faculty of Natural and Agricultural Sciences at the University of Pretoria. It has not been submitted before for any degree or examination at any other University.

Signature of candidate

_____ Day of _____ Year _____

Abstract

The aim of this work is to quantify the concentration of chromic acid (CA) in a saturated solution of chromium trioxide and sodium dichromate using Artificial Neural Networks (ANNs).

A set of titration curves was obtained by automated acid-base titration according to a factorial experimental design that was developed for this purpose. These titration curves were divided into three subsets, a learning, training and test set for use by ANNs. Once trained, ANNs have the ability to recognize, generalize and relate the input to a particular output. Concentration of chromic acid (CA), total chromium(VI) and/or dichromate was used as the outputs and titration curves as the inputs to ANNs. Our aim here was to establish whether ANNs would be able to predict the concentration of chromic acid with an absolute error below 1%. For real world problem, the neural networks are only given the inputs and are expected to produce reasonable outputs corresponding to that inputs without any prior 'knowledge' about theory involved – here, no interpretation of titration curves was performed by ANNs. The test set of data that was not used for learning process, was used to validate the performance of the neural networks, to verify whether the ANNs learned the input-output patterns properly and how well trained ANNs were able to predict the concentrations of chromic acid, dichromate and total chromium. A number of ANNs models have been considered by varying the number of neurons in the hidden layer and parameters related to the learning process. It has been shown that ANNs can predict the concentration of chromic acid with required accuracy. A number of factors that affect the performance of the neural networks, such as the number of points in a titration curve, number of test points and their distribution within the training set, has been investigated. This work demonstrates that ANNs can be used for online monitoring of an electrolytic industrial process to manufacture chromic acid.

Keywords: chromic acid, sodium dichromate, Artificial Neural Networks, electrolytic process.

Dedication

To my grandparents and parents



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List of Abbreviations and Symbols

AI	Artificial Intelligence
ANNs	Artificial Neural Networks
aq	Aqueous solution
b_j	Bias from neuron j
CA	Chromic acid (H_2CrO_4 or CrO_3)
CISA	Chrome International South Africa
cm^{-1}	per centimetre (wave number)
^{13}C NMR	carbon 13 nuclear magnetic resonance
$^{\circ}C$	Degree Celsius
Cr	Chromium
DC	Dichromate
DNA	De-ribose Nucleic Acid
e^{-}	Elementary charge of an electron ($1.6021764 \times 10^{-19}$ coulombs)
EP	End-point of titration curve
EP ₁	First end-point in the titration of chromic acid against NaOH solution.
EP ₂	Second end-point in the titration of chromic acid against NaOH solution.
EP ₃	End-point in the titration of dichromate solution against NaOH solution.
EP ₄	Second end-point in the titration of a solution mixture of chromic acid and dichromate against NaOH solution.
ES	Expert system

FORTRAN A word derives from IBM mathematical **Formula Translating** systems. It is a general-purpose, procedure, imperative programming languages that is especially suited for numerical computation.

F.W. Formula Weight

g gram

gmol⁻¹ gram per mole

g/L gram per litre

g gas phase

GC-MS Gas chromatography-mass spectrometry

GSH Glutathione

i Number of neurons

ICP Inductively coupled plasma

IR Infrared spectrum

Ka Acid dissociation constant

KHP Potassium Hydrogen Phthalate

LISP The word LISP derives from LISt processing language. It was originally created as a practical mathematical notation for computer programs based on lambda calculus and it became the favoured programming languages for artificial intelligence.

LOOPs Lisp Object- Oriented Programming System.

M Molar concentration

min Minute

mL Millilitre

mM Millimolar concentration

MOLGEN Molecular Structure Generator is devoted to generating all structures (connectivity isomers, constitutions) that correspond to a given molecular formula, with optional further restrictions, e.g. presence or absence of particular substructures.

molL^{-1} Concentration in mole per litre

mV MilliVolts

NaDC Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$)

pH Negative logarithm of proton concentration

pH_{max} Maximum negative logarithm of proton concentration

pKa Negative logarithm of the acid dissociation constant

PROLOG Is a logic programming language. The name prolog was chosen by Philippe Roussel as an abbreviation for programming in logic. It is a general purpose language often associated with artificial intelligence and computational linguistics.

Redox Reduction-Oxidation

RMS Relative Mean Square error

s second

STDEV Standard Deviation

UV-vis Ultra violet visible absorption spectra

V Volume

W_{ij} Weight connection between the input neuron i and hidden neuron j

WinNNs Neural networks software for windows.

X_i input node

$Y_{k, \ell}$ Weight connection between the hidden neuron k and output ℓ .

Y_i Weight sum of all inputs.



% Percentage unit

Σ Summation

CHAPTER 1

1. INTRODUCTION

1.1 Analysis and control of the industrial electrolytic process

During the industrial electrolytic process used to produce chromic acid, sodium dichromate solution is electrolytically converted into chromic acid in two compartment electrolytic cells arranged in series; the process will be described in detail in the following section. Traditionally, chromic acid was produced by the reaction of sodium dichromate with concentrated sulphuric acid either via wet or melt process. Concentrated sulphuric acid was combined with sodium dichromate crystals during melt process. In the wet process, sulphuric acid was combined with concentrated aqueous sodium dichromate solution.

Electrolytic process depends on many parameters that need to be controlled and monitored in order to maintain and to optimise the performance of the process. Among other things, the process was maintained or controlled in a traditional way of taking a sample from the operating plant and transporting it to the analytical laboratory, which is often far from the operating plant. During transportation, the composition of the sample might be altered, for example, temperature of the sample might be changed. The sample then undergoes a series of treatments; it is weighed, diluted and titrated automatically with a sodium hydroxide solution. Titration data is analysed accordingly before it can be sent to the relevant personnel at the operating plant. To mention few, these results include the concentration of chromic acid, total chromium(VI) and dichromate concentration.

Whenever is required, the information (analysis) is send to the quality control personnel and used for corrective purpose in the process. Based on the analysis, the concentration of the feed solution or electrolyte solution at some stages of the process might be increased by adding more dichromate, or

might be reduced by dilution with water. The concentrations of chromic acid and alkali metal ions in a solution leaving the anode compartment may be adjusted to various values, or levels, by varying the quantity of the feed solution introduced into the cell. The temperature of the cells might also be changed. The overall idea behind corrective action is to improve the quality of the product (chromic acid), to optimise the performance and the capacity of the process and also to reduce emission of mist (waste) into the workplace environment.

Unfortunately, the time taken during sampling, transportation, sample treatment, data analysis and reporting back to the operating personnel is usually beyond the time frame required for corrective action to take place, since the production process was in a continuous state. Delayed time monitoring has a negative impact on the quality of the product and may lead to ineffective production process. There is a need for a quick on-line or in-line monitoring system that will help to monitor the conversion of sodium dichromate solution into chromic acid in the industrial electrolytic process.

1.2 Electrolysis of sodium dichromate in the production of chromic acid

Electrolysis may be referred to as separation of substances by electricity. In chemistry and manufacturing industries it is used for the production of compounds and to separate compounds by passing electric current through them. Usually a substance to be electrolysed should be in solution or in a molten form, but electrolysis can also takes place in gases [1].

Chromic acid (H_2CrO_4) is now produced by electrolysis of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) solution in a two-compartmental cell [2, 3]. The lining of the cell is constructed from a suitable material that is resistant to corrosive action of chromium(VI) solutions involved. These materials include glass, stoneware and tantalum [4]. In a multistage electrolytic process the cells are arranged in series and may be referred to as stages. This kind of arrangement is shown in Figure 1.1.

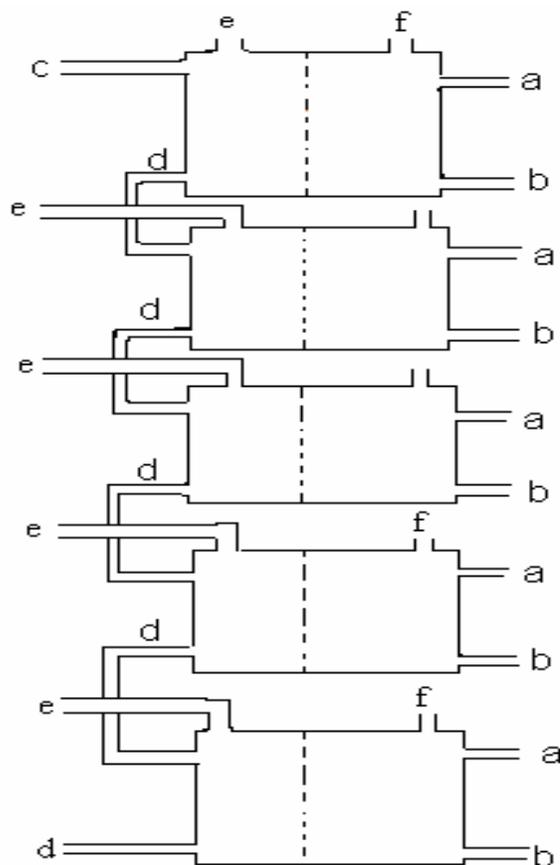


Figure 1.1 Representation of electrolytic cells arranged in series. a – inlet for catholyte feed, b – outlet for catholyte product, c – inlet for anolyte feed, d – communicating tube (for the transport of electrolyte from cell to cell), e – outlet for oxygen gas, f – outlet for hydrogen gas.

Each cell consists of anode and cathode compartments containing anode and cathode electrodes, respectively. All electrodes are connected to a suitable voltage and current source. Anode electrode might be made of electrocatalytically active material such as titanium structure coated with a layer of titanium oxide, tantalum oxide or iridium oxide. It must be resistant to acidic chromium(VI) solution and to electrolytically produced oxygen gas. There is a chance that oxygen might react with the anode electrode instead of being released as a gas. Cathode electrode can be made out of a material resistant to sodium hydroxide solution attack. This includes stainless steel and nickel.

The two compartments are separated, or divided, by a hydraulically semi-permeable cation-exchange membrane. In most cases, the membrane is produced from acid resistant filter papers, ceramics and from co-polymers of fluorocarbon and fluorinated sulfonyl vinyl ether [5]. During cell operation, this membrane facilitates the movement of sodium ions into the cathode compartment. It does not allow the transport of hydroxyl ions, dichromate ions, or any polyvalent anions, that might be present in the solution.

A multistage electrolytic process is designed in such a way that each cell is connected to the next cell via a tube that carries electrolytes (chromium) solution to a following cell. This tube is found at the anode compartment of the cells. In the cathode compartment of each cell there is an inlet which is used for catholyte solution delivery. It can also be connected from cell to cell. The outlets are used for the collection of the end-products of the process. In the anode compartment, chromium solution is withdrawn and another outlet is used to collect oxygen gas. Hydrogen gas and sodium hydroxide solution are collected from the cathode compartment using different outlets. Gases generated during the process are collected or discharged into the atmosphere. Alternatively, they can be used in the digestion of chrome ore during the production of dichromate. Hydrogen gas is useful for the production of ammonia fertilizers via Haber process and for converting petroleum sources to lighter fractions via hydrocracking.

The number of cells in the electrolytic process may be varied. It depends mostly on the concentration of chromic acid solution required and on the capacity of the electrolytic process.

The process starts with the introduction of sodium dichromate solution in the anode compartment of the first cell through the sodium dichromate feed inlet. Water is introduced into the cathode compartment containing sodium hydroxide solution; via the feed inlet. These inlets can be seen in Figure 1.2. Electrolysis takes place as soon as voltage is applied across the terminals of the electrodes. During electrolysis, reduction takes place in the cathode

compartment of the cell and results in the production of hydrogen gas and hydroxide ions, equation 1.1.



Oxidation takes place in the anode compartment, generating oxygen gas and protons [6], equation 1.2.



Sodium ions in the anode compartment migrate through hydraulically semi-permeable cation-exchange membrane under the influence of an electric field, towards the cathode compartment where sodium hydroxide solution is formed. Dichromate ions remain behind and are neutralised by hydrogen ions formed in the anode compartment. In summary, the process comes down to the substitution of sodium ions in sodium dichromate solution by hydrogen ions to form chromic acid.



In fact, hydrogen ions substitute sodium ions from sodium dichromate solution and form chromic acid. They combine with bichromate ($HCrO_4^-$) ions formed when sodium dichromate dissolves in water at low pH, see equations 1.3 to 1.4.

The electrolyte solution in the anode compartment is always a mixture of sodium dichromate and chromic acid solution. The amount of chromium as dichromate is greater than chromium from chromic acid. This solution is then allowed to flow to the anode compartment of the next cell where it is processed in the same fashion. The process continues until the amount of

chromium(VI) as chromic acid exceeds chromium as dichromate at a particular stage of the process.

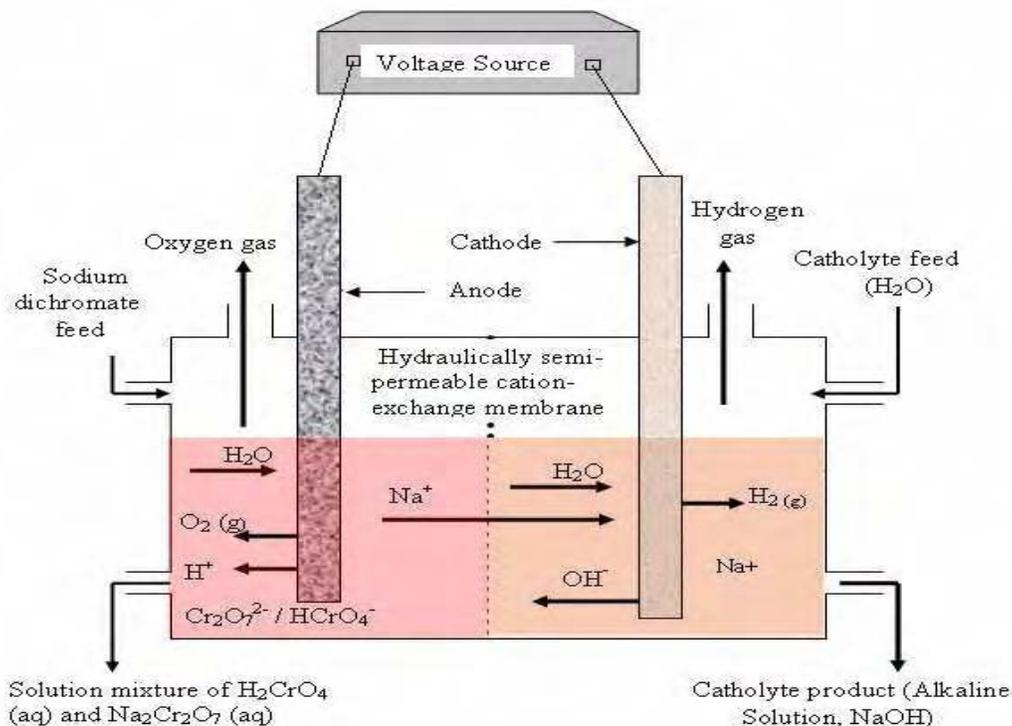


Figure 1.2 A cell used in multistage electrolytic production of chromic acid.

In stage eight of multistage electrolytic process, more sodium dichromate solution has been converted to chromic acid solution. This stage is considered to be the last stage of the process and yields concentrated chromic acid solution. During electrolysis, sodium dichromate solution cannot be converted completely into chromic acid.

For the production of chromic acid crystals (CrO_3), the solution in the anode compartment of the last stage of the process is concentrated by evaporation so that crystallisation takes place at a temperature range from 60 to 185°C. The crystallised chromic acid is then separated from the mother liquor by centrifugation. The mother liquor is then diluted with water and returned to a suitable electrolytic stage. Chromic acid crystals are dried by heating with hot air that is free from reducing agents. The crystals are then cooled and packed for sale.

Electrolytic process requires maintaining temperature and pH of electrolyte solution compartment. This helps to prevent the formation of the precipitates on the membrane separating the cathode and anode compartments of the cells. Temperature in the range of 50 to 90°C is recommended. Sodium dichromate solution introduced in the process, as a feed, usually contains impurities of polyvalent cations. As a result of pH and temperature change, insoluble hydroxides and salts of those cations form and this leads to destruction of the membrane separating cell compartments [7]. The down-time required for the regeneration or replacement of the membrane and or the electrodes causes unwanted disturbances to the process and this affects plant capacity or production.

1.3 Chromium and speciation of chromium(VI) in aqueous solution

Chromium does not occur by itself in nature but always in compounds/complexes. It occurs in the oxidation states 0, 2, 3, 4, 5 and 6. Trivalent and hexavalent oxidation states of chromium are most stable [8]. Chromium forms several commercially valuable oxygen containing compounds, the most important of which are chromium trioxide (CrO_3) and dichromate [9]. Both chromic acid and dichromate are in hexavalent form of chromium. It is due to the excellent properties of chromium that lead to the application of chromium compounds in the industries. For example:

- Manufacturing – chromium compounds are used in the production of chemicals, inks, pigments, glass, ceramics and in the production of glues [10, 11]. Chromated copper arsenate is manufactured from chromic acid and is used as a wood preservative [12].
- Leather industries – chromium compounds are applied in cloth dyeing, rubber and in leather tanning [13].
- Electroplating industries – chromium is used as decorative element, corrosion inhibitor in iron, in steel and nonferrous alloys to improve their hardenability [14].

- Organic laboratory – chromic acid and dichromate are very powerful oxidizing agents. They are widely used to oxidize primary or secondary alcohols to the corresponding aldehydes and ketones. The solution of chromic acid in sulphuric acid was used in the chemical laboratories to clean glassware. This application has declined because chromic acid leaves residues that can interfere with other applications, for example, in the stripping voltammetric determination of chromium.

Chromic acid is sometimes called chromium trioxide, particularly in the electroplating industries [15, 16]. Chromium trioxide is an odorless red deliquescent solid; when dissolved in water or in sulphuric acid, chromic acid is formed. Chromic acid also refers to a collection of compounds (species) generated by the acidification of solutions containing chromate and dichromate ions [17, 18]. Thus the species generated by the acidification of chromate and dichromate are dihydrogen chromate and dihydrogen dichromate, therefore the formula of chromic acid is either H_2CrO_4 or $H_2Cr_2O_7$.

The chemical nature of chromic acid has been a subject of investigation in the literature. The conductivity determination experiments of chromic acid conducted by Walden [19] indicated that chromic acid exists in solution as H_2CrO_4 and it dissociates as follows:



Furthermore, an experiment by Britton showed that the salts formed, when chromic acid solution is titrated against sodium hydroxide solution, contain sodium and chromium in the atomic ratios 1:1 and 2:1. These ratios correspond closely to the formulae $NaHCrO_4$ and Na_2CrO_4 [20].

On the other hand, the results from a freezing point experiment, on a chromic acid solution conducted by Ostwald, corresponded very closely to the existence of dichromic acid in solution. Costa came to the same conclusion

that in aqueous solution chromic acid contains the acid dihydrogen dichromate ($H_2Cr_2O_7$) and not dihydrogen chromate (H_2CrO_4) [19, 21].

If chromic acid is considered to exist as $H_2Cr_2O_7$, it will dissociate as follows:



The existence of chromic acid in solution as dihydrogen dichromate has been accepted by many investigators, but the existence of chromic acid in aqueous solution has not been considered settled. In the study of the constitution of chromic acid in aqueous solution both forms have to be taken into account.

Regardless of the true chemical formula of chromic acid in aqueous solution, chromic acid is a polyprotic acid. Its titration with sodium hydroxide solution yields two well defined end-points. The end-point of a titration is determined from a rapid change in pH of the solution with addition of sodium hydroxide solution.

Knowledge of chromium speciation is important for a number of reasons. The interest in chromium speciation originates from widespread use of chromium metal in the industries as already mentioned. Due to these industrial processes, large quantities of chromium compounds are discharged in liquid, solid and gaseous waste into the environment and if not treated can cause adverse effect on the environment and humans.

However, not all forms of chromium are harmful. Chromium(III) is considered to be responsible for the proper functioning of living organisms, but only in trace amount. It is involved in the control of glucose and lipid metabolism in mammals. In high concentration, chromium(III) has the ability of coordinating with various organic compounds, resulting in the inhibition of some metallo-enzyme systems [22]. Chromium(VI) is toxic, mutagenic and carcinogenic. It is responsible for lung disease, skin lesions and various forms of cancer among workers in chromium based industries.

The toxicity of chromium(VI) species depends on their ability to cross cell membrane and to react with various components of the cell. The uptake-reduction model [23] explains the general mechanism of chromium(VI) activity in the cellular and subcellular systems. According to this model, chromium(VI) transverse the cell membrane as chromate (CrO_4^{2-}) and bichromate (HCrO_4^-) ions, through pre-existing important inorganic anions (such as SO_4^{2-} and PO_4^{3-}) transport system. Cellular reductants, e.g. glutathione (GSH), ascorbic acid, hydrogen peroxide, flavin-enzymes, GSH reductase, aldehyde oxidase and others interact with chromium(VI), finally forming stable chromium(III) complexes with the cell components.

The interaction of chromium(VI) with DNA may result in chromium-DNA adducts formation and DNA strand breakage. In fact, chromium(VI) compounds do not interact directly with DNA because the genotoxic process takes place only in the presence of organic species which reduce the ion. Metabolites of chromium: chromium(V), chromium(IV) and chromium(III) and another by-products such as the free radicals are responsible for the interaction with DNA and thus for the genotoxicity.

The physicochemical properties of chromium(VI), e.g. pH-dependent equilibria, redox and coordination properties, play a key role in understanding the interaction of chromium(VI) in living systems [24]. In order to understand the toxicity properties of chromium(VI) and to implement or to develop methods of removing chromium from contaminated water and soil, knowledge of chromium speciation is required. Chromium speciation is also important in order to understand how sodium dichromate solution is converted into chromic acid in the industrial electrolytic process.

Speciation of chromium(VI) has been a subject of considerable discussion in the literature. In an aqueous solution, chromium(VI) exists in different chemical forms/species. Depending on the pH of the solution, chromium trioxide might exist in aqueous solution as chromic acid (H_2CrO_4), bichromate ion (HCrO_4^-) and chromate (CrO_4^{2-}) ions and as well as undissociated chromium trioxide molecules (equations 1.7 to 1.9).



Bichromate ions generated from chromic acid may be converted to dichromate or remain in the solution. If the concentration of chromic acid is higher, bichromate ions formed will be converted to dichromate by dehydration. In that case, the conversion of bichromate into dichromate does not depend on the pH of the solution. However, if chromium trioxide is considered to exist in a form of dichromic acid in aqueous solution, the following equilibria must be taken into account:



When a salt of chromate (either potassium chromate, sodium chromate or aluminium chromate) dissolves in water, hydrolysis reaction takes place as follows:



Furthermore, dichromate salts dissolve in water and give rise to bichromate ($HCrO_4^-$) and chromate (CrO_4^{2-}) ions depending on the pH of the solution. Dichromate ions become hydrated to a certain extent and form bichromate ion which dissociate into proton and chromate ion when the pH of the solution increases, equation 1.13 and 1.14.





The concentration of bichromate ion depends strictly on the concentration of dichromate solution and in very dilute solution the amount of bichromate ion should be greater than that of the dichromate ion.

By means of various experiments, such as freezing point, conductivity and solubility experiments, equilibrium constant of equation 1.13 was determined to be 0.013 [19]. The value found by glass electrode experiments of Neuss *et al* [25] was 0.023 and was close to the above reported value. Neuss estimated the first and second dissociation constant (K_a), of chromic acid (H_2CrO_4) as 0.18 ($pK_a = 0.74$) and 3.20×10^{-7} ($pK_a = 6.5$) at ionic strength of about 0.16. The pK_a values for the first and second dissociations of chromic acid were estimated as -0.54 and 5.8 , respectively [26].

There are differences in opinion about the existence of bichromate ion in aqueous chromium(VI) solutions. Raman spectroscopic study [27] of chromate solution failed to prove the existence of bichromate ion in dilute chromate and dichromate solutions. The concentration of bichromate ion was expected to increase with dilution of dichromate solution but there was no spectral line that would be reasonably assigned to bichromate ion under the condition where it was expected to be dominant. For that reason the authors concluded that only chromate and dichromate ions are present in detectable amount in chromate system. They proposed the following equilibrium:



For that reaction, the equilibrium constant was calculated as $\log K = 13.77$ at $20^\circ C$ in $0.8 M KNO_3$ solution. From a theoretical point of view, if the above equilibrium does exist, there is no need to question the existence of bichromate ions in such systems. For chromate (CrO_4^{2-}) ions to dimerize by elimination of water molecule, protonation should be the first step. The

concentration of chromium(VI) solution of about 200 mM applied in their study was too low for bichromate ion to exist in higher amount.

Michel and Cahay extended their study to concentrated acidic media and still bichromate ion was not detected. Moreover, they did not find any Raman peaks that might be assigned to chromic acid (H_2CrO_4) and hydrogen dichromate ions (HCr_2O_7^-). They suggested that no protonated species exist in chromate-dichromate system. Equilibrium constant of equation/reaction 1.15 was determined as $\log \beta_{22} = 14.85$ at 25°C and zero ionic strength. In very acidic solution, two other chromium species have been detected, namely trichromate ($\text{Cr}_3\text{O}_{10}^{2-}$) and tetrachromate ($\text{Cr}_4\text{O}_{13}^{2-}$) [28, 29]. Raman spectroscopy might lack sensitivity of distinguishing between dichromate, chromate and bichromate ions.

UV-vis spectroscopic investigations also suggested the absence of bichromate ion in chromate-dichromate solutions [30]. In that investigation, the spectra of chromate solution were recorded while the pH and total chromium(VI) concentrations were varied. It was observed that if the ionic strength of the solution is varied, the spectra were also changed slightly. The dominant form of chromium(VI) species depends on chromium concentration, pH of the solution media and the ionic strength. The presence of isosbestic points and the results from factor analysis (they showed only two elements in the diagonalised matrix) were used as a proof for the existence of only chromate and dichromate ions.

The appearance of isosbestic points may arise as a result of many complications and does not guarantee the existence of only two species. In the other study, there were no crossing points which would serve as a test for only two species when perchloric acid was added to a chromate solution [31]. The spectral changes were caused by the formation of chromic acid and it was found that there was no significant difference between the UV-vis absorption spectra of bichromate and dichromate ions.

The chances that bichromate and dichromate ions have more or less identical spectra are minimal. The only reason that might be given for that observation is the change in pH at which the spectra were reported and the concentration of chromium(VI) solution used.

Other evidence that supports the existence of bichromate was obtained from UV-vis spectroscopic study at high temperature [32]. The spectra of dichromate at various temperatures and pH were recorded and it was shown that spectra change with temperature cannot be due to dichromate ion or the formation of polychromate ions. The formation of dichromate ion is not favourable at higher temperatures. The formation of polychromate ions is favourable in more concentrated chromium(VI) solutions. The spectra were recorded under the conditions at which only bichromate and chromate ions were expected in reasonable quantities.

A Raman investigation study of Heyns *et al.* [33] also showed that bichromate is an important species in chromate-dichromate solutions. In that investigation, the Raman spectra of chromium(VI) solution were recorded while the pH of the solution was slowly decreased with addition of an acid. The intense peak observed in strongly alkaline solution becomes less intense and vanishes completely upon acidification of chromium(VI) solution, see Figure 1.3.

The peak at 844 cm^{-1} was associated to chromate ions vibrations. The peak at 899 cm^{-1} was assigned to either dichromate ion alone or to both bichromate and dichromate ions. The one at 1045 cm^{-1} was for NO_3^- . It is difficult to get direct spectra of bichromate ions. It was concluded that the Raman peak of bichromate and dichromate ions coincide. Raman investigation conducted by Palmer *et al.*, at temperatures up to 245°C where bichromate ion was predicted to be dominant, also did not reveal exact bichromate ion band and then these authors suggested that the Raman symmetric stretching mode of bichromate may be coincident with the stretching mode of dichromate.

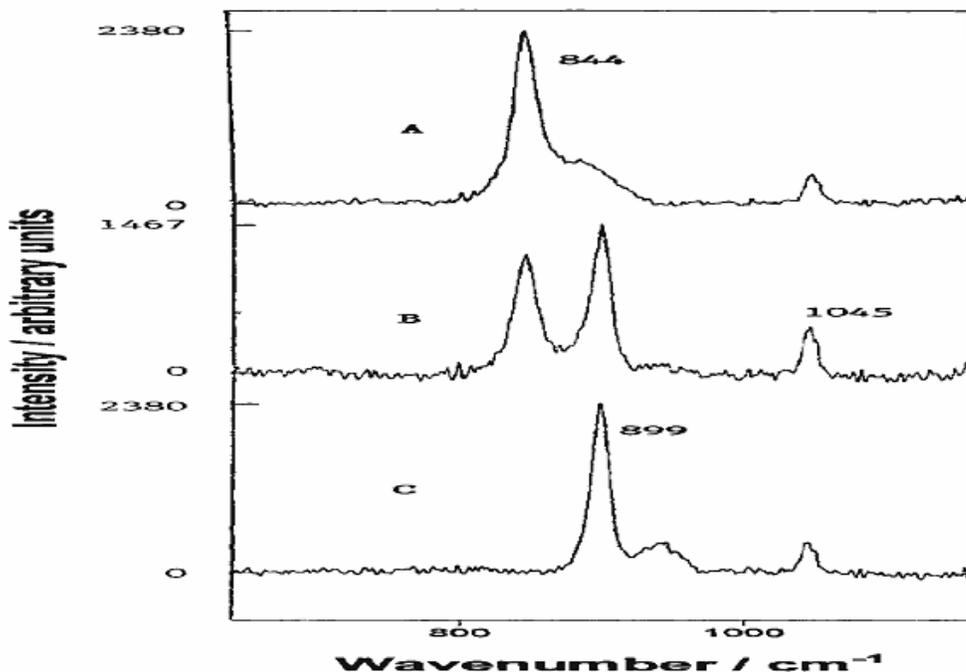


Figure 1.3 Experimental spectra (average of five exposures of 3 min each) of solution of 18 mM Cr(VI) at pH values 9.15 (A), 6.12 (B) and 3.03 (C). The peak at 1045 cm^{-1} is that of NO_3^- [33].

A bichromate ion band was estimated in the IR study of Hoffmann *et al* [34]. In that study it was revealed that at low solution pH, speciation changes from dichromate ion dominance at high total chromium(VI) concentration to bichromate ion dominance at low chromium(VI) concentration. Aqueous chromate solution was acidified to low pH and observed how changing the pH affects the IR spectrum.

The spectra were also recorded as a function of total chromium(VI) at fixed pH values of below 3. By changing the total chromium(VI) concentration the mole fraction of bichromate and dichromate ions should change. If no bichromate ion exists at low pH conditions, no spectral changes would be expected with variation of the total chromium(VI) concentration. If both bichromate and dichromate ions are present then their concentration and intensities of the IR bands should change as a function of total chromium(VI) concentration. The study supports the fact that bichromate indeed exists and must have Cr—O bond distance nearly identical to those found in the dichromate ion.

Besides the difference in the opinions about the existence of bichromate ion in aqueous solution, there is disagreement about the predominance of chromium(VI) species in aqueous solution as a function of pH. Predominance of chromium(VI) species depends both on the total chromium(VI) concentration, on the pH and the ionic strength of solution media. It was considered that dichromate ions exist in acid solution, at low pH, while chromate ions are in abundance in alkaline solution.

Chromic acid (H_2CrO_4) and hydrogen dichromate (HCr_2O_7^-) ions exist only in concentrated chromium(VI) solution at pH below 1 and bichromate ion is dominant at the pH range from 1 to 6, when the concentration of chromium(VI) is about 10^{-3} mol/L. At that pH and concentration range, bichromate and dichromate ions are in equilibrium. Chromate ion is dominant at pH of above 8 as seen in Figure 1.4.

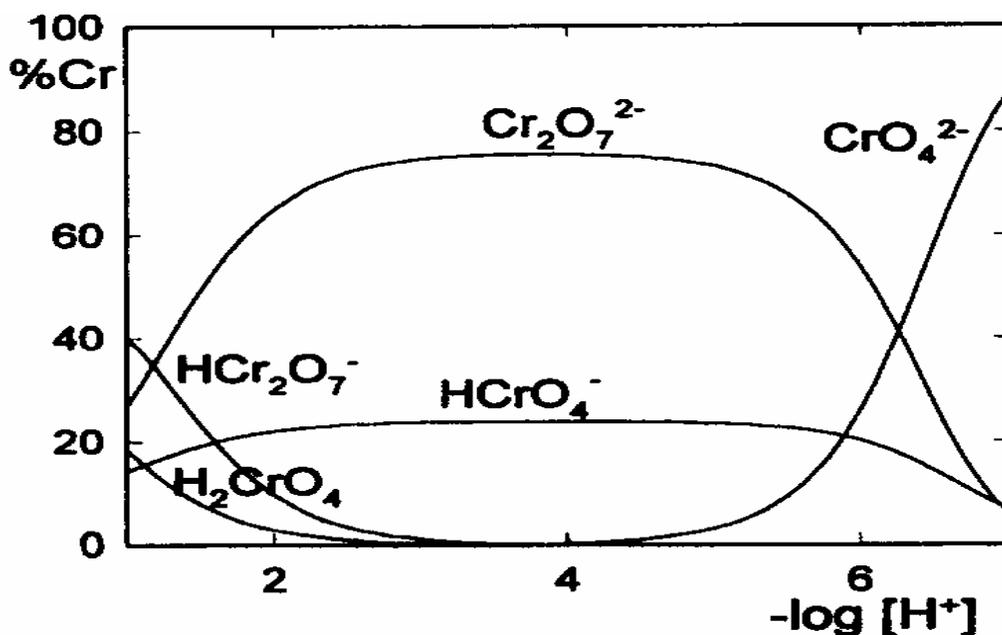


Figure 1.4 Species distribution diagram as a function of pH for total chromium(VI) concentration = 50 mM in the 3.0M KCl at 25°C [35].

To study chromium(VI) speciation one may report the spectra of chromic acid, dichromate and chromate solution with the same chromium concentration at identical pH value. Chromate solution may be acidified to a low pH and observed how changing pH affects the spectrum. The same can be done by

increasing the pH of chromic acid solution. Solution mixture of chromic acid and dichromate, alternatively chromate and dichromate solution can be prepared; by changing the total chromium concentration, the mole fraction of bichromate and dichromate species should also change.

Our study is concern with speciation in a sense of determining different forms of chromium(VI) species in concentrated electrolytic solution, not as a function of pH. These species are chromic acid and dichromate. We determined these chromium(VI) species in a solution mixture of chromium trioxide and sodium dichromate.

1.4 Objectives of the study

- To distinguish between chromic acid and dichromate in a solution mixture of chromium trioxide and sodium dichromate using redox titration.
- To develop Artificial Neural Networks models that will predict the quantity of chromic acid and dichromate in highly concentrated solutions with an accuracy of less than 1%.
- To illustrate how the number of titration points in a curve affects the accuracy of ANNs.
- To illustrate how the size of data play a role in the performance of ANNs.
- To show how distribution and number of test points within training set affect the performance of the neural networks.
- To investigate the ability of ANNs in quantitative analysis of CrO_3 and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

CHAPTER 2

2. EXPERIMENTAL

2.1 Reagents

Chromium trioxide (CrO_3), Formula Weight (F.W. 99.99 gmol^{-1}) and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, F.W. 298.05 gmol^{-1}) were obtained from Chrome International South Africa (CISA) and were used as received. Sodium hydroxide (NaOH , F.W. 40 gmol^{-1} , 98% pure), potassium hydrogen phthalate (KHP, F.W. 204.23 gmol^{-1} , 99.5% pure), potassium chloride (KCl , F.W. 74.55 gmol^{-1} , 99.0% pure), ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, F.W. 278.02 gmol^{-1}) and nitric acid (HNO_3 , 63.01 gmol^{-1} , 55 weight %) were obtained from Saarchem (Muldersdrift, South Africa). The metal salts were of analytical grade and were used without further treatment. KHP was dried out at 110°C in an oven for 2 hours; it was stored in a dessicator. De-ionized water was used throughout. It was obtained by passing distilled water through Milli-Q- water purification system (Millipore, Bedford, MA, USA).

2.2 Preparation of solutions

- Chromic acid stock solution was prepared by weighing out a required amount of chromium trioxide and dissolving in de-ionized water in 1000 ml volumetric flask.
- Dichromate stock solution was prepared by dissolving an appropriate amount of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in de-ionized water in 1000 ml volumetric flask.
- Titrant solution of approximately 0.6 M Fe(II) was prepared by dissolving an appropriate amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in dilute (0.5 M) sulphuric acid. Alternatively, a small amount (about 50 ml) of dilute sulphuric acid was added to solid ferrous sulphate before it was dissolved in de-ionized water.

- Sodium hydroxide solution was prepared by dissolving a required amount of NaOH pellets in de-ionized water in a volumetric flask. It was protected from moisture with ascarite and then stored under nitrogen gas flow (ultra-high purity nitrogen, 99.999% pure, from Afrox, South Africa) to protect against atmospheric moisture and carbon dioxide [36]. It was left for overnight before use.
- KCl solution (3 M), used to fill salt bridge and reference electrode, was prepared by dissolving KCl in de-ionized water in a volumetric flask.

2.3 Experimental set-up

In the experimental set-up as shown in Figure 2.1, the pH meter and the dosimat for NaOH or Fe(II) solution delivery have been interfaced to a personal computer and were controlled automatically using Lab View software [37]. The dosimats for dispensing chromic acid and dichromate solutions were controlled manually using dosimat keyboard.

All titrations were performed in a glass vessel fitted with a cover containing five holes. The holes were used to hold glass electrode, platinum electrode, and a salt bridge in which reference electrode was inserted. The other hole was used to fit a burette tip used to deliver NaOH or Fe(II) to a sample solution. Unused openings were closed with stopper. The salt bridge was built in “house”, because in case of commercially available salt bridge, concentrated chromium solution diffuses in rapidly, and then enters the diaphragms of the reference electrode. This results in an increase in diffusion junction potential as well as damage to the electrode when exposed to chromium solution for longer time.

Diffusion junction potential must be kept small and constant, otherwise it will make a greater contribution to a measured potential and results in errors. A measured potential should depend only on the potential at the indicator electrode/sample solution interface. Reference electrode should supply a

potential which is as independent as possible of the sample solution composition [38].

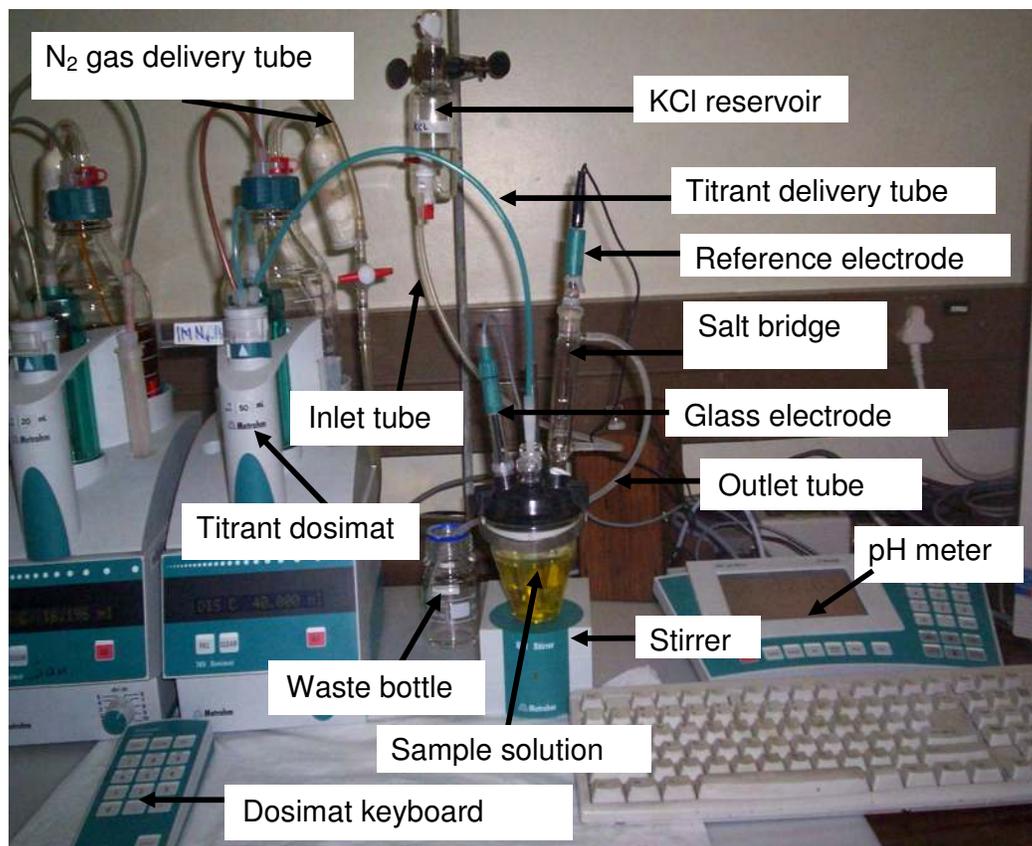


Figure 2.1 A photograph showing experimental set-up for automatic titration of chromium(VI) solutions.

A salt bridge in which reference electrode was inserted, had inlet and outlet tubes used to transport KCl solution, these tubes can be seen in Figure 2.2. The inlet tube delivers KCl solution from its reservoir to the tip of the diaphragm of external salt bridge through inner tube. This solution (KCl) flows slowly, diluting chromium that diffused from the sample solution before it reaches the reference electrode. It is then transported via the outlet tube to a waste bottle.

Only the diaphragm of external salt bridge was in contact with concentrated chromium sample solution. External diaphragm of inner salt bridge was in contact with diluted chromium sample solution while the inner diaphragm was not in contact with chromium solution.

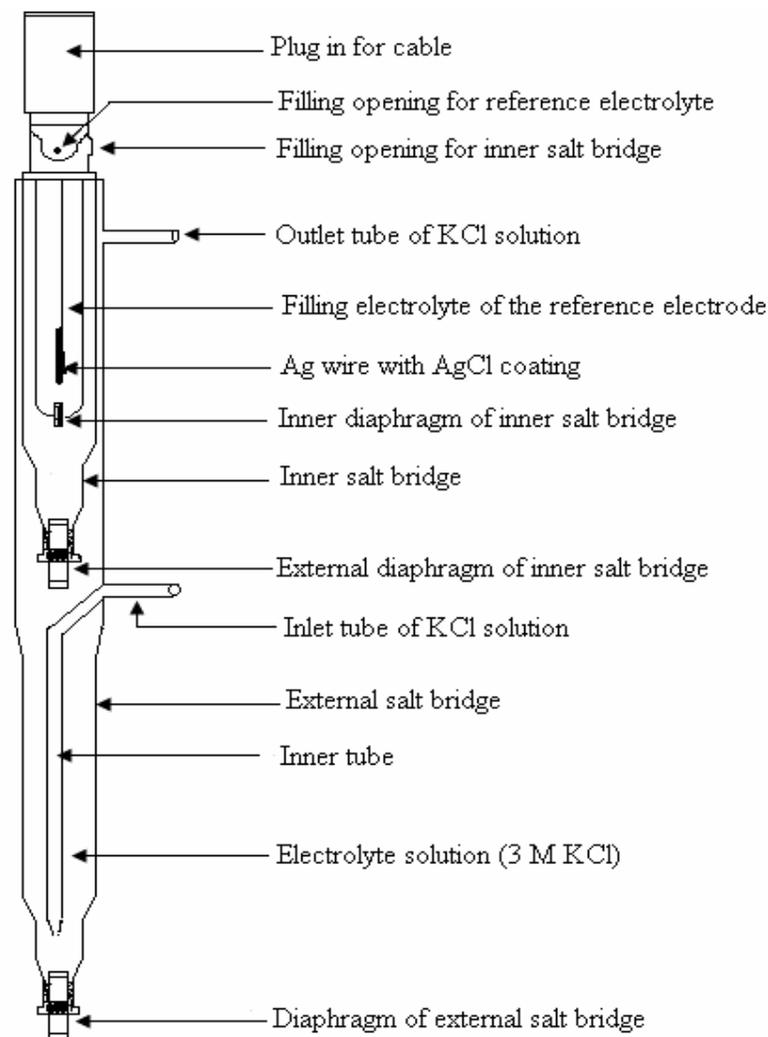


Figure 2.2 Reference electrode assembly.

All titration experiments were performed in a Metrohm (Herisau, Switzerland) glass vessel, equipped with a magnetic stirrer. The pH of the solutions was measured with glass electrode (6.0150.100) and the potential was measured with platinum electrode (6.0332.00). Ag/AgCl reference electrode (6.0726.107) was used as reference electrode. All electrodes were connected to 780 pH meter (Metrohm). Also connected to the pH meter was a Metrohm 801 magnetic stirrer which performed all stirring operations of sample solutions. Metrohm's 765 dosimat equipped with appropriate exchange unit was used to automatically deliver titrant solution to a titration vessel. During redox titration experiment, the temperature of the solution was monitored to

within $25.0 \pm 0.1^\circ\text{C}$ with temperature probe (model 6.1110.100 from Metrohm).

2.4 Experimental design

A number of experimental designs was created based on the content of chromium(VI) in the 8th stage of the industrial electrolytic process used for the production of chromic acid from dichromate. In the last stage (8th stage), the content of chromium(VI) from chromic acid solution is 320 g/L on average and fluctuates between 285 and 350 g/L, see Figure 2.3.

Average concentration of chromium(VI) from dichromate solution in stage number 8 is 210 g/L and fluctuates between 170 and 225 g/L. Total chromium(VI) concentration is 530 g/L on average and fluctuates between 475 and 550 g/L. Average chromium from chromic acid was assigned to 100% chromium and it was allowed to vary by $\pm 10\%$. By varying the content of chromium from chromic acid, other stages of the process were covered, e.g. the 6th and 7th stage of the electrolytic process. For simplicity, we referred to chromic acid solution that contains 320 g/L of chromium as 100% chromic acid solution. Chromic acid solution that contains 285 g/L of chromium was referred to as 90% chromic acid solution, and so forth.

In the experimental design developed, the total chromium concentration was maintained constant for a set of samples analysed, only the ratio of chromium from chromic acid and dichromate was varied. This means that during the preparation of the sample solutions, the concentration of chromium from chromic acid was increased whenever the content of chromium from dichromate had to be decreased. However, in other sets of data the total chromium concentration was varied within $\pm 10\%$.

Chromium(VI) stock solutions that were less concentrated compared to the industrial chromium samples were prepared, for example 30, 100 and 500 times dilution. The samples contained chromium content ranged from 90 and

110 weight % were prepared from chromic acid and dichromate stock solutions.

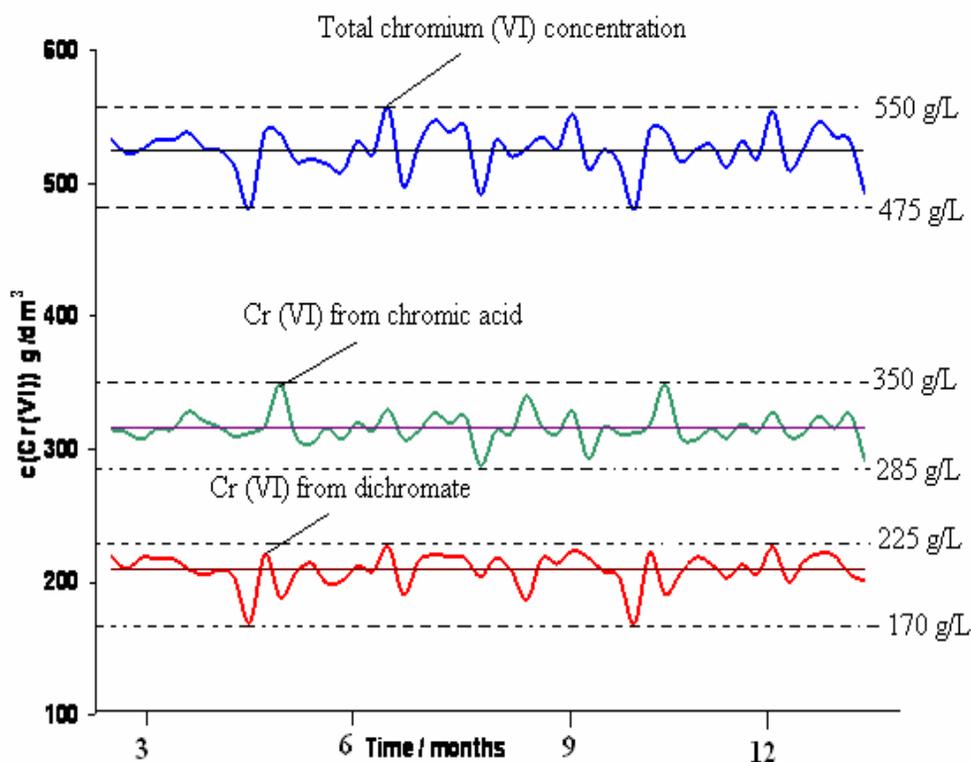


Figure 2.3 Chromium(VI) content from chromic acid and dichromate in the final stage of electrolytic process [39].

Based on the content of chromium(VI) in the last stage of the industrial electrolytic process, 20 ml chromic acid sample solution (100 weight % in chromium) contained about 0.0640 g of chromium as chromic acid, provided that it was prepared as 100 times diluted industrial sample. For the diluted industrial sample, 90 and 110% chromic acid solutions contained 0.0576 and 0.07040 g of chromium from chromic acid, respectively. For dichromate sample solution, 90, 100 and 110% solutions contained 0.0356, 0.0420 and 0.0484 g of chromium from dichromate, respectively.

In that case, a sample solution contained 90% chromium as chromic acid and 110% as dichromate contained the same total chromium concentration as compared to a sample solution contained 110% chromium as chromic acid and 90% as dichromate. However, a solution contained 90% chromium as

chromic acid and 90% as dichromate contained different total chromium concentration as compared to a solution contained 110% as chromic acid and 110% as dichromate.

The initial experimental design, as shown in Figure 2.4, was used as a guide in the preparation of chromium sample solutions used either in redox or acid-base titration experiments. The amount (volume and concentration) of sodium hydroxide solution required to complete titration was calculated. It required approximately 40 ml of sodium hydroxide (1 M) to complete titration of 40 ml chromium solution prepared according to the initial experimental design (Figure 2.4). The design shows the concentrations of chromic acid, sodium dichromate and total chromium(VI) of 500 times diluted industrial samples at the stage 8 of the industrial electrolytic process (see Figure 2.3).

Each point in the design represents a titration curve, for instance it can be a complete acid-base titration curve with two well defined end-points. The experimental design consists of subsets, namely learning, training and test set needed for ANNs. It was designed in a way that only learning points would be on the border lines (see dashed line in Figure 2.4) of a design. The total chromium(VI) concentration ranged from 90 to 110%. The ratio of chromium from chromic acid and chromium from dichromate ranged from 1.10 to 2.10.

There were no training and test points on or outside the border line of a design. ANNs do not predict well when training and test points are on or outside the border line of learning set. Training and test points were spread out within the learning set. For the training and test points, the ratio of chromic acid and dichromate was within 1.220 and 1.975 and the total chromium(VI) concentration ranged from 92.5 to 107.5%.

Every training point is in the centre of a rectangle formed by learning points. Test points are on the edge of that rectangle. A test point at the edge of a rectangle is also at the centre of a larger rectangle formed by learning points. Furthermore, every learning point that does not form part of a border lines is at the centre of a rectangle formed by training points. Learning and training

sets were used to train the neural networks and the test set was used to validate trained neural networks.

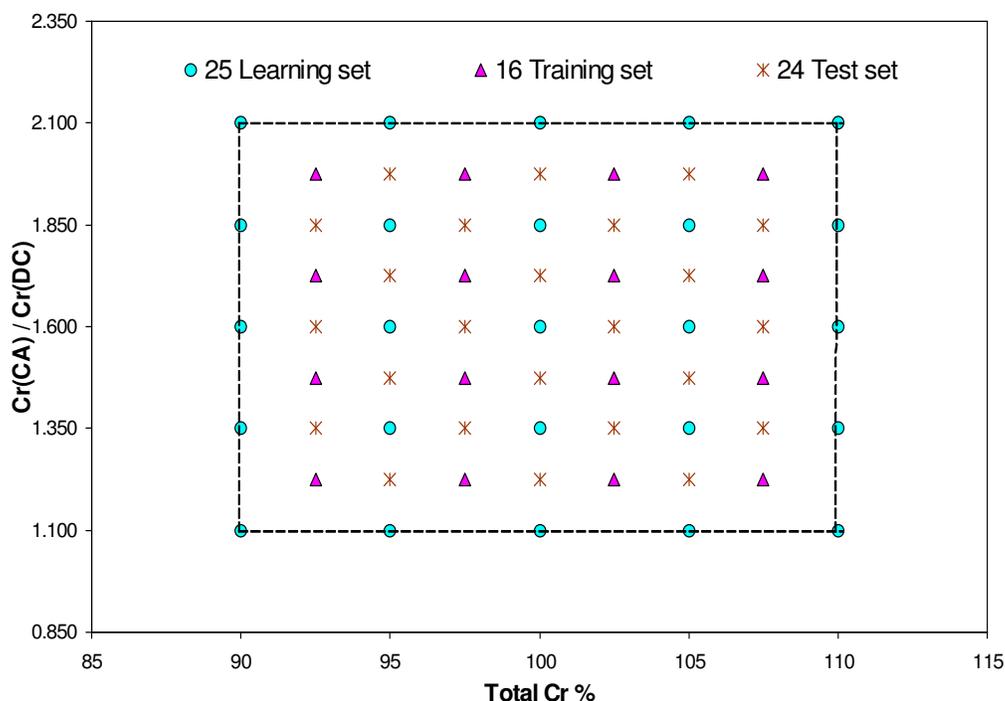


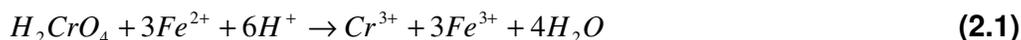
Figure 2.4 Initial experimental design

2.5 Redox titration

A required volume (ml) of chromium trioxide solution contained 90% chromium as chromic acid (referred to as 90% chromic acid) was dispensed into a clean titration vessel, followed by addition of de-ionized water. The volume of de-ionized water required was calculated according to the experimental design. The solution was stirred and purged for approximately 20 minutes with nitrogen gas, before measurements were taken. The temperature of the solution was kept constant with water circulating from the water bath maintained at 25°C. The solution was titrated automatically with Fe(II) solution delivered from an appropriate dosimat controlled in an automatic fashion. The change in potential of the solution was automatically monitored and the data were stored for analysis. Solutions referred to as

100% and 110% chromic acid solutions were also titrated. The same procedure was used in the titration of dichromate solutions.

Chromic acid and Fe^{2+} react according to the following reaction:



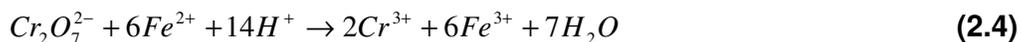
From reaction 2.1, 1 mole of chromic acid is equivalent to 3 moles of Fe^{2+} . Therefore, moles of chromic acid at the end-point of titration were given by equation 2.2 and molar concentration of chromic acid in the sample was calculated using equation 2.3.

$$(M_{Fe(II)} * V_{Fe(II)}) / 3molFe(II) \quad (2.2)$$

$$M_{H_2CrO_4} = \frac{M_{Fe(II)} * V_{Fe(II)}}{3molFe(II)} * \frac{1}{V_{H_2CrO_4}} \quad (2.3)$$

In equation 2.3, $M_{H_2CrO_4}$ is molar concentration of chromic acid solution in the sample, $M_{Fe(II)}$ is molar concentration of Fe(II) solution. $V_{Fe(II)}$ and $V_{H_2CrO_4}$ are total volume (L) of Fe(II) solution at the end-point of titration and volume (L) of chromic acid solution in a titration vessel, respectively.

Dichromate and Fe^{2+} react according to the following reaction:



At the end-point of titration, 1 mole of dichromate is equivalent to 6 moles of Fe^{2+} , equation 2.5.

$$(M_{Fe(II)} * V_{Fe(II)}) / 6molFe(II) \quad (2.5)$$

The molar concentration of dichromate solution in the sample was calculated at the end-point of titration using equation 2.6.

$$M_{Cr_2O_7^{2-}} = \frac{M_{Fe(II)} * V_{Fe(II)}}{6molFe(II)} * \frac{1}{V_{Cr_2O_7^{2-}}} \quad (2.6)$$

In equation 2.6, $M_{Cr_2O_7^{2-}}$ is molar concentration of dichromate in the sample, $V_{Cr_2O_7^{2-}}$ is the volume (L) of dichromate solution in a titration vessel. $M_{Fe(II)}$ and $V_{Fe(II)}$ are molar concentration and total volume (L) of Fe^{2+} at the end-point of titration, respectively.

2.6 Acid-base titration

2.6.1 Standardisation of sodium hydroxide (NaOH) solution

Sodium hydroxide (NaOH) solution was standardised weekly using the following procedure:

Standardisation of NaOH solution was conducted manually. A small amount of dried KHP was weighed out and dissolved in de-ionized water in an Erlenmeyer flask. Phenolphthalein indicator was added. The solution was titrated with NaOH solution from a dosimat. The end-point of titration was detected by change in colour of a sample solution. Several titrations were performed. In each titration the mass of KHP dissolved was different. Molar concentration of NaOH solution was determined at the end-point of titration using the following equation:

$$M_{NaOH} = \frac{m_{KHP}}{M_{KHP}} * \frac{1}{V_{NaOH}} \quad (2.7)$$

In equation 2.7, M_{NaOH} is molar concentration of sodium hydroxide solution; m_{KHP} is a mass of KHP (g). M_{KHP} is molar mass of KHP (g/mol) and V_{NaOH} is the total volume of NaOH added at the end-point (L) of titration.

The concentration of stock sodium hydroxide solution was found by taking the average value of the concentration values obtained from three different titrations.

2.6.2 Titration of chromic acid, dichromate and a solution mixture of chromic acid and dichromate

- A required amount of chromium trioxide solution was added into a clean titration vessel using a dosimat controlled manually. Required volume of de-ionized water was added and the solution was stirred.
- A dosimat equipped with 50 ml exchange unit containing standardised NaOH solution was automatically used to deliver NaOH solution to a titration vessel.
- During titration, NaOH solution was added in 0.25 ml increments, pH meter sampling rate of 1 s and a maximum waiting time of 5 minutes were used. Stop conditions were 40 ml of the titrant added and pH 14 of which volume was the first one to be reached. Titration data were collected and stored in a computer for analysis.

The above procedure was used in the titration of sodium dichromate and chromium solution mixture prepared from chromic acid and dichromate solutions. Data used to train and to test ANNs was obtained by titrating all chromium samples of the initial experimental design with sodium hydroxide solution.

CHAPTER 3

3. THEORY AND DATA TREATMENT

3.1 Artificial Neural Networks and Artificial Intelligence

Artificial intelligence (AI) is a branch of computer science that explores techniques for incorporating aspects of intelligence into the computer systems and seeks ways to improve the computer's ability to perform recognition and reasoning tasks [40]. It is apparent that for a computer to perform the above mentioned tasks, past experience is essential and there must be a storage house for that information and also a program(s) that allows it to do so. Artificial Intelligence programs are usually written using the following programming languages: LISP, PROLOG, FROTRAN, LOOPS and others.

Artificial Intelligence and Expert Systems (ES) are of great interest to organisations because of their ability to improve productivity and to augment work forces in many areas. ES are computer programs that use knowledge and procedure to solve problems and they are suitable for the applications that would consume time and require high level of expertise if they were performed by individual. These programs include among others MOLGEN, which is used for planning molecular genetic experiments and BACON.5, which has been used to discover law of nature [41].

If the ultimate goal of AI is to built intelligent machine or a computer that thinks like human, then it is essential to understand how human brain process information. AI should complement human intelligence but it will never replace it. Currently, it is very difficult to give a clear definition or explanation of intelligence. However, it has something to do with the ability to reason, to learn from experience and to adapt to a new situation [42].

Human brain consists of billions of biological neurons and there are thousands different kinds of neurons interconnected to one another. These

structures of brain and central nervous system control thinking, the ability of individual to learn and to react to the change in the environment [43]. A neuron consists of nucleus, cell body, axon and dendrites, see Figure 3.1. Axon and dendrites are capable of receiving and sending signal/stimuli from one neuron to the next. The axon and dendrites of a neuron are not connected directly to the axon or dendrites of the neighbouring neuron; they are connected by a small gap called synapse which helps to send stimuli or signal from neuron to neuron. This gap has the ability to increase or decrease its strength of connection and causes excitation or inhibition of a neuron.

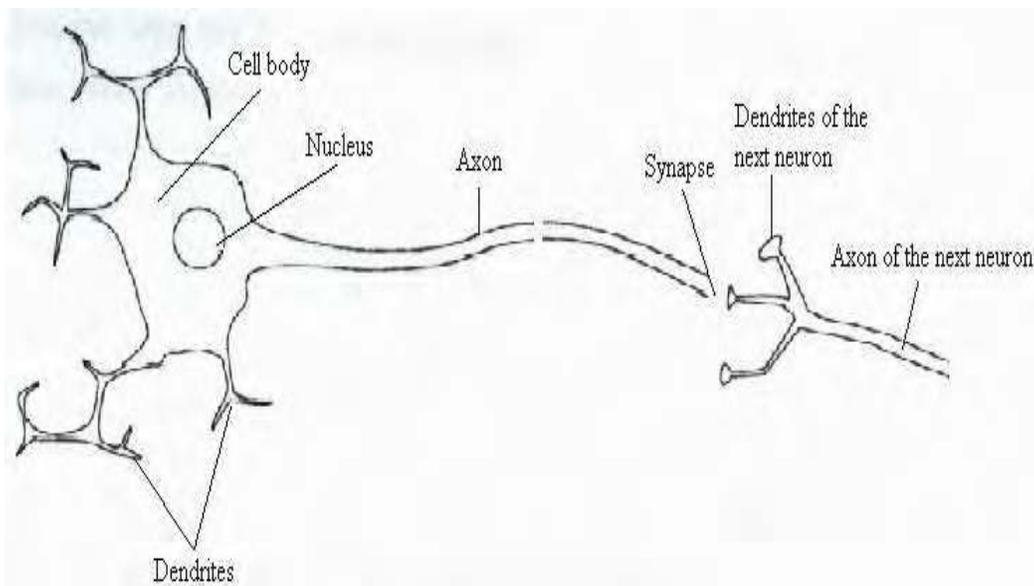


Figure 3.1 Structure of a biological neuron [44]

Artificial Neural Networks (ANNs) are models that emulate biological neural networks (the structures of brain called neurons). ANNs models are not considered as a sub area of AI but they are closely associated with AI in the area of patterns recognition for characters, speech and visual recognition. However, ANNs might be used to replace AI in areas where definite solution cannot be reached with AI systems. On the other hand, ANNs models might be integrated into the expert systems.

3.1.1 Applications of Artificial Neural Networks in chemistry and other fields

The value of ANNs technology includes their usefulness for pattern recognition, learning, classification, generalization and the interpretation of incomplete and noisy inputs. ANNs have been applied in many areas and below are few examples where ANNs have been successful.

ANNs were used to monitor galacto-oligosaccharides (GOS) and lactose concentrations in a GOS production fermentation process. During that process, the level of lactose (substrate) decreases while that of the product (GOS) increases. ANNs models generated from absorbance spectra data of the fermentation samples gave the best performance, being able to accurately and precisely predict lactose and total GOS concentrations as the fermentation process continues. The method is very fast, simple and inexpensive in monitoring the concentration of GOS in the fermentation process; it helps the operator to verify if the process is running as needed and whether some corrections are required [45].

Ivana Lukec *et al* [46] applied ANNs in the development of models which were used to determine sulphur content in hydrotreatment products. The models were developed for light gas oil and vacuum gas oil. Some models predict sulphur content in the hydrotreatment process very well and might be used on-line or in-line for continuous monitoring and optimization of the process.

ANNs were also used to develop models that would be used to predict total solar irradiation on the horizontal surface. The models were developed based on a number of factors which include latitude, longitude, altitude, sunshine duration, humidity and temperature. The results obtained might help modellers and designers of solar energy systems in their tasks of developing better solar systems [47].

Abbas Afkhami *et al* [48] applied ANNs in the simultaneous determination of new complexes of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} with synthesized Schiff base. The

base was derived from 3, 6-bis ((aminoethyl) thio) pyridazine. The absorption spectra of the metal complexes were evaluated with respect to the Schiff base concentration, pH and time of colour formation and were processed by ANNs. The proposed ANNs models were successful in the simultaneous determination of the above mentioned metal ions in different vegetables, foodstuffs and pharmaceutical samples.

Furthermore, ANNs were applied as screening tools for cancer [49, 50]. The concentrations of copper, iron, selenium and zinc determined by total reflection X-ray fluorescence spectrometry in the samples of blood were used as chemical indicators of the physical status of the individuals. Blood samples were obtained from individuals, who have been diagnosed positively or negatively for various forms of cancer. The analyses were used as the inputs to the neural networks which showed good performance in terms of distinguishing between healthy or unhealthy individuals. An estimation of 94 % was achieved and that makes ANNs to be the first tool in the evaluation of the health status of a person as far as cancer is concerned.

Dasa Kruzlicova *et al* [51] used ANNs for the classification of varieties of white wines. The developed models were used to classify Slovak white wines of different varieties, year of production and from different producers. The wine samples were analyzed by GC-MS (gas chromatography–mass spectrometry) taking into consideration mainly volatile species which highly influence the wine aroma (terpens, esters and alcohols) and the analytical data were evaluated by ANNs.

The ANNs were also used in the classification of chemotherapeutic agents, antibacterial, antifungal and antineoplastics based on the asymmetric and symmetric structure of these agents [52].

Fernando *et al* [53] applied ANNs in the prediction of ^1H NMR (proton nuclear magnetic resonance) chemical shifts of sesquiterpene lactones, and they were also used for patterns recognition of the proton NMR spectra of alditols

[54]. Kvasnička, [55] used ANNs to predict ^{13}C NMR chemical shifts of secondary carbons in acyclic alkanes.

A paper by Otto *et al* [56] illustrates how ANNs were applied to the development of expert systems for automatic qualitative analysis in X-ray fluorescence spectroscopy and ICP-AES (inductively coupled plasma-atomic emission spectroscopy).

3.1.2 Artificial Neural Networks architecture

In their basic form, ANNs consist of layers of neurons interconnected to each other's neuron by the networks. The first layer is called the input layer, the intermediate one is the hidden layer and the last layer is the output layer. The number of hidden layers and neurons in the networks may vary in different applications and it depends on the user and the application. There are no techniques available to decide the number of neurons and the hidden layers, and this is usually done by trial and error [57]. In Figure 3.2, the neural networks representing the arrangement of the input layer, one hidden layer and the output layer is shown.

The input neurons or nodes receive independent variables and are only used to distribute the weights. The hidden neurons run the learning process before passing the signals to the output neurons (dependent variables) for prediction [58]. The information or data of interest is fed into the input layer and flows in the hidden layer(s), then to the output layer where the results of the neural networks are presented.

With exception to the neurons in the input layer, all neurons in the neural networks have activation function. Hidden neurons and the output neurons might have identical or different activation functions. As an example, sigmoid activation function can be used for the neurons in the hidden layer and linear activation function can be used for the neurons in the output layer. Each neuron in the hidden layer has a threshold value and its incoming lines carry weights that represent a stimulus. In the neural networks, both the knowledge

representations and also the “programming” are stored in the networks themselves as the weight connections and the threshold values of the neurons.

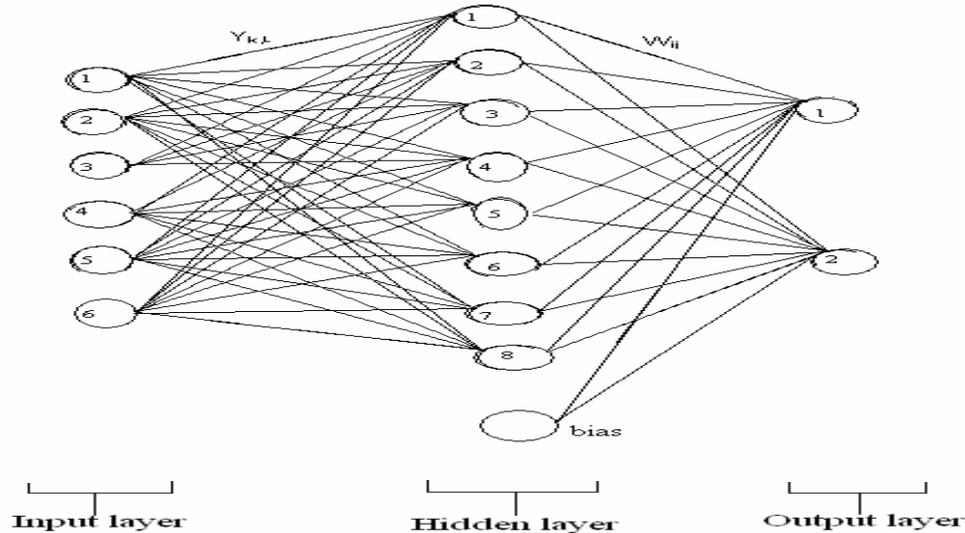


Figure 3.2 Artificial Neural Networks architecture with a single hidden layer

A neuron receives stimuli in a form of data or numerical information that should be transferred to the next layer through weight connections. To summarise the structure of the neural networks, the following important elements have been considered: the inputs, the outputs, weight connections, weighted summation function, threshold value and transformation function.

- The inputs and the outputs of the neural networks are values of the attribute of the problem and the solution of the problem, respectively.
- The weights express the strength of data connection; they transfer data from layer to layer. It is through repeated adjustment of the weights that the neural networks learn.
- The summation function finds the weighted average of all the input elements and multiplies each input value (x_i) by its weight (w_i) and total them together for a weighted sum.

$$\text{Weighted sum } (y_i) = \sum_{j=1}^i x_j w_{ij} + b_j \quad (3.1)$$

In equation 3.1, x_i - is an input to the neuron in the input layer, w_{ij} is the weight representing the strength of connection between neurons i and j , i is the number of neurons and b_j is a bias from neuron j ; it can be regarded as the nonzero offset in the data.

Threshold values are determine by a neuron's threshold functions. Based on the sum of the incoming weights, a neuron may or may not produce the outputs and we say the neuron does or does not fire. A neuron fires when the sum of its incoming weights equals or exceeds its threshold value, see Figure 3.3. The weight connections or the input lines of other neurons are activated when a neuron fires.

An activation function, also called a transformation function, computes the internal stimulation of the neurons. The internal activation function may be linear or nonlinear. The most widely used activation function is a sigmoid function represented by equation 3.2. Other activation functions include hyperbolic tangent, gaussian, and linear functions.

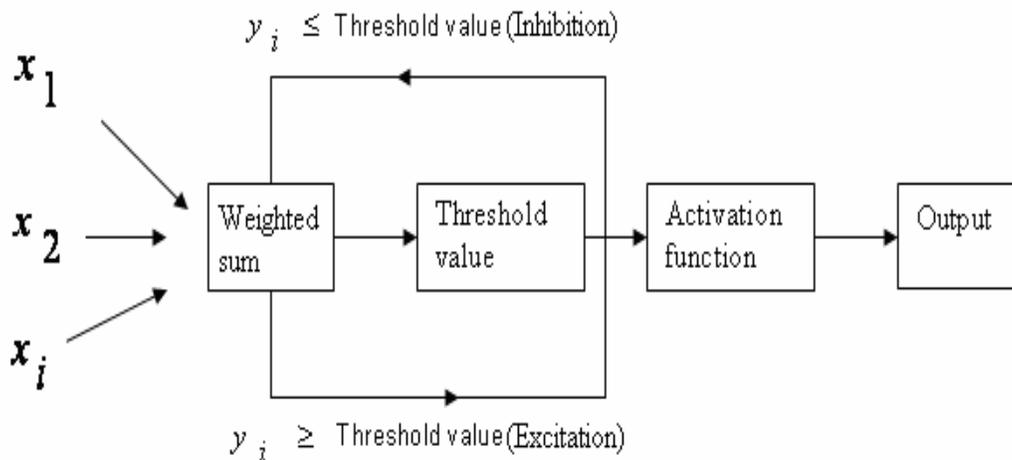


Figure 3.3 Artificial neuron [59, 60]

$$Y_j = \frac{1}{1 + e^{-y}} \quad (3.2)$$

In equation 3.2, Y_j is a neuron activation function that modifies the outputs level to a reasonable value before the outputs reach the next level.

3.1.3 How do Artificial Neural Networks learn?

In the area of ANNs technology, learning is define as a process that settles the parameters of the neural networks, namely the weight connections and the threshold values so that the neural networks yield wanted outputs for given input. The values of the weight connections and the thresholds are determined during training and testing operations using sets of data.

A learning process is classified into unsupervised and supervised learning. During unsupervised learning or self organizing process, the neural networks rearrange themselves and determine the number of the hidden layers and hidden neurons. They organize their internal learning algorithm based on the size of the input data [61]. They are not provided with “correct” or meaningful outputs. Sometimes they are not provided with the outputs at all. In our study, we considered only supervised learning and our neural networks were given relevant outputs.

A learning process, or training as sometimes called, is divided into several steps and only few of them will be noted. The first step consists of a data collection step. These data will be provided to the neural networks as the inputs. In our study, the data used as the inputs were collected via an acid-base titration experiment. Collected data must cover the widest range of problem domain. Meanwhile, care must be taken when collecting the data because large data sets increase processing time during training operation. The only advantage is that they improve the accuracy of the neural networks and would lead to good sets of weights. In that case, it is possible for the neural networks to minimize the difference between the actual and the predicted outputs and predict well when provided with the test set of data. However, the performance of the neural networks depends on many factors,

e.g. the quality of data used and on how the neural networks (the “experiments”) were designed.

In the second step, the data have to be divided into training and test sets. During a learning process, the training set is used to adjust the weights and the test set is used to test the performance of the neural networks. The testing operation is very important to insure that the neural networks did not simply memorize a given set of data but learned the general patterns involved within the application.

Figure 3.4 shows a flow chart with some of the main steps involved during the training and testing of the neural networks. In the third step, the data have to be treated and transformed into a format required by the neural networks and their algorithms. Before the training process starts choice must be made on what type of learning will be applied e.g. supervised or unsupervised learning. The number of the hidden layers must also be taken into account. Other parameters including the target error, learning parameters (η and α), epoch length and the number of iterations should also be considered.

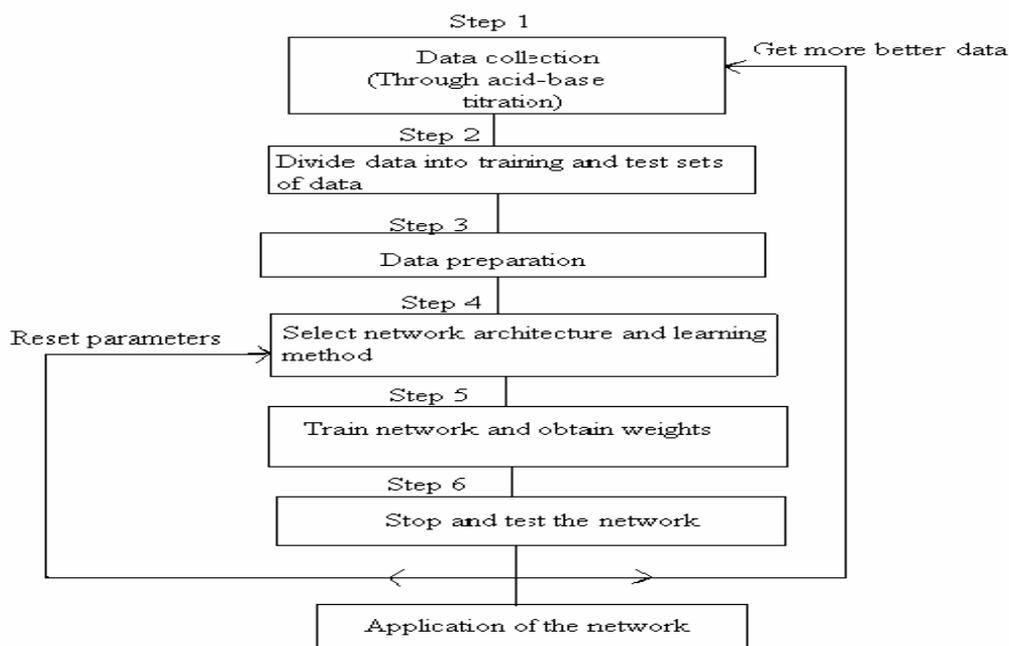


Figure 3.4 A flow chart illustrating the main steps involved during learning of ANNs.

During the training of ANNs, the number of neurons in the hidden layer(s), learning parameters and, if needed, the number of the inputs would be changed until better weights connection are established. The main objective is to find the values of the weights that minimize the difference between the actual outputs and the predicted outputs [62]. This happens when all or most trained patterns have errors (difference between the actual and the predicted outputs) below the target level set by the operator.

The performance of the neural networks is tested or validated with the test set of data which have never been used in the training patterns. Usually, the test data belong to the same “family” as the training set of data. The neural networks that perform well lead to good set of weights and have smaller RMS (relative mean square) error, both in the training and testing operations. But this does not mean that the neural networks with smaller RMS errors obtained during the training operation will predict very well. They might not result in reasonable predictions during testing operation. It is not possible that the neural networks with larger RMS errors obtained during training would predict well, since they did not learn effectively. Once the neural networks performed well in the test process, they are now ready for the applications and they can be used as part of software systems or integrated into the expert systems.

3.1.4 Problems associated with training Artificial Neural Networks

As already mentioned, the performance of ANNs depends on a number of factors used to train the neural networks. These factors include the size of the data (networks) and other parameters associated with training operation. During the data collection step, large amount of data that cover a large area of the problem is needed. Despite the fact that the neural networks trained with large set of data learned effectively, they will learn slowly and may get stuck while the RMS errors are still on the maximum level and they may stop earlier. On the other hand, small neural networks might not learn what you want them to learn.

Early stopping is the main problem associated with the process of training the neural networks with a large set of data. This effect is called over-fitting. During over-fitting, the neural networks might produce very small RMS errors as quickly as possible, but predict with very large errors when tested [63].

The rate parameter called alpha (α), also affects the performance of the neural networks equally as other parameters in the networks. A smaller rate parameter may waste time and a larger rate parameter may promote instability or provide poor predictions. Other factors that cause problem during the training of the neural networks are the neurons that do not fire to produce outputs and those that fire when they are not suppose to. This activation and deactivation of the neurons also leads to large errors during the testing process.

Most of these faults are minimized through back propagation (back error) procedure. This supervised learning method [64] is the most commonly used [65]. It is called back propagation because it computes changes to the weight connections from the final layer towards the hidden layer and back to the initial layer, using the difference between the predicted and the actual outputs to change the weights so that the neural networks can give reasonable predictions. The overall idea behind back propagation is to make large changes to the particular weights, if the changes lead to a reduction in the errors observed at the output neurons. The process of learning is repeated over and over until desired or reasonable errors are established [66].

3.2 Fitting acid-base titration curves

The concentrations of chromic acid and dichromate at the end-point of titration of chromium sample contained chromium trioxide and sodium dichromate against sodium hydroxide, were determined by fitting titration curves with a modified sigmoid equation, see equation 3.3 [67, 68]. A normal sigmoid equation is represented by equation 3.2. Applying that modified equation, the

total volume of sodium hydroxide solution added at the equivalence point of titration was estimated.

$$y = \frac{pH_{\max}}{(1 + \text{EXP}((-1) * ((x - EP) / \text{slope})))} + (a + k * \text{EXP}(b * x)) \quad (3.3)$$

In equation 3.3, pH_{\max} is maximum pH (a plateau of acid-base titration curve), EP is equivalence point of titration (total volume of sodium hydroxide solution added at the end-point). The parameters x and y are volume (ml) of sodium hydroxide solution added and pH value at point x , respectively. The slope defines the steepness of acid-base titration curve. The parameters a , b and k are variables needed to be established for a better fitting of a titration curve.

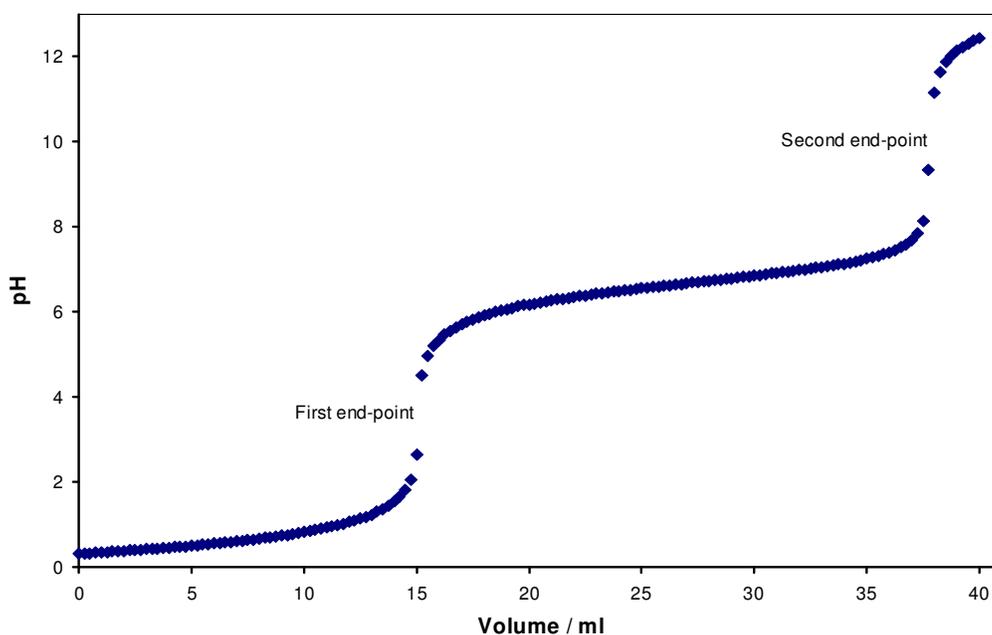


Figure 3.5 An example of acid-base titration curve fitted with modified sigmoid equation. Chromium sample contained chromic acid and dichromate was titrated against 1 M sodium hydroxide solution.

Figure 3.5 shows acid-base titration curve obtained when chromium sample contained chromic acid and dichromate was titrated against sodium hydroxide solution. This titration curve was fitted with equation 3.3. For fitting purpose, a titration curve was divided into two equal halves which were fitted separately,

because equation 3.3 was designed to fit acid-base titration curves with only one jump.

The first end-point in the titration of a sample contained chromic acid and dichromate was as a result of a neutralization reaction between chromic acid and sodium hydroxide solution. Chromic acid releases the first proton and forms bichromate ion (equation 3.4). To determine the concentration of chromic acid in that sample, firstly, the volume of sodium hydroxide solution at the end-point of titration was estimated by fitting the first half of titration curve as shown in Figure 3.6. Secondly, the concentration of chromic acid was calculated at the end-point of titration using equation 3.5.



$$M_{H_2CrO_4} = \frac{M_{NaOH} * V_{NaOH}}{V_{H_2CrO_4}} \quad (3.5)$$

In equation 3.5, $M_{H_2CrO_4}$ is molar concentration of chromic acid in the sample (mol/L). $V_{H_2CrO_4}$ is volume of chromic acid in the sample (L), M_{NaOH} and V_{NaOH} are molar concentration and total volume (L) of sodium hydroxide solution at the equivalence point of titration, respectively.

The second half of titration curve was also fitted, see Figure 3.7. Both first and the second end-points of titration were used to calculate the end-point of titration due to dichromate in a sample containing chromic acid and sodium dichromate.

The volume of sodium hydroxide solution that reacted with dichromate can be calculated using equation 4.8 as would be discussed in the next chapter. The overall reaction of dichromate with sodium hydroxide is given by equation 3.6. In that case, the concentration of dichromate in the sample can be calculated using equation 3.7.

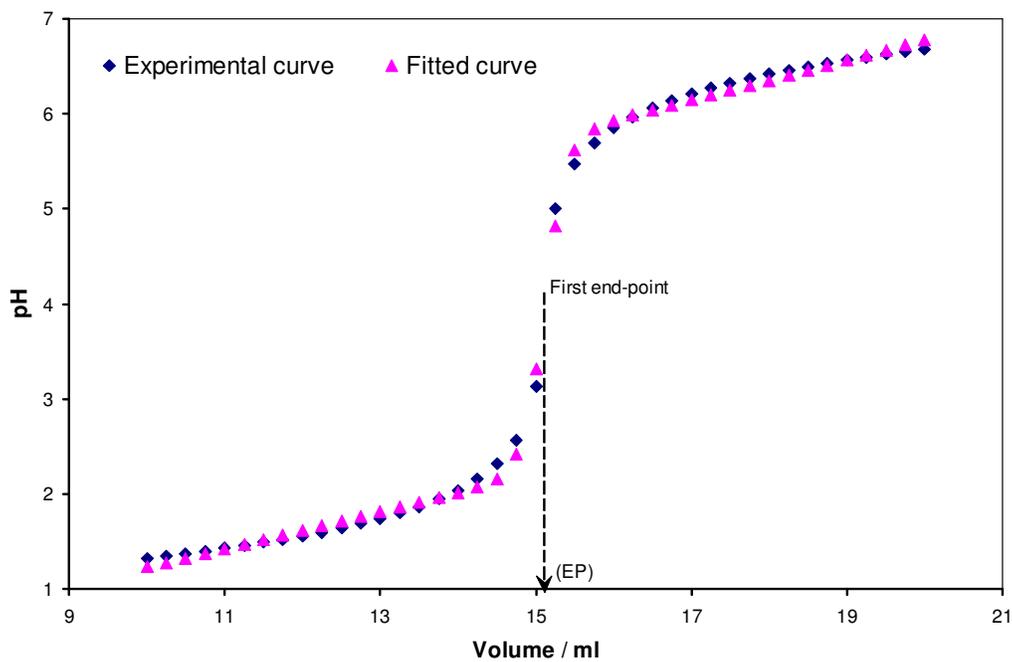


Figure 3.6 The first half of acid-base titration curve.

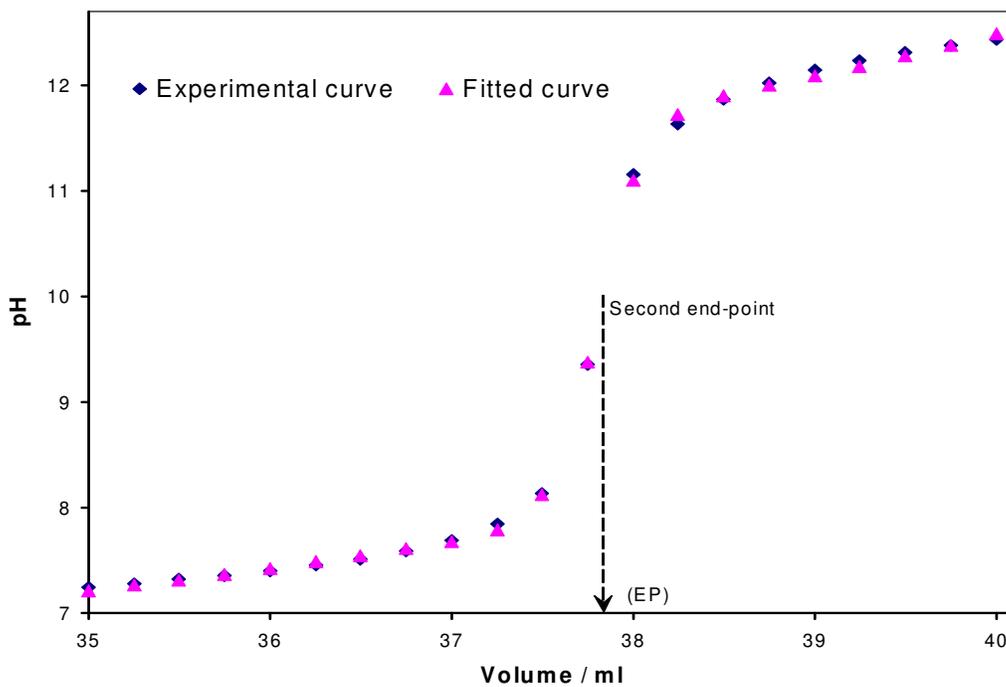


Figure 3.7 The second half of acid-base titration curve.

$$M_{Cr_2O_7^{2-}} = \frac{M_{NaOH} * V_{NaOH} / 2}{EP_4 - 2EP_1} \quad (3.7)$$

In equation 3.7, $M_{Cr_2O_7^{2-}}$ is molar concentration of dichromate in a sample, M_{NaOH} and V_{NaOH} are the molar concentration and total volume (L) of sodium hydroxide solution at the end-point (EP_4). EP_1 and EP_4 are first and second end-points observed during the titration of a sample containing chromic acid and dichromate, respectively. The end-point of titration due to dichromate in that sample is the difference between the second end-point (EP_4) and twice the first end-point ($2EP_1$). The first end-point (EP_1) is doubled because it takes only two protons for chromic acid to dissociate completely. This means that the second end-point (EP_2) in the titration of chromic acid must be twice the volume as the first one. See the titration curve of chromic acid in Figure 4.6.

3.3 Training and testing ANNs.

ANNs were trained and tested before they could be useful for their application, i.e. to predict the concentrations of chromic acid and dichromate in the samples. For that purpose, they were provided with sets of acid-base titration curves as the inputs. Training and testing operations were performed with Windows Neural Networks (WinNNs) 32 version 1.6 written by Yaron Dagon [69]. WinNNs 32 are windows based neural networks simulators with back-propagation learning method. When neural networks were loaded, neural networks control panel windows were displayed, as can be seen in Figure 3.8.

In Figure 3.8, the upper left-side window is the neural networks control window. It consists of the most important features of the neural networks and it allows the operator to specify and enter the learning parameters. The other upper window is the plot outputs window. This window provides the results (training and testing) of the neural networks in a form of plots. Examples of the plots which can be displayed in the plot outputs window are patterns

outputs, patterns errors, RMS errors, test outputs and test errors plots. The lower window is the test neural networks window. This window displays the predicted outputs in a form of a table. These are the most important results of the neural networks and are usually copied to the spreadsheet for the analysis.

Titration curves were divided into learning, training and test sets. All sets have the inputs and the outputs. The inputs were sets of acid-base titration curves in the form of titration points (vol/pH) and the outputs were chromic acid and the total chromium concentrations. In other cases, dichromate and chromic acid concentrations were provided as the outputs and sometimes only one output was provided. Learning and training sets were used to train the neural networks, to adjust the weights so that the neural networks can recognize and generalise the input-output patterns provided. Test set was used to validate the performance of the neural networks, to check whether the neural networks learned the input-output patterns properly. If they memorized the patterns, RMS error would be larger as compared to the one obtained during the training operation.

The neural networks were composed of three layers, the input layer, the hidden layer and the output layer. As already mentioned, the input layer consists of acid-base titration curves and the output layer consists of chromic acid and total chromium concentrations (two outputs). The number of neurons in the hidden layer was varied from 10 to 20 neurons and for every number the neural networks were ran several times. Sigmoid function was chosen as the neurons' activation function for both hidden and output layers.

Initially, the learning parameters, Eta (η) and Alpha (α) were set to 0.0001 and 0.5, respectively. Eta was set to increase by 1.0002 per iteration when the relative mean square error (RMS) of the neural networks decreases. This value multiplies the initial Eta value. Eta was also decreased by 0.9996 when RMS error increased for a particular iteration. The target error was set to either 0.01 or 0.005. This is the error requirement of the neural networks,

training operation stops when all patterns have error smaller or equals to the target error. The initial minimum and maximum neural networks weights were set to be between -1 and 1 , respectively. The weights were set within this region because the activation function used can only have the output node values between 0 and 1 , and the input to a sigmoid function must be between -2 and 2 . However, the actual weight values were shown and updated when the training operation started or stopped.

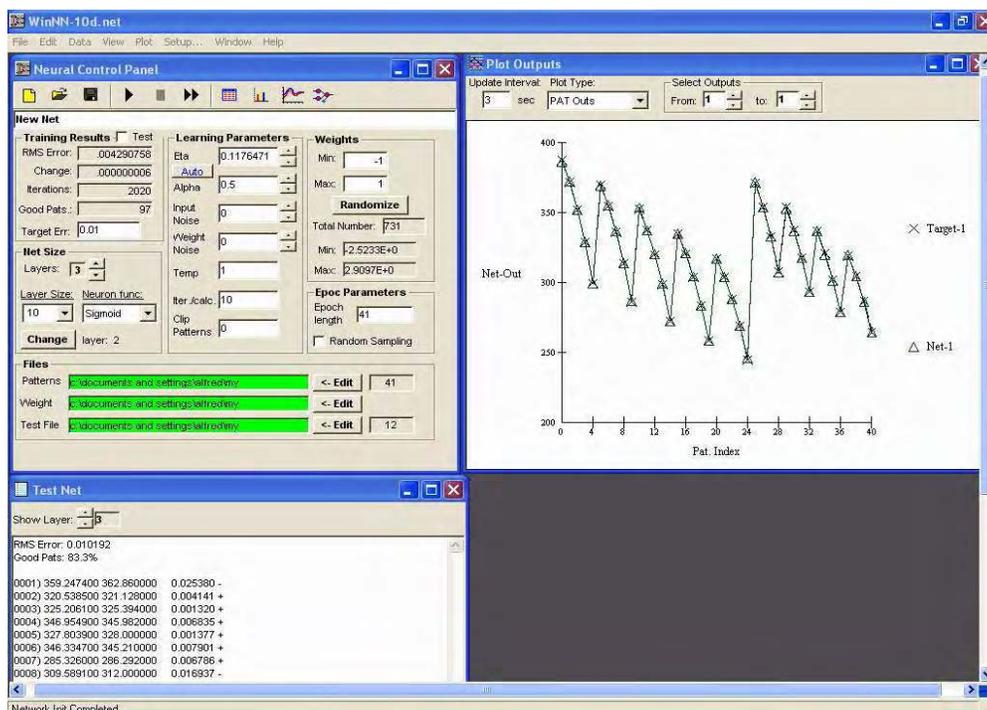


Figure 3.8 WinNNs 32 windows; the upper left-side is neural networks control window, the right one is plot outputs window and the lower one is test networks window.

Global normalization method was chosen to normalize the neural networks' patterns to an effective neuron input or output values. The neural networks were trained with back-propagation method. Once trained, they were tested with the test set of data contained test patterns which were not in the training set. The results of the neural networks (see test neural networks window in Figure 3.8) were copied to spreadsheet for analysis. These results were predicted concentrations of chromic acid, dichromate and total chromium, depending on the output(s) provided to the neural networks.

3.3.1 Experimental designs

3.3.1.1 Initial experimental design

Figure 3.9 shows the initial experimental design and is the same as the one shown previously in Figure 2.4 of chapter 2. Ideas about how this experimental design came about were presented in chapter 2. It consists of learning points which form part of border line of a design (dashed line seen in Figure 3.9). There were no training and test points on the border line. ANNs are not very good in prediction when the training and test points are on or outside a border line, out of the limits of the variables. Here the total chromium is within 90 and 110% and the ratio of Cr(CA)/Cr(DC) is in the range of 1.10 and 2.10.

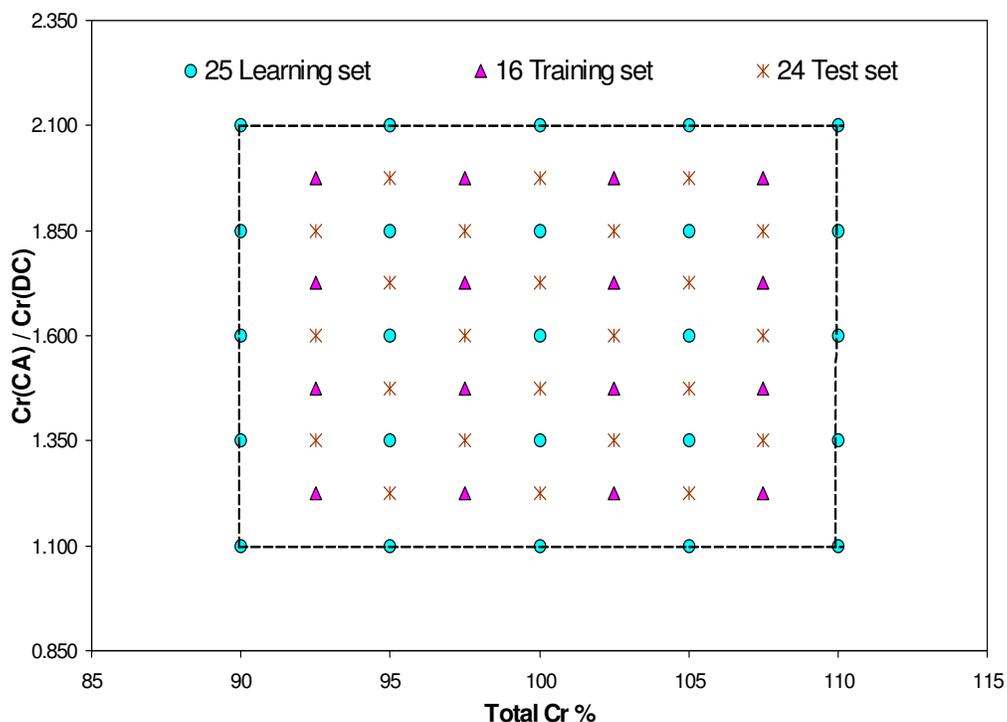


Figure 3.9 Initial experimental design

a) *Titration curves with all collected points*

ANNs were trained and tested with sets of data from the initial experimental design. Acid-base titration curves with collected points starting from 2.50 mL (exactly 151 points) were provided as the inputs to the neural networks. An example of acid-base titration curve with all collected points is provided in Figure 3.10. The outputs were the expected chromium from chromic acid and the total chromium concentrations. The expected chromium from chromic acid, or total chromium, is the theoretical concentration of chromium from chromic acid, or total chromium, that was calculated according to the experimental design. These values were calculated for each and every acid-base titration curve (a single point seen in Figure 3.9) provided as the input to the neural networks. Each curve (as an input to ANNs) must have the same number of titration points in the learning, training and test set of data.

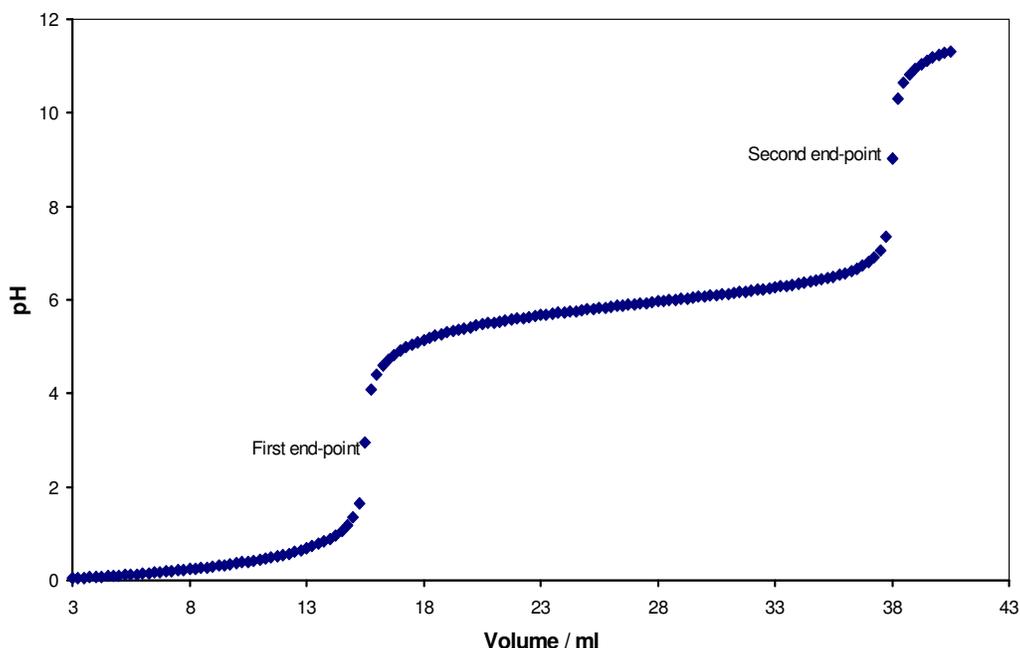


Figure 3.10 An example of acid-base titration curve with all collected points.

The neural networks were also trained and tested with titration curves with all collected points as the inputs (as before) but with the experimental concentrations of chromic acid and dichromate as the outputs. The experimental concentrations of chromic acid and dichromate were obtained by fitting titration curves with modified sigmoid equation as seen in equation 3.3. All titration curves provided as the inputs were fitted.

The performance of the neural networks was expected to be better, when the experimental concentrations were used as the outputs. The same titration curves used as the inputs were fitted to obtain the outputs. Therefore, one would expect the networks to predict better. They should simply generalize a given patterns and relate the inputs to the outputs.

b) Titration curves with reduced or fewer points

The neural networks were trained and tested also with sets of titration curves with reduced points (exactly 33 points as seen in Figure 3.11). Those titration curves were obtained by removing every four points in succession and retain every fifth point in the titration curves with all collected points. Such curves are equivalent to the titration curves obtained when the titrant is added in larger increments. When the titrant was added in larger increments, then titration experiments were completed rapidly and faster, but when added in smaller increments, the experiments took significantly longer.

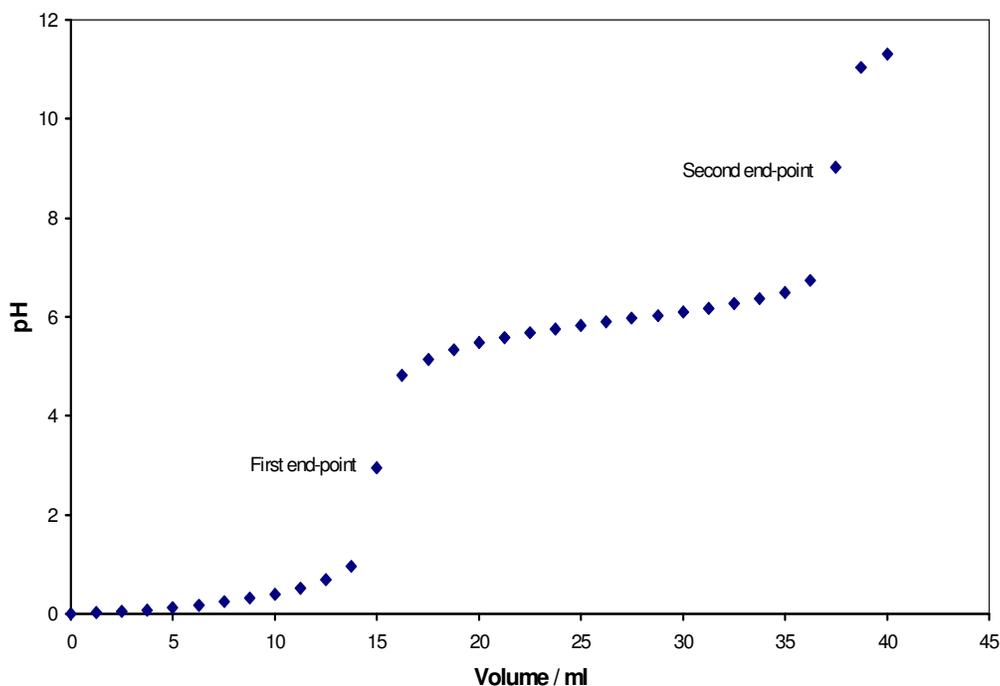


Figure 3.11 An example of acid-base titration curve with reduced or fewer points.

The time required for the analysis would be minimized, if the neural networks were able to predict the concentrations of chromic acid and dichromate with accuracy of less than 1%.

3.3.1.2 Increased learning density experimental design

This experimental design was created from the initial experimental design. No additional titration curves were collected. The size of the learning set was increased, as seen in Figure 3.12. The learning set was created by combining learning and training sets of the initial experimental design. New training and test sets were created from the previous test set of the initial experimental design; because of that the size of these sets was significantly reduced.

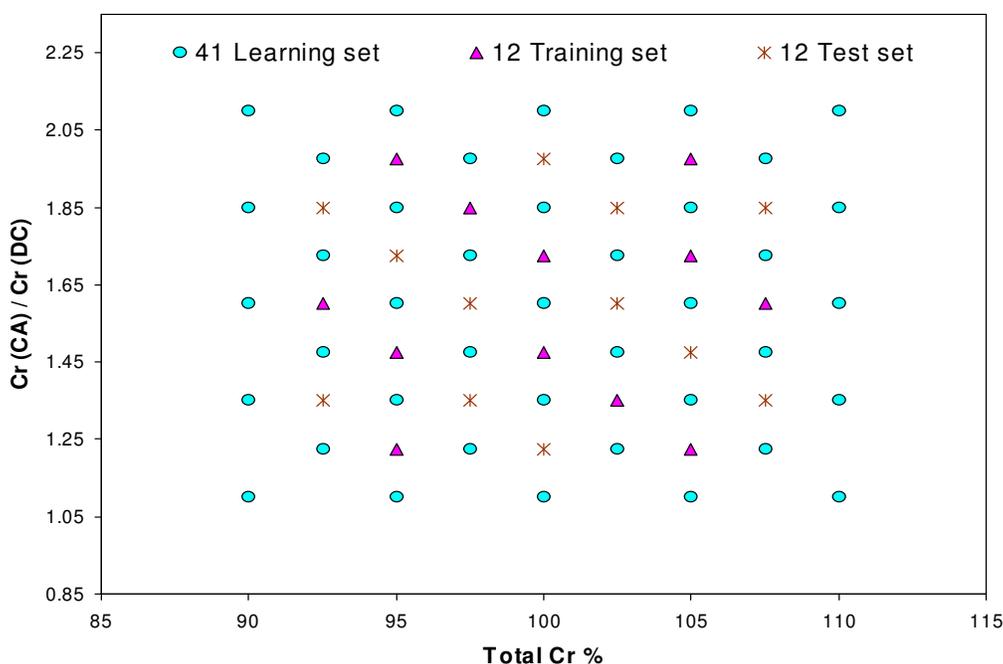


Figure 3.12 Increased learning density experimental design

When the size of learning set increases, the neural networks is expected to learn well and be able to minimize the errors between the expected and the predicted outputs. The ANNs were expected to predict the concentrations of chromic acid and dichromate with accuracy of less or equal to 1%. However, larger networks may learn slowly and overfit. The size and the placement of

training and test points within the learning set play an important role as far as the performance of the neural networks is concerned. The performance of the neural networks was tested for the following:

a) *Titration curves with all collected and reduced points*

The networks were provided with a set of titration curves with all collected points as the inputs. These titration curves were from increased learning density experimental design. In the other training and testing operations, titration curves with reduced number of titration points were provided as the inputs to the neural networks. In both cases, the expected concentrations of chromium from chromic acid and the total chromium were the outputs of the networks.

b) *Chromium from chromic acid or from dichromate as the single output*

The networks were trained and tested with titration curves with all collected points as the inputs and the expected chromium from chromic acid as the output (only one output). In the other operation, only the expected chromium from dichromate was provided as the output.

c) *Chromium from chromic acid and the first half of titration curve*

The networks were trained and tested with first halves of titration curves (the part of titration curves with the first end-point) as the inputs. These halves of titration curves were from curves with all collected points. The corresponding output was the expected chromium from chromic acid. The accuracy of the neural networks was expected to improve. The first end-point in the titration of a sample solution containing chromic acid and dichromate is only due to the first dissociation of chromic acid.

3.3.1.3 Decreased range experimental design

A learning set in a decreased range experimental design, as seen in Figure 3.13, was formed by selection of some points of learning, training and test sets of the initial experimental design. The size of the learning set was the same as in the initial experimental design (25 points). Training and test sets (reduced in size) were obtained by additional acid-base titration experiments. Learning points formed rectangles with alternating training and test points in their centre (see an example of dashed rectangles in Figure 3.13).

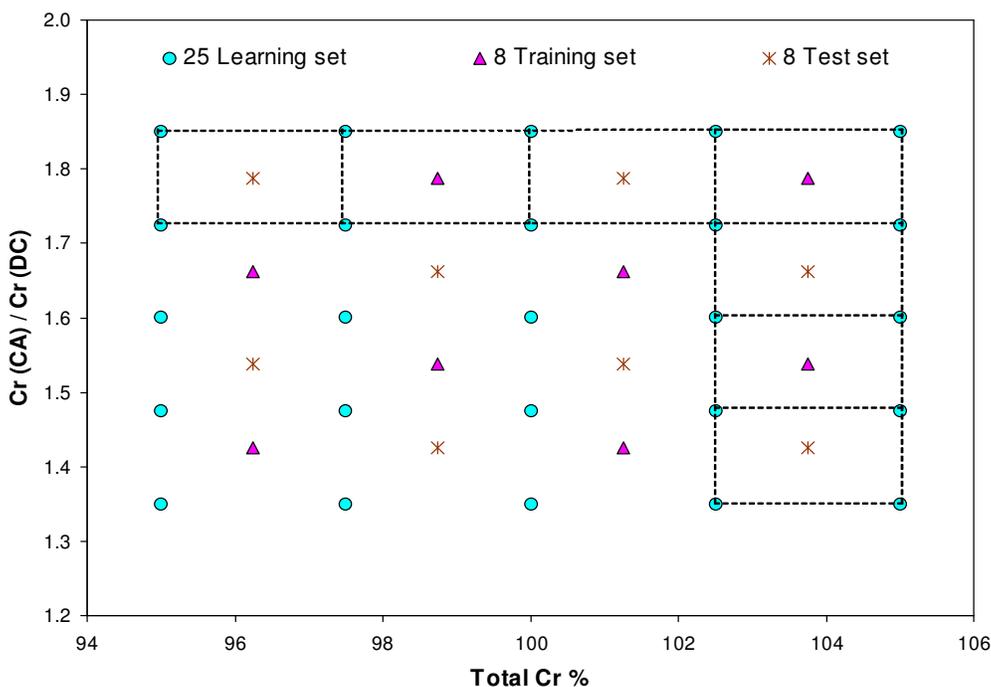


Figure 3.13 Decreased range experimental design

Only titration curves with all collected points were used as the inputs to the neural networks. The corresponding outputs were the expected chromium from chromic acid and total chromium concentrations.

3.3.1.4 Increased learning and test sets of the experimental design

In this experimental design, learning and training sets were from increased learning density experimental design. Test set was created by combining training and test sets of a decreased range experimental design. Some test points formed rectangles with learning points at their centres, but there are

two rectangles with training points at their centres and the two remaining rectangles have no points at their centres.

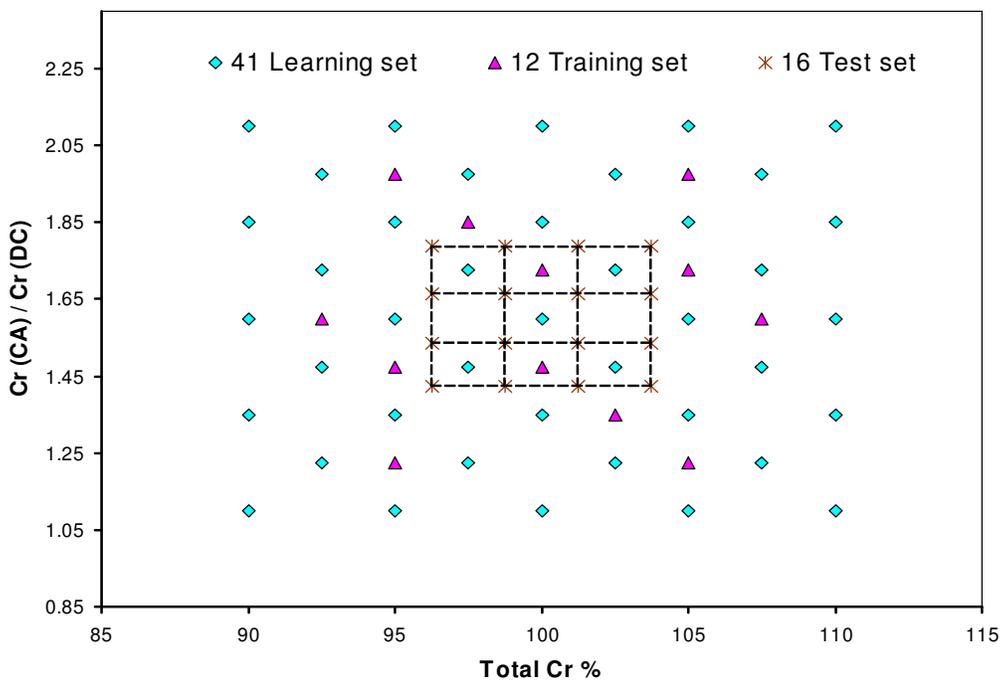


Figure 3.14 Increased learning and test sets of the experimental design

Since the neural networks were already trained with titration curves with all collected points as the inputs and chromium from chromic acid and total chromium concentrations as the inputs, they were just validated with the new test set of data.

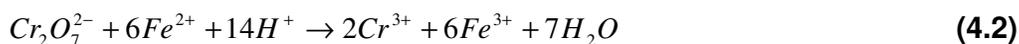
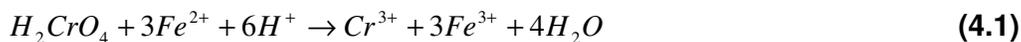
CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 Redox potentiometric titration

Redox titration experiment was performed with the aim of quantifying the concentrations of chromic acid and dichromate, in a sample solution containing chromium trioxide (CrO_3) and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$). These chromium solutions were titrated against Fe(II) solution as titrant. Chromium(VI) solutions are very oxidizing and when titrated with Fe(II) solution, hexavalent chromium was reduced to green trivalent chromium. Fe(II) is a reducing agent and it was oxidized to Fe(III).

Equations 4.1 and 4.2 apply when chromic acid (H_2CrO_4) and dichromate react with Fe(II), respectively.



Both reactions are pH dependent. The experiment was performed in acidic medium, H_2SO_4 , and in the presence of nitrogen gas to prevent hydrolysis as well as unnecessary oxidation due to atmospheric oxygen.

Figure 4.1 shows redox titration results obtained when sodium dichromate samples were titrated with a Fe(II) solution. These samples were 200 times less concentrated than the chromium samples at the 8th stage of the industrial electrolytic process. At the 8th stage of the industrial electrolytic process, the average content of chromium from chromic acid is 320 g/L and for simplicity, this is here referred to as 100% chromium content. The average content of chromium from dichromate at the 8th stage is 210 g/L.

In Figure 4.1, curve A is for a sodium dichromate sample containing 1.210 g/L of chromium and this is equivalent to 110% chromium content from dichromate of the 8th stage of the industrial process. Curve B corresponds to a sodium dichromate sample containing 1.050 g/L of chromium and this is equivalent to 100% chromium content from dichromate in the industrial process. Curve C is for a sodium dichromate sample containing 0.890 g/L of chromium and this is equivalent to 90% chromium content of the 8th stage of industrial process.

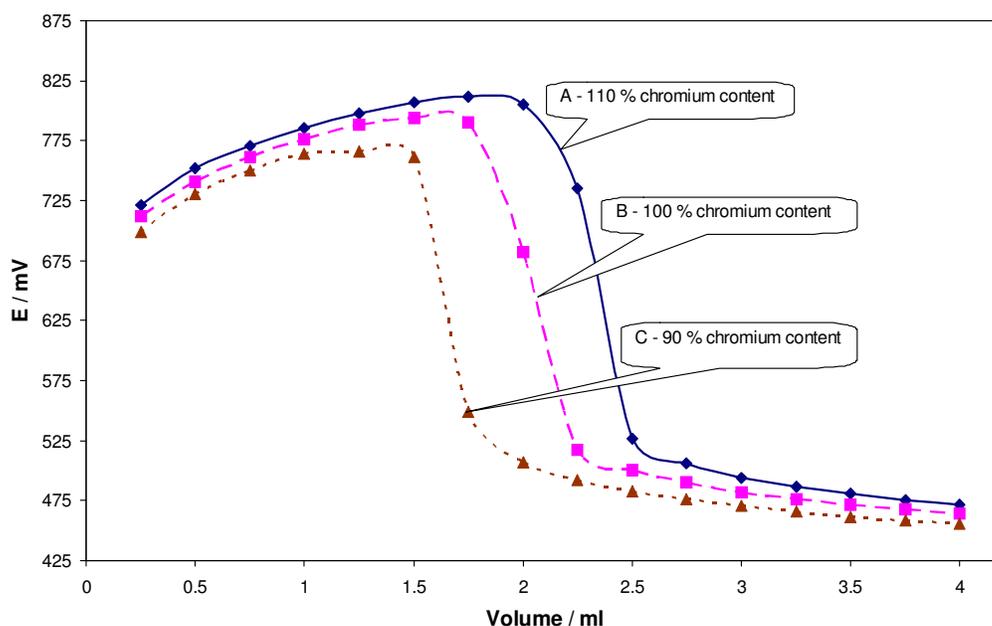


Figure 4.1 Redox titration of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ samples against 0.6 M Fe(II) solution in 1.4 M H_2SO_4 solution. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

Figure 4.2 shows the results obtained when 200 times less concentrated chromic acid samples were titrated with Fe(II) solution. Curve A is for a chromic acid sample containing 1.76 g/L of chromium and this is equivalent to 110% chromium content of the 8th stage of the industrial electrolytic process. Curve B corresponds to chromic acid sample containing 1.60 g/L and is equivalent to 100% chromium content from chromic acid in the industrial process. Curve C is for a chromic acid sample containing 1.44 g/L of chromium and this is equivalent to 90% chromium content from chromic acid in the 8th stage of the industrial electrolytic process.

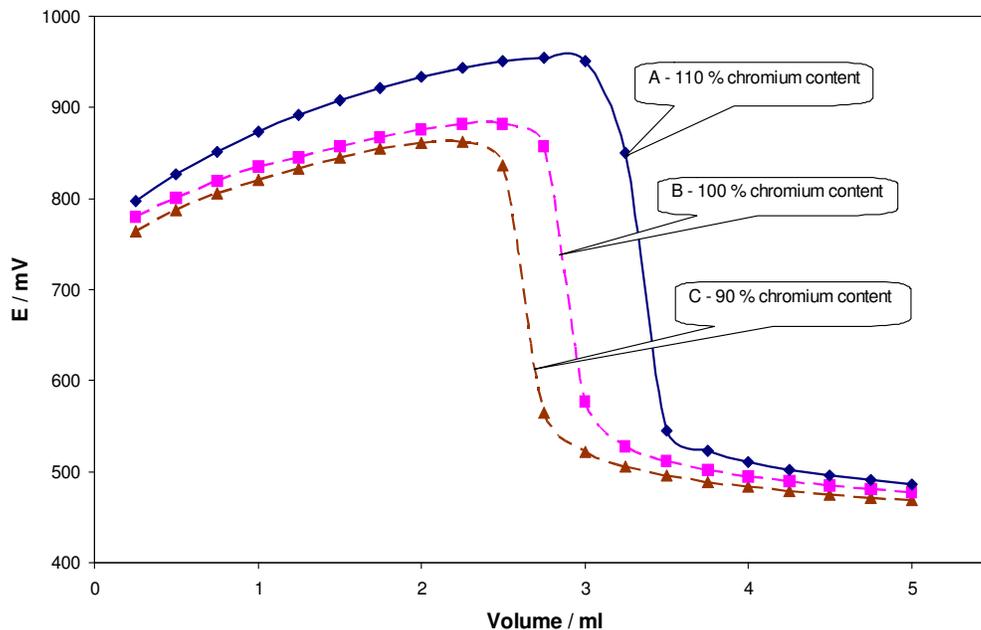


Figure 4.2 Redox titration of H_2CrO_4 samples against 0.6 M Fe(II) solution in 1.4 M H_2SO_4 solution. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

For simplicity, dichromate sample containing 0.890 g/L of chromium (this is equivalent to 90% of average chromium content at the 8th stage of the industrial process) was referred here to as 90% dichromate sample. Dichromate solution containing 1.050 g/L of chromium (equivalent to 100% of average chromium content of the industrial sample) was referred to as 100% dichromate sample. Dichromate sample containing 1.210 g/L of chromium that is equivalent to 110% chromium content of the industrial samples was referred to as 110% dichromate sample. The same nomenclature was used for chromic acid samples.

Chromium concentration in 90% dichromate sample is not equal to chromium concentration in 90% chromic acid sample. Chromium concentrations in 100% dichromate sample and 100% chromic acid sample are also not equal. The same applies to 110 % dichromate and 110% chromic acid samples.

On the other hand, a sample containing 8.900 g/L of chromium from dichromate (equivalent to 90% chromium content of the 8th stage of the industrial process) and 17.600 g/L of chromium from chromic acid (equivalent

to 110% chromium content), contains the same amount of total chromium as a sample containing 12.100 g/L of chromium from dichromate (equivalent to 110% chromium content) and 14.400 g/L of chromium from chromic acid (equivalent to 90% chromium content of the 8th stage of the industrial process). A sample that was 100% dichromate and 100% chromic acid contains the same total chromium as the above chromium samples. These samples were 20 times less concentrated than chromium samples of the 8th stage of the industrial electrolytic process.

Titration of these chromium samples against Fe(II) solution resulted in the titration curves with identical equivalence points, see Figure 4.3. Total chromium concentration was the same in all three samples and it was equal to 26.500 g/L. Redox titration did not distinguish between chromic acid and dichromate in a sample contained chromium trioxide and dichromate.

Redox titration cannot distinguish chromium samples with constant total chromium concentration. In other words, a sample containing 90% of chromium from chromic acid and 110% of chromium from dichromate cannot be distinguished from a sample containing 110% of chromium from chromic acid and 90% of chromium from dichromate. These samples cannot be distinguished from a sample containing 100% of chromium from chromic acid and 100% of chromium from dichromate.

Titration of separate chromic acid and dichromate samples with equal chromium concentration also results in titration curves with identical equivalence points, see Figure 4.4. Prior to the equivalence point of the titration, there is a difference in the potential of chromic acid and dichromate samples. The difference occurred as a result of the difference in the acidity of the samples. Chromic acid solution is more acidic than dichromate solution that contains the same amount of chromium concentration. The difference in potential of chromic acid and dichromate is too small to be used for speciation purpose.

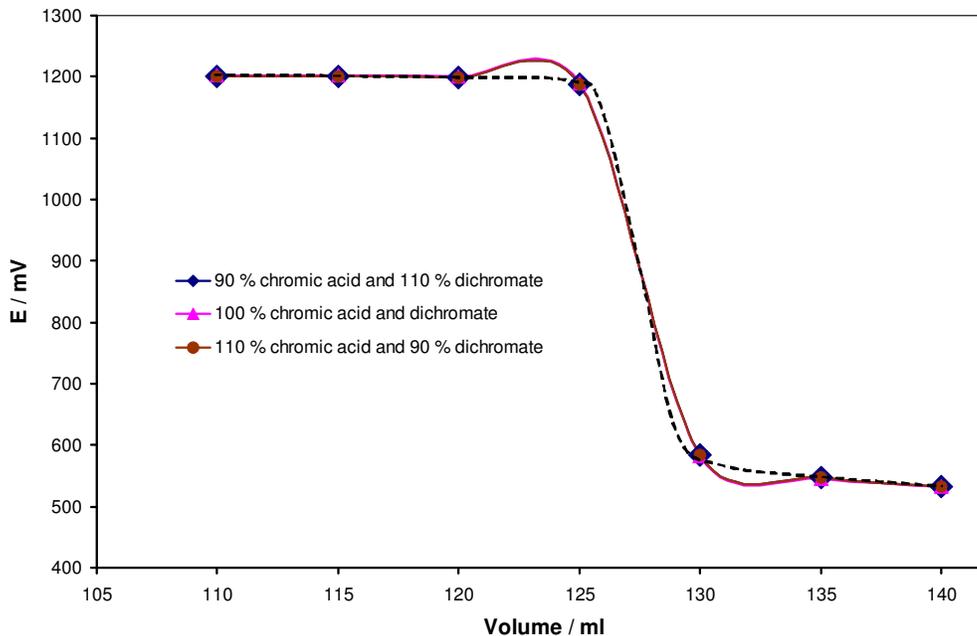


Figure 4.3 Redox titration of chromium samples against 0.6 M Fe(II) solution in 3 M H_2SO_4 solution. The total chromium concentration was equal in all three samples. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution). (Solid lines were generated by MS Excel)

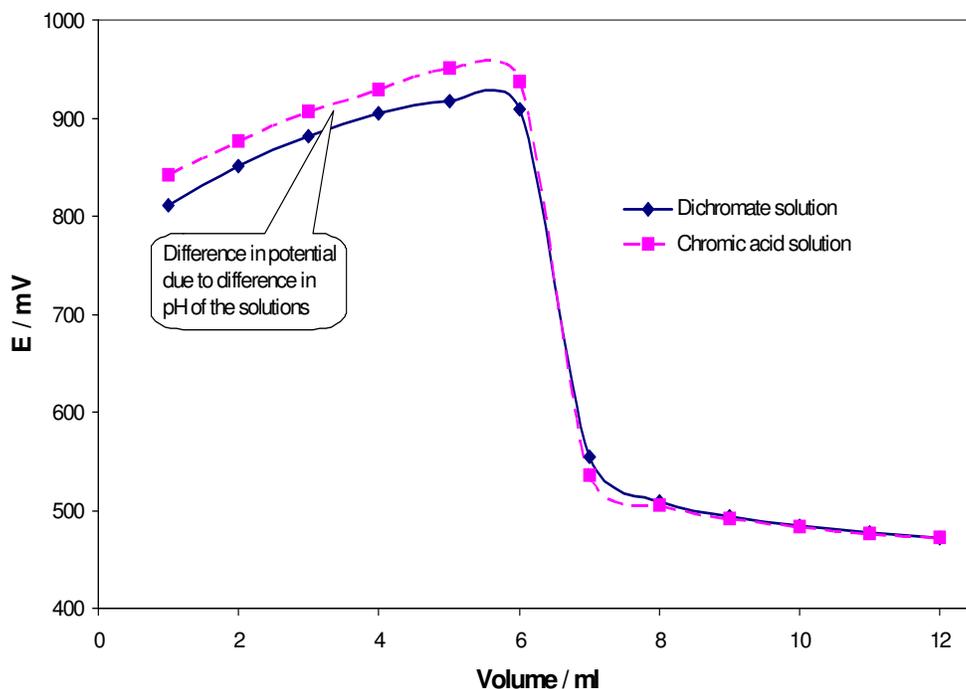


Figure 4.4 Redox titration of chromic acid and dichromate samples against 0.5 M Fe(II) solution in 1.4 M H_2SO_4 solution. Chromium concentration in chromic acid sample was equal to chromium concentration in dichromate sample. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

A redox titration can be used to distinguish chromium samples that do not contain the same amount of the total chromium concentration. However, they cannot be used to distinguish between chromic acid and dichromate in those samples. Figure 4.5 shows titration results obtained when chromium samples containing different total chromium concentration were titrated against a Fe(II) solution. Curve A corresponds to chromium sample contained 6.5100 g/L of the total chromium concentration and this is equivalent to 110% chromium content of the industrial process. Curve B and C correspond to 100% and 90% of the total chromium content of the 8th stage of the industrial process. These samples contain 5.8700 and 5.2300 g/L of the total chromium concentration, respectively. These samples are 100 times diluted as compared to the industrial samples at the 8th stage of the process.

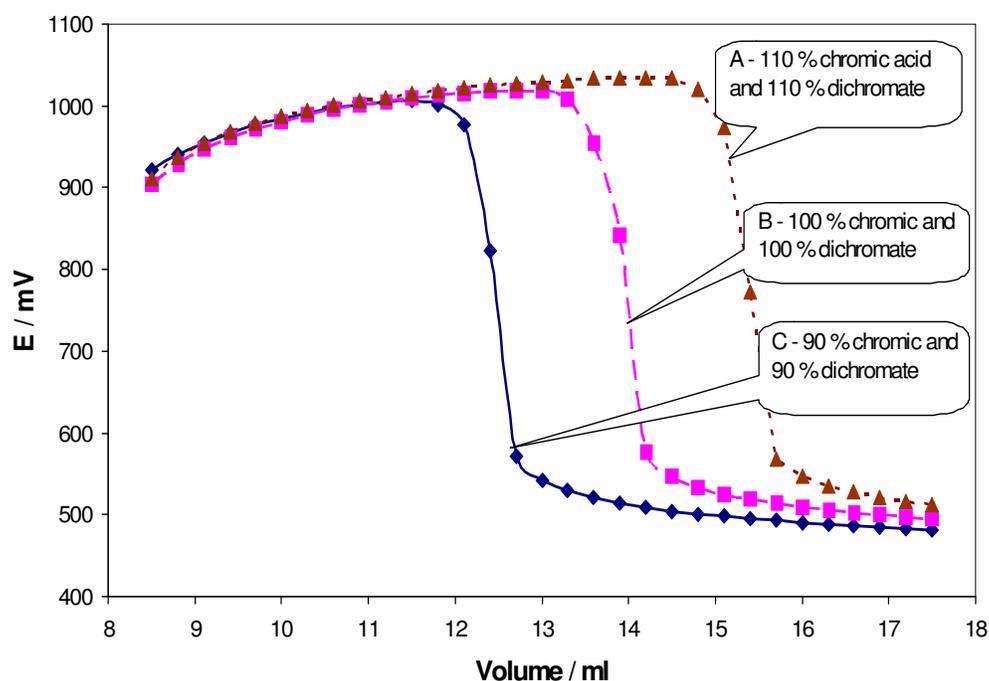


Figure 4.5 Redox titration of chromium samples against 0.5 M Fe(II) solution in 1 M H₂SO₄ solution. The total chromium concentration in all three samples was different. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

4.2 Titration of chromium(VI) sample solutions against sodium hydroxide solution.

Both chromium trioxide and sodium dichromate are soluble in water and give rise to a variety of chemical species. Predominance and concentration of those species depend on the concentration of chromium(VI) and pH of the solution [70]. When dissolved in water, chromium trioxide forms chromic acid (H_2CrO_4), equation 4.3. Titration of chromic acid solution with sodium hydroxide as a titrant yields two well defined end-points; each end-point was determined from a rapid change in pH with addition of sodium hydroxide solution.



The first end-point of the titration was reached when chromic acid (H_2CrO_4) was partly neutralized to form bichromate ion ($HCrO_4^-$), equation 4.4. Further increase in the pH of the solution caused total neutralization of chromic acid and formation of chromate ion (CrO_4^{2-}), equation 4.5. Figure 4.6 shows an example of acid-base titration curves obtained when chromic acid and dichromate solutions were titrated against sodium hydroxide solution.

In the titration of chromic acid against sodium hydroxide, the first end-point is indicated as EP_1 as shown in Figure 4.6. The second end-point is indicated as EP_2 . The second end-point is twice the volume of the first end-point; this is expected since it takes two protons for chromic acid to dissociate completely. Depending on the initial concentration of chromium trioxide solution, chromic acid is dominant at pH below 1; around pH 6, bichromate ion is the main chromium(VI) species. Chromate ion is dominant at pH above 12. The initial concentration of chromium trioxide was 0.0554 M for the curves shown in Figure 4.6. At higher chromic acid concentration, bichromate ion dimerizes and forms dichromate ion. At such condition, both bichromate and dichromate ions are at equilibrium.

When dichromate is dissolved in water, bichromate ion is formed to some extent, equation 4.6. The concentration of bichromate ion in that solution depends on the initial concentration of dichromate. Titration of dichromate solution against sodium hydroxide caused bichromate ion to deprotonate and form chromate ion, equation 4.7.



Only one jump is observed when dichromate solution is titrated with sodium hydroxide solution and it is seen as EP₃ in Figure 4.6. The initial concentration of dichromate solution was 0.0233 M.

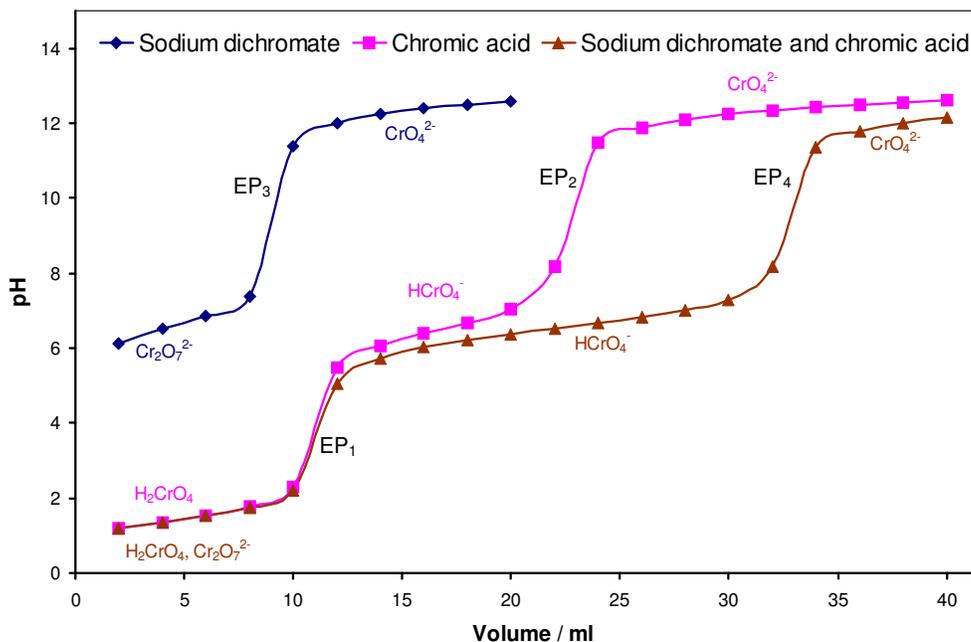


Figure 4.6 Titration of chromium(VI) solutions against 0.1 M sodium hydroxide solution as a titrant. \diamond = 0.0233 M dichromate sample and \square = 0.0554 M chromic acid sample. Δ = chromic acid and dichromate sample.

The titration of a sample solution containing a mixture of chromic acid and dichromate against sodium hydroxide resulted in two end-points of titration. This chromium(VI) sample was prepared by mixing 0.0233 M dichromate

sample and 0.0554 M chromic acid sample. The first end-point was equivalent to the first end-point (EP_1) observed during the titration of separate chromic acid sample. This was expected because the concentration of chromic acid in both samples was identical.

During the titration of a sample mixture of chromic acid and dichromate, chromic acid was neutralized to form bichromate ion. This resulted in the first end-point of the titration. The second end-point (EP_4) was not reached at the same volume of titrant added as the second end-point (EP_2), observed in the titration of a separate chromic acid sample. It was also not equivalent to the end-point (EP_3) observed in the titration of separate dichromate sample. Dichromate did not affect the first end-point (EP_1) of the titration because it unchanged. The second end-point has shifted far to the right. This indicates that dichromate had contributed to the second end-point (EP_4).

The pH of a separate chromic acid sample was around 1 and that of dichromate sample was around 6. The pH of chromium sample containing a mixture of chromic acid and dichromate was around 1. In fact, it was the same as the pH of chromic acid sample before mixing. Neutralization of bichromate ion formed from both chromic acid and dichromate, took place at pH above 6. The concentration of bichromate ion in the solution has increased. An increase in the pH of the solution caused bichromate ion to deprotonate and form chromate ion, and that resulted in the second end-point (EP_4) of the titration. This end-point (EP_4), was not due to the second neutralization of just chromic acid or due to dichromate ion in the sample mixture. It was as a result of neutralization of bichromate ion formed from both chromic acid and dichromate in a sample, at the pH above 6.

To determine the volume of the titrant consumed due to the dichromate content in a sample of chromic acid and dichromate, the following equation was applied:

$$EP_{DC} = EP_4 - 2EP_1 \quad (4.8)$$

In equation 4.8, EP_{DC} is the end-point (ml) of the titration due to dichromate in a sample of chromic acid and dichromate. EP_1 is the first end-point (ml) observed during the titration of a sample of chromic acid and dichromate and is equivalent to the first end-point (EP_1) observed in the titration of separate chromic acid solution. EP_4 is the second end-point (ml) observed during the titration of a sample of chromic acid and dichromate against sodium hydroxide solution.

The acid-base titration permitted the quantification of the concentrations of chromic acid and dichromate in a sample of chromium trioxide and sodium dichromate. It is a suitable technique to be used in the determination of chromic acid and dichromate in concentrated electrolyte samples of chromic acid and dichromate in the industrial electrolytic process used to produce chromic acid.

The concentrations of chromic acid and dichromate were determined in a samples mixture of chromic acid and dichromate following the initial experimental design (see Figure 2.4). All titration curves generated according to the initial experimental design, were fitted with a modified sigmoid equation (equation 3.3). The results obtained for the concentrations of chromic acid and dichromate in the training, learning and test sets are shown in the Tables 4.1 to 4.6.

In the training set, the concentration of chromic acid was determined with an absolute percentage error of 1.21 ± 0.12 , see Table 4.1. There were 16 points (acid-base titration curves) in the training set. The concentration of chromic acid was determined with an absolute percentage error of greater than 1%. An absolute percentage error of greater than 1% is not acceptable to the manufacturer of chromic acid.

The concentration of dichromate was determined with an absolute percentage

Table 4.1 The comparison of the expected and experimentally determined concentrations of chromic acid (H_2CrO_4) in the training set of data of the initial experimental design.

Sample number	Concentration of chromic acid (H_2CrO_4)/ M		Error	Absolute % error
	Expected	Experimental		
1	0.3568	0.3530	-0.0038	1.0600
2	0.3403	0.3359	-0.0043	1.2708
3	0.3203	0.3162	-0.0042	1.2979
4	0.2959	0.2923	-0.0037	1.2404
5	0.3402	0.3365	-0.0038	1.1065
6	0.3244	0.3208	-0.0036	1.1127
7	0.3054	0.3024	-0.0030	0.9985
8	0.2822	0.2787	-0.0035	1.2239
9	0.3236	0.3204	-0.0033	1.0066
10	0.3086	0.3044	-0.0042	1.3662
11	0.2905	0.2867	-0.0039	1.3333
12	0.2684	0.2650	-0.0034	1.2512
13	0.3070	0.3031	-0.0039	1.2782
14	0.2928	0.2894	-0.0034	1.1461
15	0.2756	0.2719	-0.0038	1.3672
16	0.2546	0.2513	-0.0033	1.2911
No. of curves in a set = 16	Average errors		-0.0037	1.21 ± 0.12

Table 4.2 The comparison of the expected and experimentally determined concentrations of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) in the training set of data of the initial experimental design.

Sample number	Concentration of $Na_2Cr_2O_7 \cdot 2H_2O$ / M		Error	Absolute % error
	Expected	Experimental		
1	0.0903	0.0949	0.0045	4.9981
2	0.0986	0.1031	0.0045	4.5302
3	0.1086	0.1131	0.0045	4.1844
4	0.1208	0.1248	0.0040	3.3274
5	0.0861	0.0905	0.0044	5.0526
6	0.0940	0.0979	0.0038	4.0776
7	0.1035	0.1069	0.0033	3.2323
8	0.1152	0.1191	0.0040	3.4313
9	0.0819	0.0859	0.0039	4.7993
10	0.0894	0.0938	0.0044	4.9044
11	0.0985	0.1026	0.0041	4.1564
12	0.1096	0.1131	0.0035	3.2334
13	0.0777	0.0819	0.0042	5.3522
14	0.0849	0.0882	0.0034	3.9908
15	0.0934	0.0973	0.0038	4.1074
16	0.1039	0.1078	0.0039	3.7435
No. of curves in a set = 16	Average errors		0.0040	4.20 ± 0.69

error of 4.20 ± 0.69 . This is shown in Table 4.2. The determination of dichromate concentration is significantly less accurate when compared with accuracy achieved for chromic acid.

An absolute percentage error of 0.90 ± 0.21 was obtained in the determination of chromic acid concentration (as shown in Table 4.3). In the determination of dichromate concentration, an absolute percentage error of $< 1\%$ was not achieved in the learning set of data. Dichromate was determined with an absolute percentage error of 3.57 ± 0.82 as shown in Table 4.4. There were 25 points in the learning set of the initial experimental design.

Table 4.3 The comparison of the expected and experimentally determined concentrations of chromic acid (H_2CrO_4) in the learning set of data of the initial experimental design.

Sample number	Concentration of chromic acid (H_2CrO_4)/ M		Error	Absolute % error
	Expected	Experimental		
1	0.3726	0.3667	-0.0059	1.5877
2	0.3570	0.3535	-0.0035	0.9757
3	0.3385	0.3347	-0.0038	1.1241
4	0.3160	0.3138	-0.0021	0.6677
5	0.2881	0.2858	-0.0023	0.8134
6	0.3556	0.3521	-0.0035	0.9855
7	0.3408	0.3389	-0.0019	0.5582
8	0.3231	0.3208	-0.0023	0.6996
9	0.3016	0.2991	-0.0025	0.8427
10	0.2750	0.2729	-0.0021	0.7495
11	0.3387	0.3357	-0.0030	0.8789
12	0.3246	0.3219	-0.0026	0.8147
13	0.3077	0.3049	-0.0028	0.9081
14	0.2872	0.2849	-0.0023	0.7969
15	0.2619	0.2593	-0.0026	0.9780
16	0.3218	0.3186	-0.0031	0.9739
17	0.3083	0.3048	-0.0036	1.1617
18	0.2923	0.2898	-0.0025	0.8625
19	0.2729	0.2706	-0.0023	0.8270
20	0.2488	0.2467	-0.0021	0.8375
21	0.3048	0.3025	-0.0023	0.7666
22	0.2921	0.2903	-0.0018	0.6012
23	0.2769	0.2739	-0.0031	1.1032
24	0.2585	0.2556	-0.0030	1.1441
25	0.2357	0.2337	-0.0020	0.8681
No. of curves in a set = 25	Average errors		-0.0028	0.90 ± 0.21

Table 4.4 The comparison of the expected and experimentally determined concentrations of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) in the learning set of data of the initial experimental design.

Sample number	Concentration of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ / M		Error	Absolute % error
	Expected	Experimental		
1	0.0887	0.0916	0.0029	3.2530
2	0.0965	0.1007	0.0043	4.4077
3	0.1058	0.1096	0.0038	3.5950
4	0.1170	0.1199	0.0028	2.4311
5	0.1310	0.1346	0.0037	2.7939
6	0.0847	0.0890	0.0043	5.0698
7	0.0921	0.0950	0.0029	3.1937
8	0.1010	0.1040	0.0031	3.0424
9	0.1117	0.1152	0.0035	3.1385
10	0.1250	0.1285	0.0035	2.7983
11	0.0806	0.0845	0.0039	4.8352
12	0.0877	0.0912	0.0035	4.0187
13	0.0962	0.1000	0.0038	3.9730
14	0.1064	0.1098	0.0034	3.1812
15	0.1190	0.1226	0.0035	2.9778
16	0.0766	0.0803	0.0037	4.8153
17	0.0833	0.0876	0.0042	5.0626
18	0.0913	0.0945	0.0032	3.4490
19	0.1011	0.1041	0.0031	3.0470
20	0.1131	0.1158	0.0027	2.4302
21	0.0726	0.0751	0.0025	3.4960
22	0.0789	0.0811	0.0022	2.7690
23	0.0865	0.0905	0.0039	4.5480
24	0.0957	0.0996	0.0039	4.0470
25	0.1071	0.1103	0.0032	2.9630
No. of curves in a set = 25	Average errors		0.0034	3.57 ± 0.82

In the test set of data, the concentration of chromic acid was determined with an absolute percentage error of 0.35 ± 0.15 as shown in Table 4.5. An absolute percentage error of $\leq 1\%$ was not achieved in the determination of dichromate concentration, since it was determined with an absolute percentage error of 4.16 ± 0.61 , see Table 4.6.

Table 4.5 The comparison of the expected and experimentally determined concentrations of chromic acid (H_2CrO_4) in the test set of data of the initial experimental design.

Sample number	Concentration of chromic acid (H_2CrO_4)/ M		Error	Absolute % error
	Expected	Experimental		
1	0.3489	0.3472	-0.0017	0.4847
2	0.3308	0.3295	-0.0013	0.3930
3	0.3088	0.3071	-0.0017	0.5552
4	0.3485	0.3472	-0.0014	0.3920
5	0.3323	0.3311	-0.0012	0.3735
6	0.3129	0.3118	-0.0011	0.3447
7	0.2890	0.2880	-0.0011	0.3662
8	0.3327	0.3312	-0.0015	0.4519
9	0.3154	0.3148	-0.0006	0.1819
10	0.2944	0.2936	-0.0008	0.2808
11	0.3319	0.3305	-0.0015	0.4448
12	0.3165	0.3158	-0.0007	0.2261
13	0.2980	0.2979	-0.0001	0.0411
14	0.2753	0.2743	-0.0010	0.3598
15	0.3164	0.3154	-0.0011	0.3378
16	0.3000	0.2992	-0.0008	0.2618
17	0.2801	0.2796	-0.0005	0.1632
18	0.3153	0.3141	-0.0012	0.3935
19	0.3007	0.2996	-0.0011	0.3505
20	0.2831	0.2824	-0.0007	0.2372
21	0.2615	0.2608	-0.0007	0.2584
22	0.3002	0.2994	-0.0008	0.2689
23	0.2846	0.2835	-0.0011	0.3936
24	0.2657	0.2636	-0.0021	0.7946
No. of curves in a set = 24	Average errors		-0.0011	0.35 ± 0.15

All absolute errors obtained in the determination of chromic acid were negative. It means that the experimental concentrations of chromic acid were lower than expected. On the other hand, all absolute errors obtained in the determination of dichromate were positive, showing that the experimental concentrations of dichromate were more than expected. This is an indication of a systematic error, which may arise, for instance from curve fitting operation. Errors may also come from the experimental equipments or were introduced during sample preparation. They may also be introduced when the solutions were dispensed in a titration vessel, as a result of the bubbles in the tubing of the dosimat exchange units.

Table 4.6 The comparison the expected and experimentally determined concentrations of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) in the test set of data of the initial experimental design.

Sample number	Concentration of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ / M		Error	Absolute % error
	Expected	Experimental		
1	0.0943	0.0982	0.0039	4.1551
2	0.1034	0.1069	0.0036	3.4582
3	0.1144	0.1183	0.0039	3.4040
4	0.0882	0.0909	0.0027	3.0754
5	0.0963	0.1002	0.0038	3.9690
6	0.1061	0.1104	0.0043	4.0633
7	0.1180	0.1226	0.0046	3.9267
8	0.0899	0.0945	0.0046	5.0778
9	0.0986	0.1028	0.0042	4.2609
10	0.1090	0.1132	0.0041	3.7748
11	0.0840	0.0886	0.0046	5.4688
12	0.0917	0.0958	0.0041	4.4199
13	0.1010	0.1049	0.0039	3.8917
14	0.1124	0.1166	0.0043	3.7860
15	0.0855	0.0896	0.0041	4.8110
16	0.0938	0.0975	0.0038	4.0403
17	0.1037	0.1074	0.0037	3.5888
18	0.0798	0.0840	0.0042	5.2084
19	0.0872	0.0910	0.0039	4.4510
20	0.0960	0.1001	0.0042	4.3449
21	0.1067	0.1103	0.0035	3.2953
22	0.0811	0.0849	0.0038	4.6371
23	0.0889	0.0927	0.0038	4.2399
24	0.0984	0.1029	0.0039	4.5488
No. of curves in a set = 24	Average errors		0.0040	4.16 ± 0.61

Other possible causes of this systematic error are the reagents (sodium dichromate and chromium trioxide from CISA). Chromium trioxide might be contaminated with sodium dichromate. One should keep in mind that in the industrial electrolytic process used to produce chromic acid from dichromate solution; sodium dichromate cannot be converted completely into chromic acid and has to be separated from “chromic acid” (CrO_3). Therefore, there is high possibility that chromic acid might be contaminated with sodium dichromate.

Neither CrO_3 , nor $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ are 100% reagents, they are of technical and not reagent grade purity. CrO_3 must contain $\text{Cr}_2\text{O}_7^{2-}$ and vice versa.

These two systematic errors (negative and small for CrO_3 , positive and large for $\text{Cr}_2\text{O}_7^{2-}$) also indicate that CrO_3 is relatively clean. It contains small quantities of impurities. Since the presence of $\text{Cr}_2\text{O}_7^{2-}$ does not interfere in NaOH titration, it should be possible to determine CrO_3 from ANNs quite exactly. Unfortunately, large error for $\text{Cr}_2\text{O}_7^{2-}$ indicates significant impurities by CrO_3 and other forms of chromium. Because the presence of CrO_3 has influence on the $\text{Cr}_2\text{O}_7^{2-}$ determination, one cannot expect exact predictions by ANNs in this case.

4.3 Performance tests of ANNs models

After the neural networks were trained, they were tested with patterns that were not included in the training set. Testing operation was performed to check whether the neural networks had learned the patterns. When tested, the neural networks were expected to predict the concentrations of chromium from chromic acid and chromium from dichromate with an accuracy of $\leq 1\%$, on average. Percentage error of $\leq 1\%$ is the target error required by the manufacturer of chromic acid or CrO_3 ; they required that any developed ANNs model would be accepted, only if it can predict the concentrations of chromium from chromic acid or/and chromium from dichromate with an average percentage error of $\leq 1\%$. It was interesting to find out whether ANNs predictions for the sodium dichromate content could be better than results obtained for acid-base titrations

4.3.1 Initial experimental design

- a) *Titration curves with all collected titration points as the inputs; the expected chromium concentration from chromic acid and total chromium were the outputs.*

The following results were obtained when the neural networks were tested with the set of data from the initial experimental design. Titration curves with all collected points were used as the inputs and the outputs were the expected chromium concentrations from chromic acid and total chromium (chromium concentrations were calculated according to the experimental design).

The comparison of the expected and the predicted concentrations of chromium from chromic acid can be seen in Figure 4.7. There was good agreement between the expected and the predicted concentrations of chromium from chromic acid. Trained ANNs model that has 10 neurons in the hidden layer, relative mean square error (RMS) of 0.017257 and good patterns of 37.50% was able to predict the concentration of chromium from chromic acid with an accuracy of 0.72 ± 0.54 , on average. There were 24 points in the test set. The predicted absolute percentage error is below the target error of $\leq 1\%$, as required in the industrial electrolytic process.

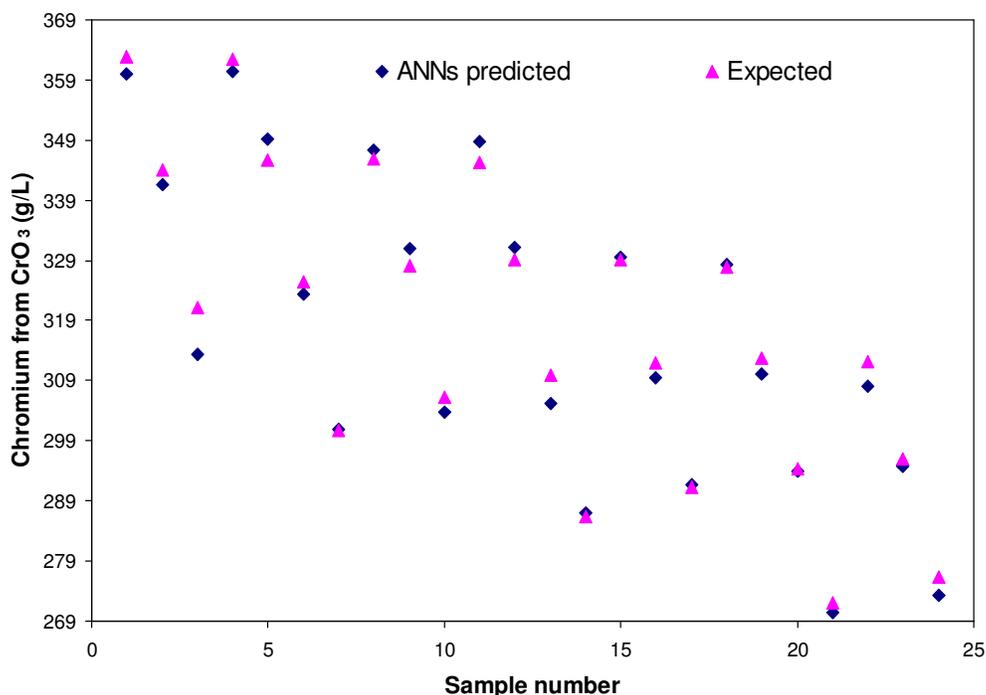


Figure 4.7 Test results obtained for chromium from chromic acid from the neural networks in which the titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the expected total chromium concentration.

During the testing process, RMS error of 0.012692 and good patterns of 41.70% were obtained (see brown dots in Figure 4.10). This showed that the number of patterns with errors less or equal to the target error of the neural networks had increased during the testing process. There would always be an RMS error and good patterns for both training and testing operations.

Since the outputs of the neural networks were only chromium from chromic acid and the total chromium concentrations, the contribution of chromium from dichromate was calculated as the difference between the two outputs. The comparison of the predicted and the expected concentrations of chromium from dichromate is shown in Figure 4.8.

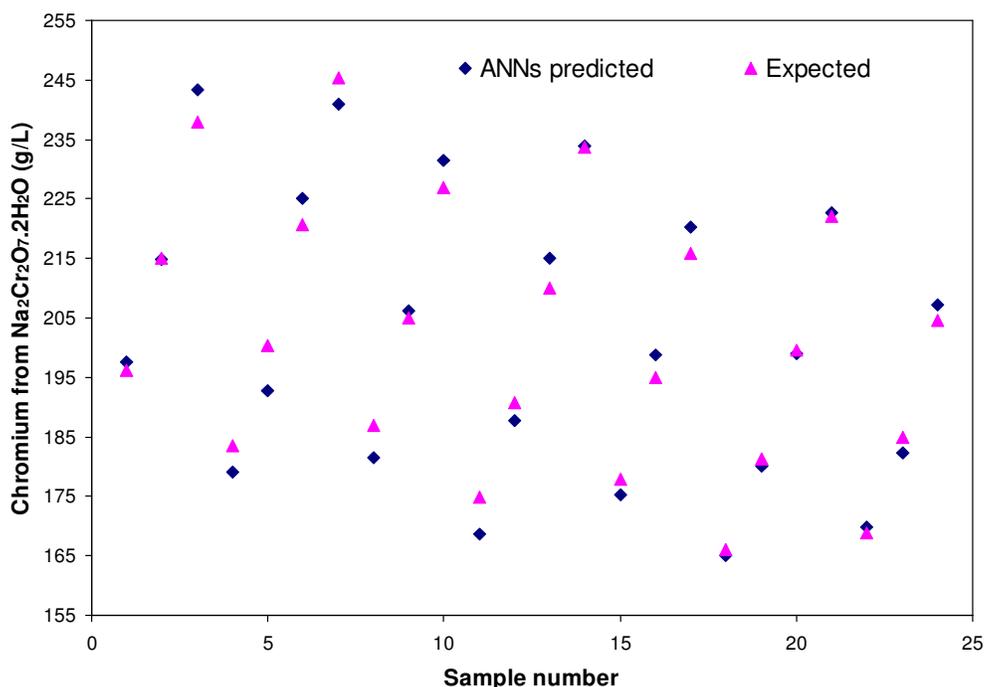


Figure 4.8 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium concentration. Concentration of chromium from dichromate was calculated as the difference between the total chromium and chromium from chromic acid.

Selected ANNs model was not able to predict the concentration of chromium from dichromate with required accuracy. The concentration of chromium from dichromate was predicted with an absolute percentage error of 1.54 ± 1.05 .

There was no good agreement between the predicted and the expected concentrations of chromium from dichromate. The total chromium concentration was predicted with an absolute percentage error of 0.486 ± 0.308 . From acid-base titration percentage error was greater than 4% and when the same titration curves were used as the inputs, Artificial Neural Networks gave much smaller absolute percentage error. ANNs work better than simple interpretation of acid-base titration curves.

The neural networks were able to predict chromium from chromic acid and total chromium with required accuracy. This accuracy was not achieved in the determination of dichromate. It appears that, particularly when industrial environment is considered, an error of between 1 to 3% should be expected, with more accurate estimate for chromic acid concentration.

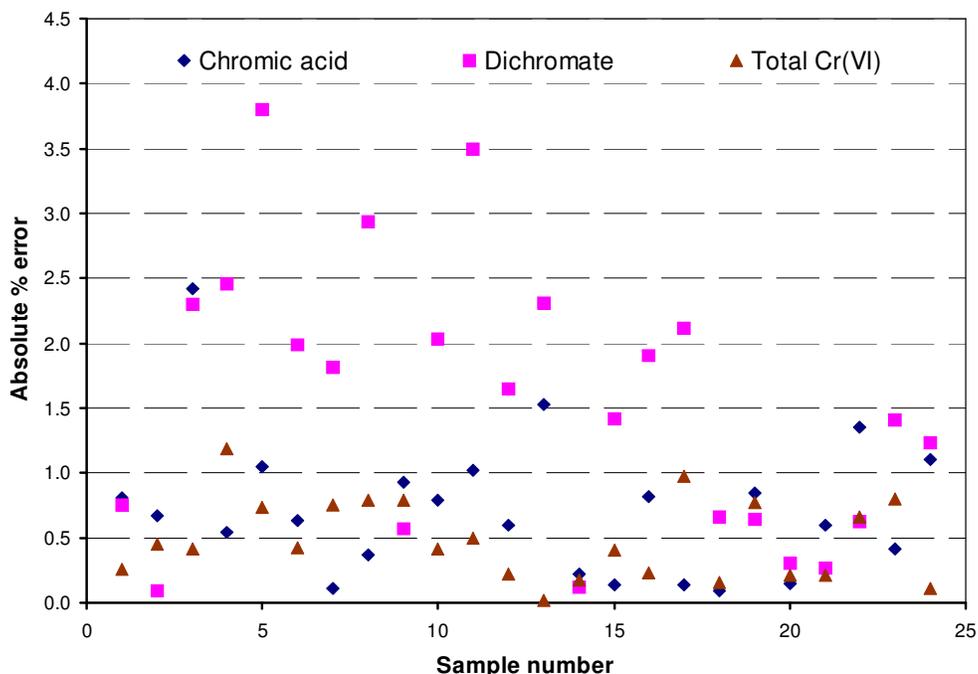


Figure 4.9 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium. The titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

The absolute percentage errors in the determination of chromium from chromic acid were between 0 and 2.5%. In the determination of chromium

concentration from dichromate, absolute percentage errors were between 0 and 4%. These variations are shown in Figure 4.9.

ANNs models were selected based on their generalization ability. Generalization is the ability of the neural networks that have been trained with a set of patterns to respond properly to the other patterns not belonging to the trained set. A model that results into the lowest RMS error during the testing operation was selected; only RMS error was considered initially when selecting ANNs model. It was noticed that the number of good patterns also has an effect on the accuracy of the neural networks.

Therefore, when selecting the best ANNs model, both RMS error and the number of good patterns (obtained during the testing operation) must be considered. Once again, trained neural networks with lowest RMS error and higher number of good patterns do not guarantee good prediction. A model that results into the highest number of good patterns during the testing operation seems to be the best one. Good pattern is the percentage of patterns with RMS error of less or equals to the error requirement of the neural networks (target error).

Figure 4.10 illustrates an RMS error and a number of good patterns obtained during the test operation, when trained networks models with similar number of good patterns but different RMS errors were tested. The number of good patterns was 37.50% in both models. An RMS error obtained in the third run of the trained networks was 0.13926. A model resulted from the fourth run of the trained networks had an RMS error of 0.017257.

During the testing operation, the number of good patterns had increased to 62.50% (see green dot in Figure 4.10) in the model obtained in the third run of the neural networks. The accuracy of the neural networks had increased, but not much, when the number of good patterns increased to 62.50%. This model predicted chromium from chromic acid with an absolute percentage error of 0.67 ± 0.53 . Chromium from dichromate was predicted with an absolute percentage error of 1.29 ± 0.95 . The relationship between RMS error

and the number of good patterns must be noted when selecting the best ANNs model. One must also take into consideration that there is no correlation between the accuracy of the neural networks and how many times they were trained. The neural networks may be trained as many times as possible, until the lowest or required RMS error is achieved. However, it is possible to obtain the lowest RMS error with just a single run.

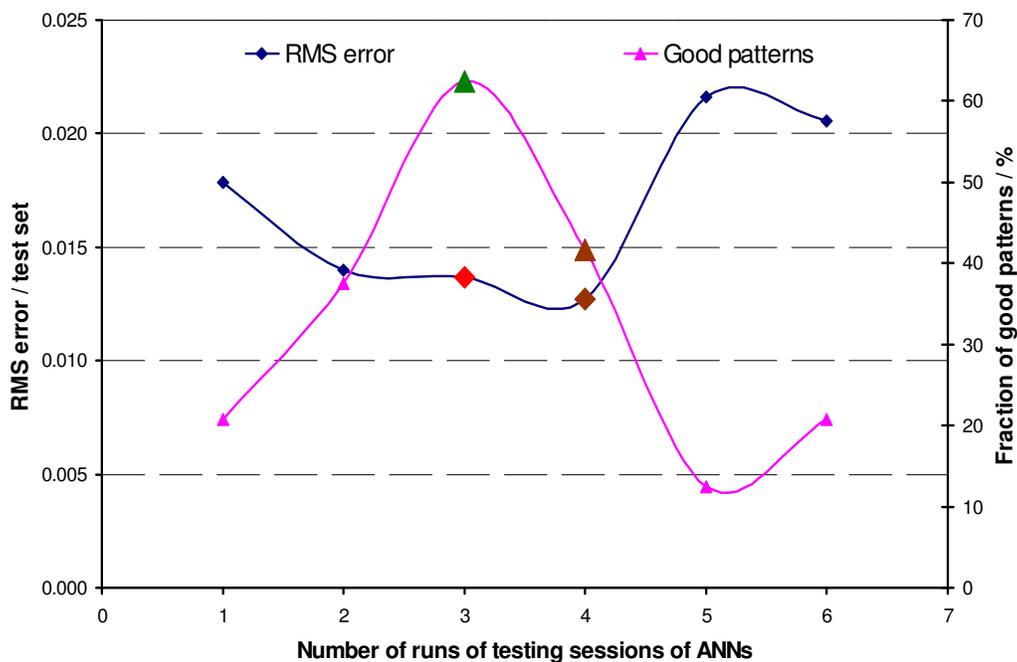


Figure 4.10 An example of variation in RMS error and number of good patterns with consecutive training/testing of ANNs. There were 10 neurons in the hidden layer. The titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were the expected concentrations of chromium from chromic acid and the total chromium. Chromium from dichromate was calculated as the difference between the total chromium and chromium from chromic acid.

- b) *Titration curves with all collected points as the inputs and the experimental concentrations of chromic acid and dichromate as the outputs.*

The neural networks were expected to predict better when provided with a set of titration curves with all collected points as the inputs and the experimental concentrations of chromic acid and dichromate as the outputs. The experimental concentrations of chromic acid and dichromate were obtained by

fitting acid-base titration curves (the inputs). One would expect better predictions in that case.

ANNs model with 10 neurons in the hidden layer, an RMS error of 0.01121 and good patterns of 50.00% predicted the concentration of chromic acid with an absolute percentage error of 0.93 ± 0.60 , for 24 points in the test set. The comparison of the predicted and the experimental concentrations of chromic acid is shown in Figure 4.11. The concentration of chromic acid was predicted with percentage error of $< 1\%$; but this percentage error is above the percentage error obtained when the expected chromium from chromic acid and the total chromium were used as the outputs of the neural networks. These results were not expected.

Similar results were obtained in the determination of chromium from dichromate. The concentration of dichromate was predicted with percentage error of 2.15 ± 1.27 . Percentage error predicted for the concentration of dichromate is above the percentage error predicted when the expected chromium from chromic acid and total chromium were used as the outputs of the neural networks. It was also above the target accuracy of $\leq 1\%$. The comparison of the predicted and the experimental concentrations of dichromate is show in Figure 4.12.

In the case where the experimental concentrations of chromic acid and dichromate were used as the outputs, the neural networks were not able to minimize the errors between the given and the predicted outputs, as in the case where the expected chromium from chromic acid and total chromium were used as the outputs of the networks. Percentage error has increased, particularly for dichromate determination.

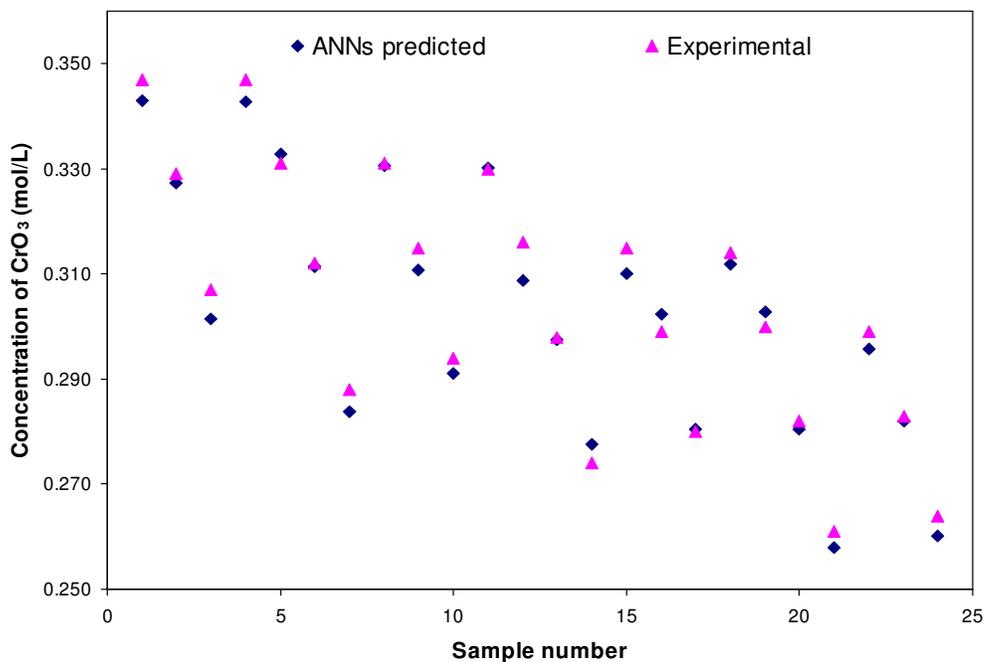


Figure 4.11 Test results obtained for chromic acid in the neural networks in which titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the concentrations of chromic acid and dichromate obtained by fitting titration curves (experimental concentrations).

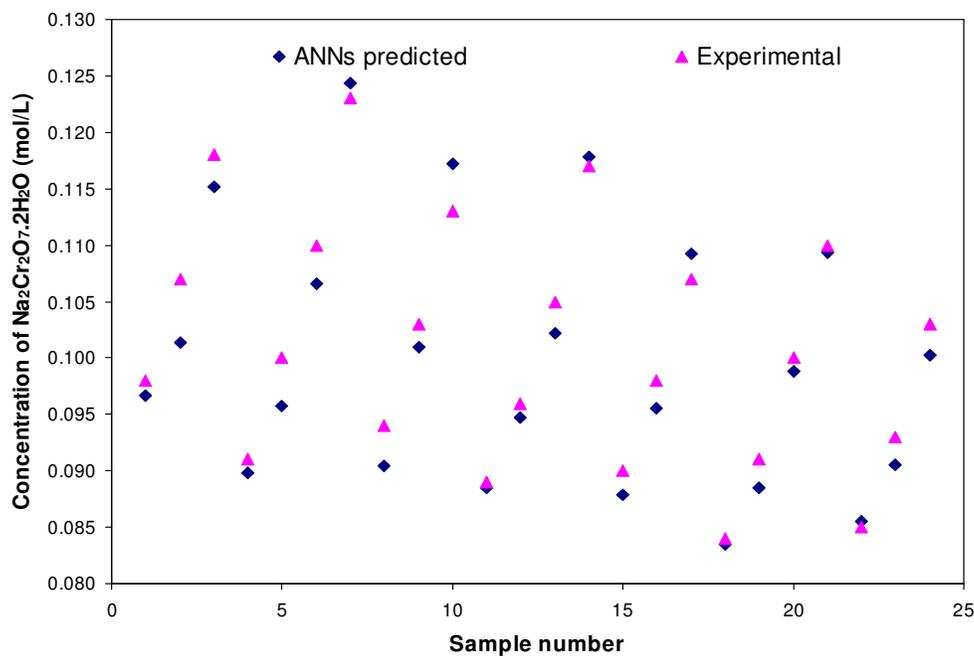


Figure 4.12 Test results obtained for dichromate concentration in the neural networks in which titration curves with all collected points from the initial experimental design were provided as the inputs. The outputs were the concentrations of chromic acid and dichromate obtained by fitting titration curves (experimental concentrations).

In the determination of chromic acid concentration, an absolute percentage error fluctuated between 0 and 2.5%. It was between 0 and 5.5% for dichromate concentration determination. These variations in absolute percentage errors can be seen in Figure 4.13.

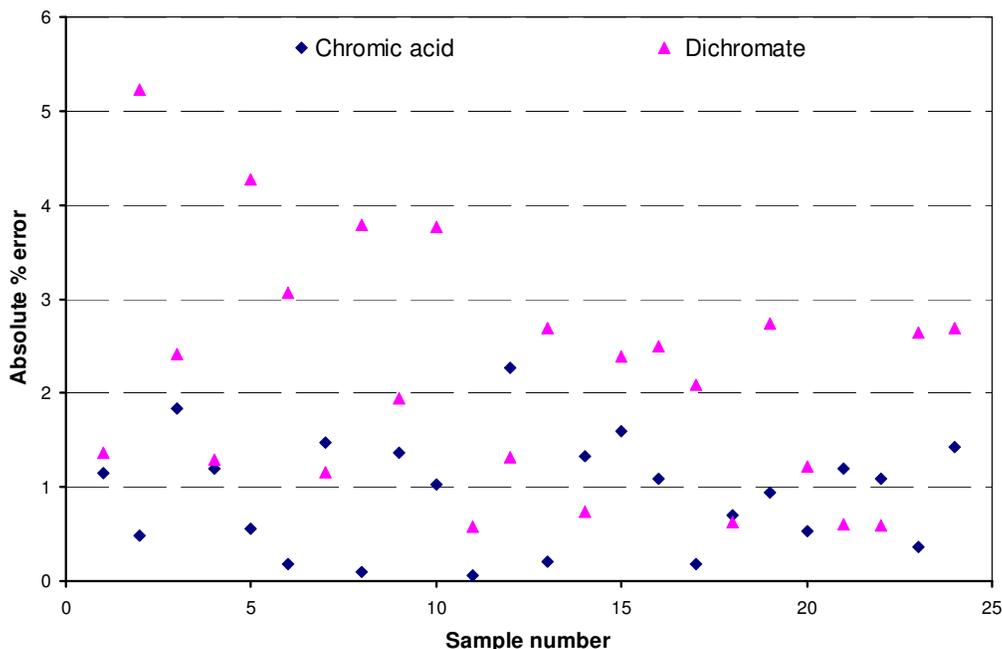


Figure 4.13 Variation in absolute percentage error of chromic acid and dichromate concentration. Titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were the concentrations of chromic acid and dichromate obtained by fitting the titration curves.

- c) *Titration curves with fewer points as the inputs and the expected chromium from chromic acid and total chromium as the outputs.*

The performance of the neural networks was reduced when titration curves (from the initial experimental design) with fewer points were provided as the inputs. The corresponding outputs were the expected chromium from chromic acid and total chromium concentrations. Trained ANNs model with 13 neurons in the hidden layer, RMS error of 0.017972 and good patterns of 12.50% predicted the concentration of chromium from chromic acid with absolute percentage error of 1.10 ± 0.74 . There were 24 points in the test set.

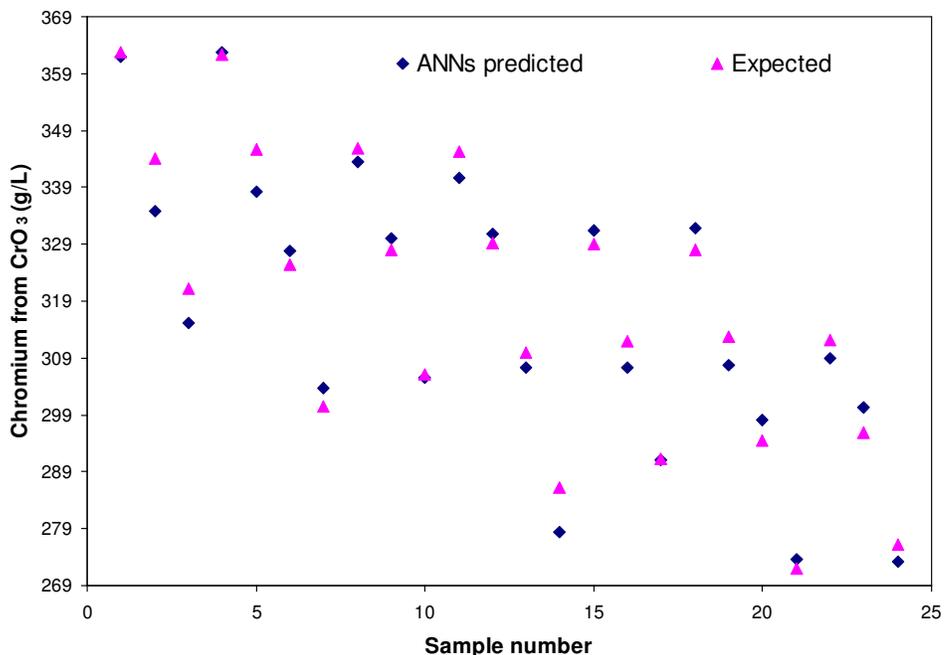


Figure 4.14 Test results obtained for chromium from chromic acid in the neural networks in which titration curves with fewer points from the initial experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium.

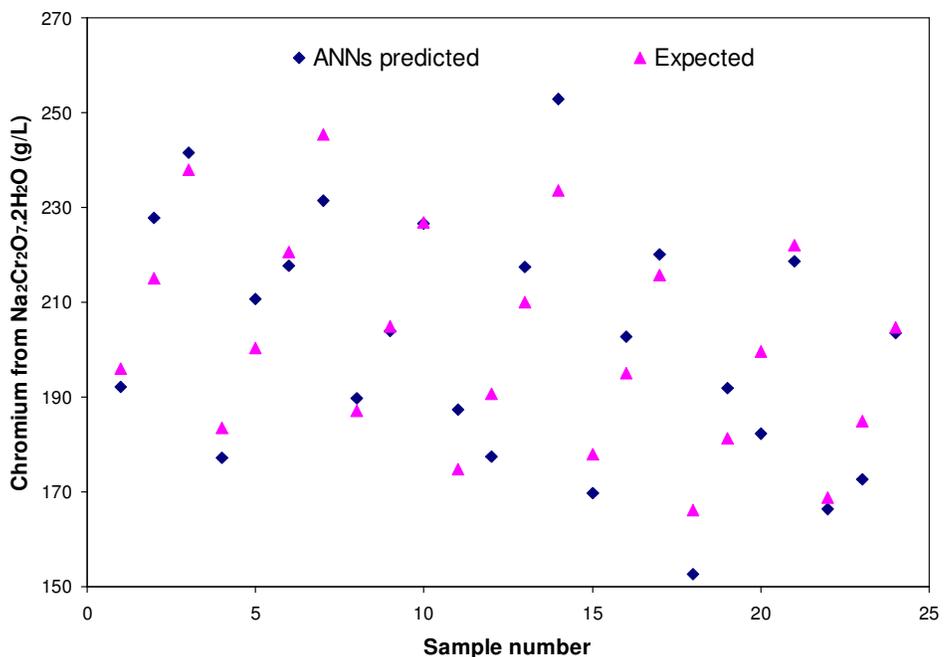


Figure 4.15 Test results obtained for chromium from dichromate in the neural networks in which titration curves with fewer points from the initial experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium. The concentration of chromium from dichromate was calculated as the difference between total chromium and chromium from chromic acid.

The comparison of the predicted and the expected concentrations of chromium from chromic acid is shown in Figure 4.14.

The concentration of chromium from dichromate was predicted with absolute percentage error of 4.03 ± 2.76 . There is no good agreement between the expected and the predicted concentrations of chromium from dichromate and these can be seen in Figure 4.15. The total chromium concentration was predicted with percentage error of 1.06 ± 0.75 .

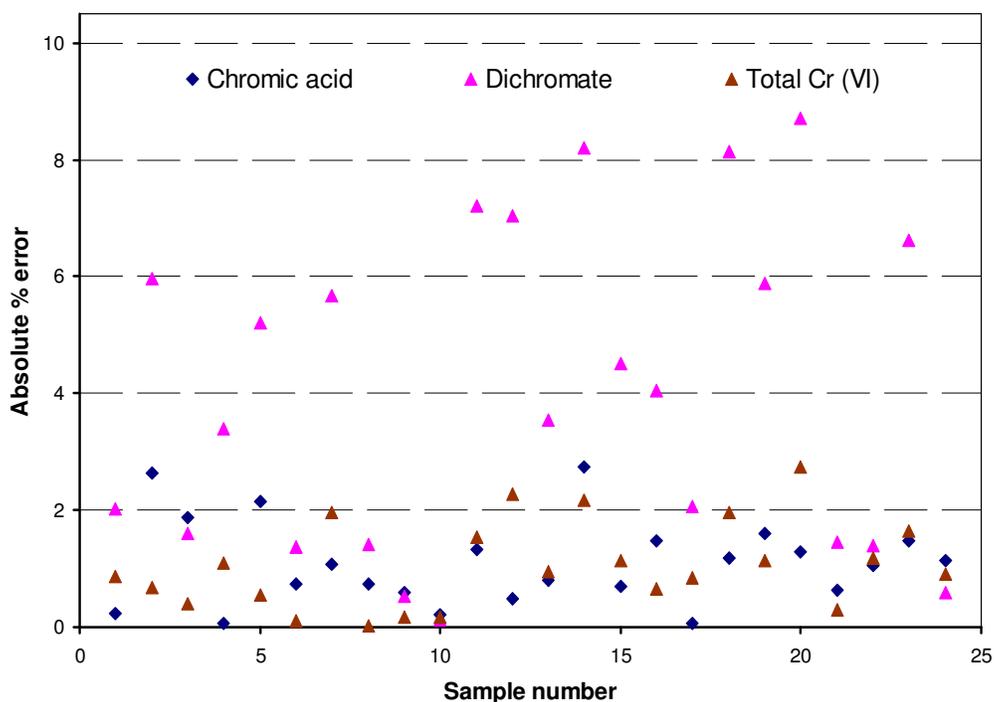


Figure 4.16 Variation in percentage error of chromium from chromic acid, dichromate concentration and total chromium concentration. Titration curves with fewer points from the initial experimental design were the inputs of the neural networks. The outputs were the expected concentrations of chromium from chromic acid and total chromium.

Absolute percentage error of $\leq 1\%$ was not achieved, both in the determination of chromic acid and dichromate concentrations. When the titration curves with fewer points were used as the inputs of the neural networks, the networks did not predict reasonably well. Training or testing the neural networks with acid-base titration curves with fewer points reduces the

time needed for the analysis or data collection steps; unfortunately, the accuracy of the neural networks also decreases.

In the determination of chromium concentration from chromic acid and total chromium concentration an absolute percentage error was fluctuating between 0 and 2.5%. It was fluctuating between 0 and 9% in the determination of chromium concentration from dichromate. These variations in absolute percentage errors are shown in Figure 4.16.

4.3.2 Increased learning data set in the experimental design

- a) *Titration curves with all collected points as the inputs and the expected chromium from chromic acid and the total chromium as the outputs.*

Trained ANNs model with 18 neurons in the hidden layer, RMS error of 0.012558 and good patterns of 50.0% predicted the concentration of chromium from chromic acid with absolute percentage error of 0.84 ± 0.50 , for 12 points in the test set. The inputs of the networks were acid-base titration curves with all collected points (from increased learning data in the experimental design). The outputs were the expected concentrations of chromium from chromic acid and total chromium.

The concentration of chromium from dichromate was predicted with absolute percentage error of 2.30 ± 1.45 . The total chromium concentration was predicted with absolute percentage error of 0.50 ± 0.29 . The concentration of chromium from chromic acid and total chromium were predicted well, but dichromate was predicted poorly. The comparisons of the expected and the predicted concentrations of chromium from chromic acid and from dichromate are shown in Figure A1 and Figure A2, respectively.

An absolute percentage error in the determination of concentrations of chromium from chromic acid and total chromium was fluctuating between 0 and 1.5%. In the determination of the concentration of chromium form dichromate, absolute percentage error was fluctuating between 0 and 5%.

These variations in an absolute percentage error in the determination of chromium from chromic acid, dichromate and total chromium can be seen in Figure A3.

Regardless of an average absolute percentage error obtained in the prediction of chromium concentration from chromic acid, which is less than 1%; these results were not expected in the neural networks with large learning set. Larger networks are expected to learn properly because they have large 'storage house' of data. Therefore, it should not be difficult for them to generalize a given set of patterns when tested.

It is important to keep the size of the training set larger, in the neural networks with large learning set. The performance of the networks would not improve as required, if the size of learning set was increased but the training set reduced. The size of the sets should not be too large to an extent that the networks might over-fit. The placement and the size of the test set must also be considered. Generally, the size of all sets play an important role as far as the accuracy of the neural networks is concerned.

It was noticed that when the number of good patterns (in the test operation) increased from 33.3 to 58.30% (see brown and green dots in Figure 4.17); the concentration of chromium from chromic acid was predicted with an absolute percentage error of 0.45 ± 0.59 . The concentration of chromium from dichromate was predicted with an absolute percentage error of 1.51 ± 1.21 , see Figure 4.17. The accuracy of the neural networks was enhanced, particularly in the prediction of chromium concentration from chromic acid. Trained ANNs model with an RMS error of 0.013807 and good patterns of 41.70% predicted chromium from chromic acid with good accuracy. However, this model was not able to predict the concentration of chromium from dichromate with an absolute percentage error of $\leq 1\%$ as required.

A model that had an RMS error of 0.12558 and good patterns of 50.0% did not predict both chromium from chromic acid and dichromate very well when

compared with a model with an RMS error of 0.013807 and good patterns of 41.70%.

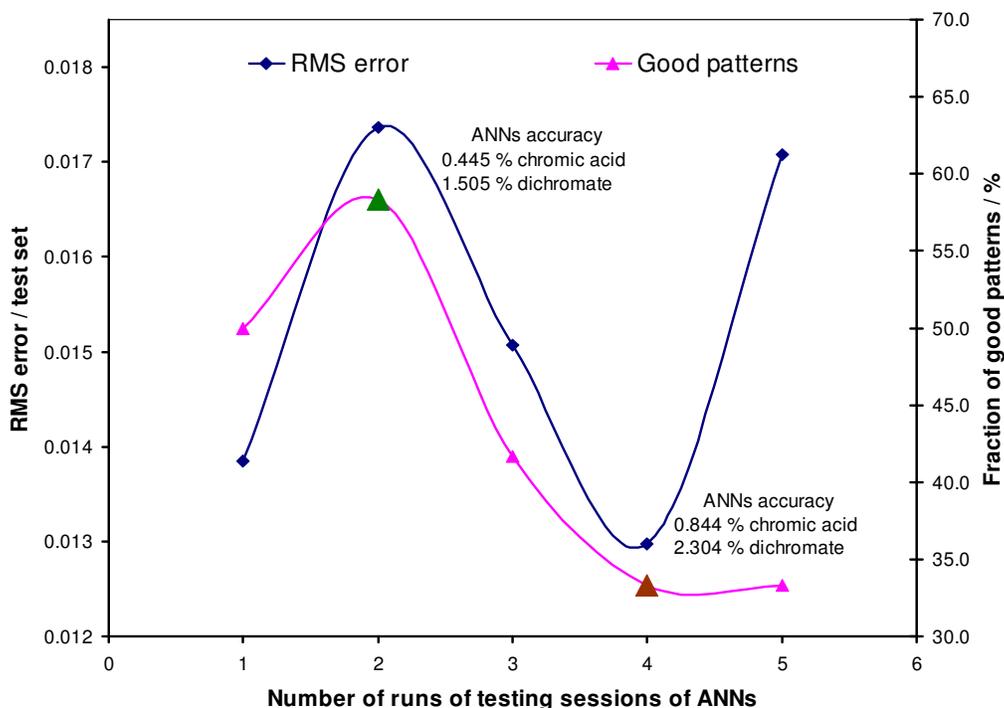


Figure 4.17 An example of variation in an RMS error and number of good patterns with consecutive training/testing of ANNs. There were 18 neurons in the hidden layer. Titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium. The concentration of chromium from dichromate was calculated as the difference between the total chromium and chromium from chromic acid.

A model obtained from the fourth run of the networks was selected because of its lower RMS error and higher number of good patterns (obtained during the training operation). When tested, that model resulted into the lower RMS error and lower number of good patterns. A model resulted from a second run of the neural networks was selected because of its higher number of good patterns (obtained in the test operation) which improved the performance of the neural networks. This model had higher RMS errors both in the training and testing operations, but is the best ANNs model. Note the RMS errors and the number of good patterns of these two models in the training operation.

- b) *Titration curves with fewer/reduced points as the inputs and the expected chromium from chromic acid and the total chromium as the outputs.*

ANNs model with 15 neurons in the hidden layer, an RMS error of 0.027606 and good patterns of 9.10% predicted the concentration of chromium from chromic acid with an absolute percentage error of 0.89 ± 0.36 , for 12 points in a test set. The total chromium concentration was predicted with an absolute percentage error of 0.77 ± 0.46 .

Titration curves with reduced or fewer points from an increased learning data set in the experimental design were the inputs. The outputs were the expected chromium from chromic acid and total chromium. The concentration of chromium from dichromate was predicted with percentage error of 2.60 ± 1.91 . However, it is less than an absolute percentage error predicted for chromium from dichromate in the neural networks from the initial experimental design, in which the titration curves with fewer or reduced points were used as the inputs.

Comparison of these results with the one obtained in the initial experimental design in the neural networks in which the inputs were the titration curves with fewer points, clearly illustrated how the size of the learning set influenced the performance of the neural networks. The concentration of chromium from chromic acid was predicted with an absolute percentage error of $> 1\%$, in the networks from the initial experimental design, but with $< 1\%$ in the networks from an increased learning data set in the experimental design. The only difference between these networks is the size of the sets.

The comparisons of the expected and the predicted concentrations of chromium from chromic acid and from dichromate in the networks from an increased learning data set in the experimental design are shown in Figures A4 and A5, respectively. An absolute percentage error was between 0 and 2% in the determination of chromium concentration from chromic acid and total

chromium concentration. It was fluctuating between 0 and 6% in the determination of chromium concentration from dichromate, see Figure A6.

c) *Titration curves with all collected points as the inputs and the expected chromium from chromic acid as the only output*

ANNs model with 10 neurons in the hidden layer, an RMS error of 0.011815 and good patterns of 50.0% predicted the concentration of chromium from chromic acid with an absolute percentage error of 0.42 ± 0.31 , for 12 points in the test set. The inputs were the titration curves with all collected points and the output was the expected concentration of chromium from chromic acid (from increased learning data set in the experimental design).

The comparison of the expected and the predicted concentrations of chromium from chromic acid can be seen in Figure A7. In this case an absolute percentage error was fluctuating between 0 and 1% and is shown in Figure A8. When the whole titration curves were used as the inputs and only chromium concentration from chromic acid as output, the prediction was very good.

d) *Titration curves with all collected points as the inputs and the expected chromium from dichromate as the only output*

In the neural networks with 10 neurons in the hidden layer, an RMS error of 0.02811 and good patterns of 16.70%, the concentration of chromium from dichromate was predicted with an absolute percentage error of 1.48 ± 0.87 , for 12 points in the test set. The inputs were acid-base titration curves with all collected points and the output was the expected chromium concentration from dichromate (from an increased learning data set in the experimental design). The agreement between the expected and the predicted concentrations of chromium from dichromate was not satisfactory, see Figure A9. Variation in an absolute percentage error is shown in Figure A10 and it fluctuated between 0 and 3%.

e) *The first halves of the titration curves as the inputs and the expected chromium from chromic acid as the output*

ANNs model with 20 neurons in the hidden layer, an RMS error of 0.00447 and good patterns of 100.0%, was able to predict the concentration of chromium from chromic acid with an accuracy of 0.24 ± 0.16 , for 12 points in the test set. This is the lowest absolute percentage error predicted for chromic acid so far. A chosen model predicted chromium from chromic acid very well and it showed that there was good agreement between the expected and the predicted concentrations of chromium from chromic acid, see Figure A11. Variation in an absolute percentage error was between 0 and 0.7% and is shown in Figure A12.

Halves of the titration curves (curves with all collected points) were used as the inputs and the expected chromium from chromic acid as the output. Each half of the titration curves had first equivalence point of the titration. In the titration of chromium trioxide and dichromate sample solution against sodium hydroxide, the first equivalence point was due to chromic acid. Chromic acid released the first proton and form bichromate and that resulted into the first equivalence point of the titration.

4.3.3 Decreased range of experimental design

ANNs model with 18 neurons in the hidden layer, an RMS error of 0.040088 and good patterns of 0.0% predicted the concentration of chromium from chromic acid with an absolute percentage error of 2.11 ± 0.74 , for 8 points in the test set. The concentration of chromium from dichromate and total chromium concentration were predicted with an absolute percentage error of 1.78 ± 1.29 and 1.67 ± 0.74 , respectively. The comparison of the expected and the predicted concentrations of chromium from chromic acid is shown in Figure A13. The expected and the predicted concentrations of chromium from dichromate are shown in Figure A14. There were no patterns with an error equal or less than the target error of the neural networks in the test set of

data. An absolute percentage error was fluctuating between 0 and 3.5%, see Figure A15.

The inputs of the networks were the titration curves with all collected points and the outputs were the expected chromium from chromic acid and total chromium concentrations. A decreased range of experimental design covered a smaller area of a problem domain. The size of learning set in a decreased range of experimental design is the same as in the initial experimental design. The training and test sets of a decreased range of experimental design were reduced.

4.3.4 Increased learning and test sets of the experimental design

ANNs model with 15 neurons in the hidden layer, an RMS error of 0.013766 and good patterns of 41.70% predicted the concentration of chromium from chromic acid with an absolute percentage error of 2.11 ± 1.06 . The concentration of chromium from dichromate and total chromium concentrations were predicted with an absolute percentage error of 2.19 ± 1.50 and 1.68 ± 0.45 , respectively. The agreement between the expected and the predicted concentrations of chromium from chromic acid and from dichromate was not satisfactory and are shown in Figure A16 and A17, respectively.

The inputs of the neural networks were the titration curves with all collected points and the outputs were the expected concentration of chromium from chromic acid and the total chromium concentration. The data used when from an increased learning and test sets of the experimental design.

Absolute percentage errors in the determination of chromium concentrations from chromic acid and from dichromate were fluctuating between 0 and 5% and they are shown in Figure A18.

The following table shows different ANNs models and their accuracy in the prediction of the concentrations of chromium from chromic acid, chromium

from dichromate and total chromium concentration. This is a summary of what has been already explained about the predicting power of the neural networks.

Table 4.7 The comparison of the absolute percentage errors predicted for chromic acid, dichromate and the total chromium concentrations with different developed ANNs models.

Exp. designs	Inputs	Outputs	No. of neurons in hidden layer	RMS errors		No. of good patterns (%)		No. of points (acid-base titration curves)			ANNs predicted absolute % errors		
				Training operation	Testing operation	Training operation	Testing operation	Learning set	Training set	Test set	Cr/ CA	Cr _{Total}	Cr/ NaDC
Initial exp. design	Curves with all collected points	Expected Cr in CA & Cr _{Total}	10	0.013926	0.013645	37.50	62.50	25	16	24	0.67 ± 0.54	0.56 ± 0.47	1.29 ± 0.95
				0.017257	0.012692	37.50	41.70	25	16	24	0.72 ± 0.54	0.49 ± 0.31	1.54 ± 1.05
	Curves with all collected points	Exp. conc. of CA & NaDC	10	0.01121	0.014431	50.00	25.00	25	16	24	0.93 ± 0.60		2.15 ± 1.27
	Curves with fewer points	Expected Cr in CA & Cr _{Total}	13	0.017972	0.023904	12.50	20.80	25	16	24	1.10 ± 0.74	1.06 ± 0.75	4.03 ± 2.76

Table 4.7 Continued

Exp. designs	Inputs	Outputs	No. of neurons in hidden layer	RMS errors		No. of good patterns (%)		No. of points (acid-base titration curves)			ANNs predicted absolute % errors		
				Training operation	Testing operation	Training operation	Testing operation	Learning set	Training set	Test set	Cr/ CA	Cr _{Total}	Cr/ NaDC
Increased learning data set in the exp. design	Curves with all points	Expected Cr in CA & Cr _{Total}	18	0.013807	0.017366	41.70	58.30	41	12	12	0.45 ± 0.59	0.69 ± 0.82	1.51 ± 1.21
				0.012558	0.012977	50.00	33.30	41	12	12	0.84 ± 0.50	0.50 ± 0.29	2.31 ± 1.45
	Curves with fewer points	Expected Cr in CA & Cr _{Total}	15	0.027606	0.016853	9.10	16.70	41	12	12	0.89 ± 0.36	0.77 ± 0.46	2.59 ± 1.91
	Curves with all points	Expected Cr in CA	10	0.011815	0.011521	50.00	58.30	41	12	12	0.42 ± 0.31		
	Curves with all points	Expected Cr in NaDC	10	0.02811	0.027740	16.70	16.70	41	12	12			1.49 ± 0.87
	First halves of curves "with all points"	Expected Cr in CA	20	0.00447	0.006044	100.00	91.70	41	12	12	0.24 ± 0.16		

Table 4.7 Continued

Exp. designs	Inputs	Outputs	No. of neurons in hidden layer	RMS errors		No. of good patterns (%)		No. of points (acid-base titration curves)			ANNs predicted absolute % errors		
				Training operation	Testing operation	Training operation	Testing operation	Learning set	Training set	Test set	Cr/CA	Cr _{Total}	Cr/NaDC
Decreased range of exp. design	Curves with all points	Expected Cr in CA & Cr _{Total}	18	0.040088	0.0451	0.0	0.0	25	8	8	2.11 ± 0.74	1.67 ± 0.74	1.78 ± 1.29
Increased learning and test sets of exp. design	Curves with all points	Expected Cr in CA & Cr _{Total}	15	0.013766	0.035789	41.70	0.0	41	12	16	2.11 ± 1.06	1.68 ± 0.45	2.19 ± 1.50

Exp = Experimental; Conc = Concentration; CA = Chromic acid / CrO₃; No. = number; NaDC = Sodium dichromate (Na₂Cr₂O₇·2H₂O).

CHAPTER 5

5. CONCLUSIONS AND SUGGESTIONS

The main aim of this work was to predict the concentrations of chromic acid, total chromium and dichromate in a solution containing sodium dichromate and chromium trioxide, using Artificial Neural Networks. As required by the manufacturer of chromic acid (CrO_3), Artificial Neural Networks models, or any other model, would be accepted if they are able to predict the concentrations of chromic acid and dichromate with percentage error of less or equal to 1%, on average. Accepted ANNs model would be considered for an on-line monitoring system to monitor the concentrations of chromic acid, dichromate and total chromium in the industrial electrolytic process used to produce chromic acid from dichromate solution.

To achieve this, firstly, one needs to have a better understanding of speciation of chromium(VI) in aqueous solution. Secondly, a technique which can distinguish between chromic acid and dichromate in aqueous solution must be identified and used during the data collection step for the use of ANNs.

As already mentioned, when chromium trioxide dissolves in water, chromic acid is formed. Titration of chromic acid solution against sodium hydroxide solution results in two equivalence points. When sodium dichromate dissolves in water, bichromate ion is formed. Only one equivalence point was observed when dichromate solution was titrated against a sodium hydroxide solution. It was noticed that the pH of chromium solution prepared by mixing chromic acid and dichromate solutions was the same as the pH of chromic acid solution before mixing. When this solution was titrated against sodium hydroxide solution, neutralization of bichromate ion started at pH above 6.

Acid-base titration was identified as a suitable technique to be used in the determination of chromic acid and dichromate in a solution containing chromium trioxide and sodium dichromate. It might be useful if one needs to

prove the existence of bichromate ion in chromate-dichromate system. It can also be used to study the nature of chromic acid in aqueous solution, whether the true formula of chromic acid is H_2CrO_4 or $\text{H}_2\text{Cr}_2\text{O}_7$. Many authors concluded that bichromate ion does not exist in aqueous chromium(VI) solution [27, 28, 31].

Redox titration was also investigated as a potential technique in this study. However, it was found that redox titration cannot distinguish between chromic acid and dichromate in a solution contained chromic acid and dichromate. It can only be used to determine or to monitor the total chromium concentration. Therefore, redox titration is not preferred in this study.

Acid-base titration was used to collect the data or set of titration curves that was used as the inputs to the ANNs. Most of the developed ANNs models predicted the concentration of chromium from chromic acid with required accuracy of less than 1 %. The performance of the neural networks is totally dependent on the nature of the experimental designs, the number of points in the titration curves used as the inputs and the type of the outputs. By the nature of the experimental designs we are referring to the size of the sets i.e., learning, training and testing sets and the patterns in which these sets are placed in relative to one another.

We suggest that the first half of acid-base titration curve could be used as the input and only the concentration of chromium from chromic acid as the output, if one needs to monitor the concentration of chromic acid only. However, the concentrations of chromium from chromic acid and total chromium should be used as the outputs, whenever the concentrations of chromic acid, dichromate and total chromium have to be monitored. For a better prediction, acid-base titration curves with as many collected points as possible should be used as the inputs of the neural networks.

The concentration of chromium from dichromate was not predicted with an absolute percentage error of less or equal to 1%. The lowest percentage error predicted for the concentration of chromium from dichromate was 1.51 ± 1.21 .

It was noticed that the concentration of chromium from dichromate was predicted with an absolute percentage errors of more than those predicted for the concentration of chromium from chromic acid, in all developed models. This can be explained by considering the reagents as the source of a systematic error and we assume that if this is taken into account, ANNs can predict the concentration of chromium from dichromate with an absolute percentage error of less than 1%.

We recommend that one should prepared chromium solutions using analytical grade reagents, not chromium trioxide and sodium dichromate obtained from the factory. The concentration of titrant solution (NaOH) must be constant throughout the experiment. The response slope of a glass electrode must be checked during the titration experiment. The combination of acid-base titration technique and Artificial Neural Networks was found to be successful in the prediction of the concentrations of chromium from chromic acid, dichromate and total chromium.

The number of points in the titration curves (the inputs of the neural networks) affects the accuracy of the neural networks; when the number of points in the curves was reduced, the performance of the neural networks also decreased. The neural networks would predict better if one reduce the number of points in the titration curves and increase the size of the learning set. Decreasing the number of points in the titration curves reduce the time required to complete the titration experiment and data analysis.

We suggest that the experiment must be designed in a way that it could cover as many stages of the industrial electrolytic process as possible. The size of training and testing sets and the way they are distributed within the learning set must be considered when designing the neural networks. Good predictions were observed with training and testing points uniformly distributed within the learning set.

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APPENDICES

APPENDIX A

The comparison of the expected and predicted concentrations of chromium from chromic acid and from dichromate. Variation in an absolute percentage error in the determination of chromium concentrations from chromic acid, dichromate and total chromium is also shown. These results are for the following experimental designs: an increased learning data set in the experimental design, decreased range of experimental design, increased learning and test sets of the experimental design.

APPENDIX B

Experimental designs used during the preparation of chromium(VI) sample solutions ; the samples were less concentrated as compared to the samples of the 8th stage of the industrial electrolytic process used to produce chromic acid. The amount of chromium from chromic acid (CrO_3 or H_2CrO_4) was assigned to 100% chromium. It was varied by $\pm 10\%$. The concentration of chromium from dichromate was varied in a way that the total chromium would remain constant. In some cases the total chromium was not constant. These experimental designs are also shown as spreadsheet in Appendix B1 on an attached disc. Other experimental designs (for example, the initial experimental design and a decreased range of experimental design are in Appendix B2 also on a disc.

APPENDIX C

Data used to test reproducibility of acid-base procedure involving the same glass (pH) and (Ag/AgCl) reference electrodes. The test was performed with sample # 1 of learning set of data of 500 times diluted industrial chromium(VI) samples.

APPENDIX D

An example of acid-base titration data obtained through automated experiment performed on solution # 1 of learning set of data of 500 times diluted industrial samples. Other acid-base titration data obtained during the experiment are in Appendix D on an attached disc

APPENDIX E

An example of data loaded in the neural networks, normalized titration curves with all collected points were used as the inputs of the networks. The outputs were the total chromium and the concentration of chromium from chromic acid. Other data loaded in the networks are in Appendix E on the attached disc. The normalized titration curves were obtained by subtracting each and every pH reading from the initial pH value and the resulting pH values were referred to as normalized pH values.

APPENDIX A

The comparison of the expected and predicted concentrations of chromium from chromic acid and from dichromate. Variation in an absolute percentage error in the determination of chromium concentrations from chromic acid, dichromate and total chromium is also shown. These results are for the following experimental designs: an increased learning data set in the experimental design, decreased range of experimental design, increased learning and test sets of the experimental design.

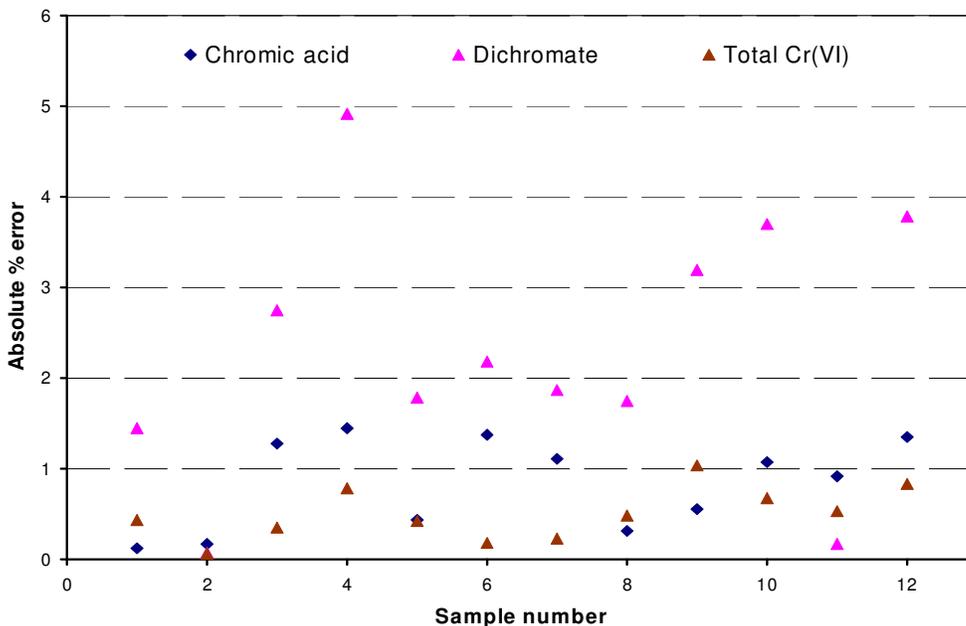


Figure A3 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

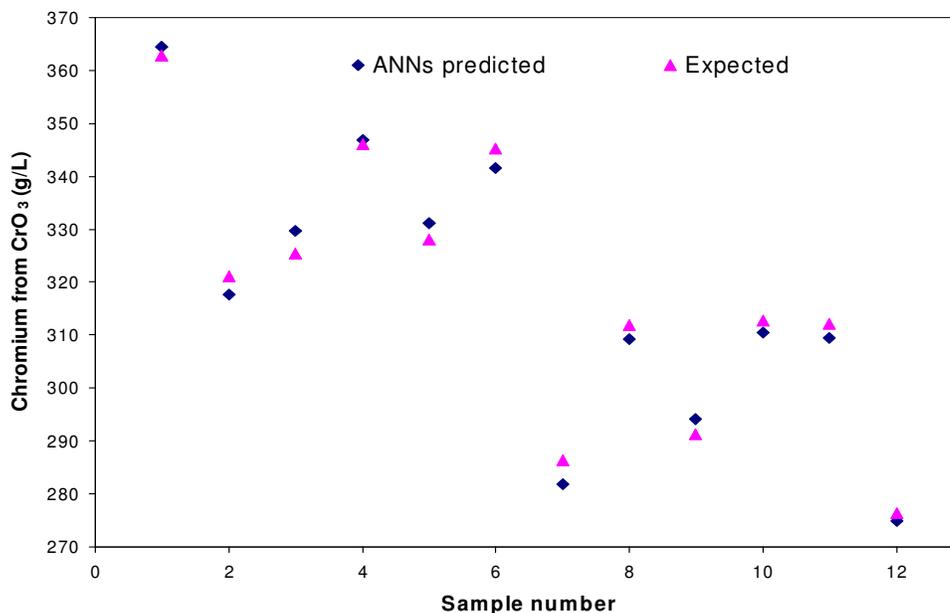


Figure A4 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with fewer or reduced points from increased learning data set in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

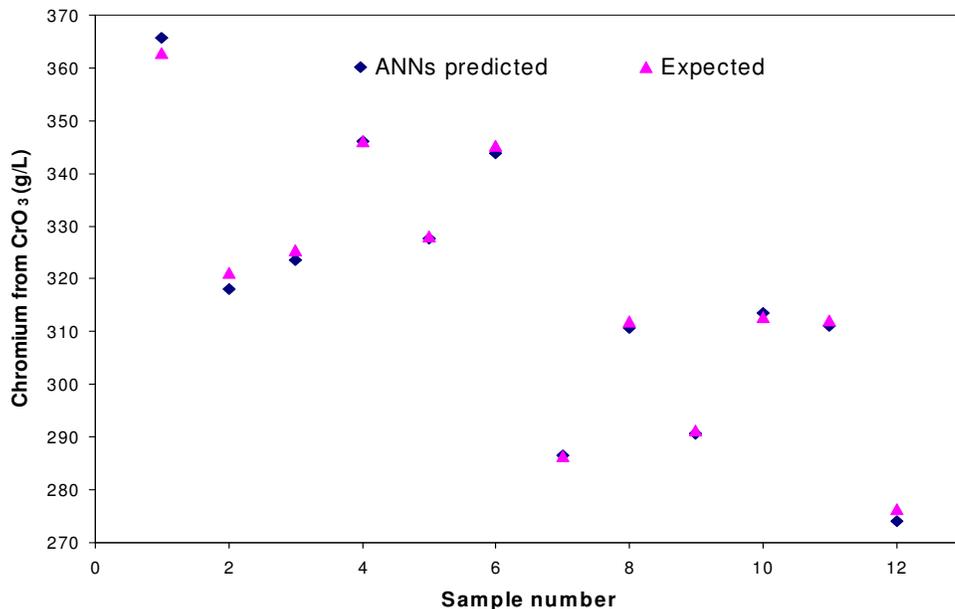


Figure A7 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

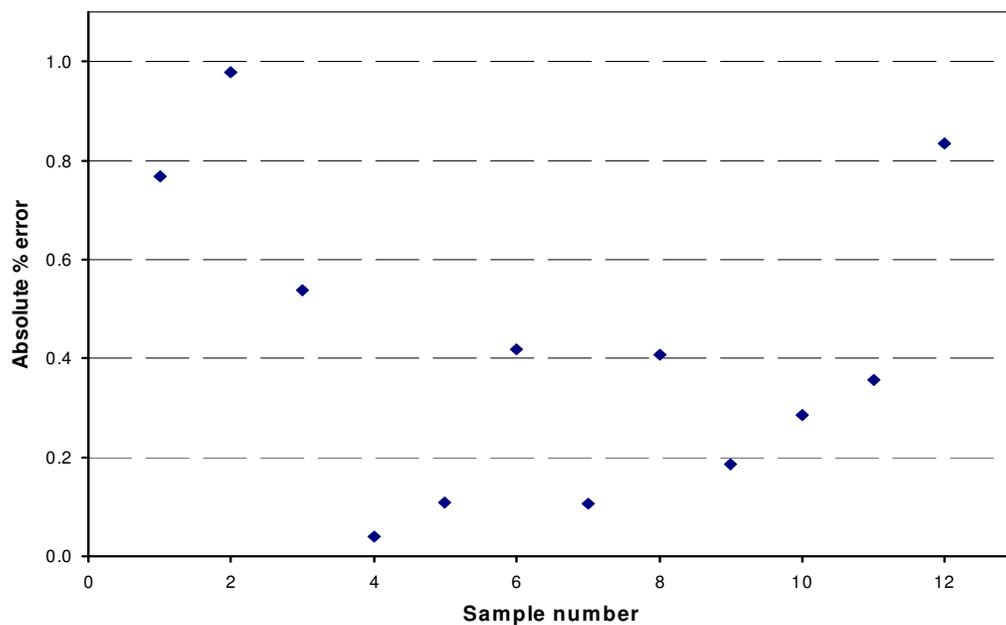


Figure A8 Variation in an absolute percentage error of chromium from chromic acid. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

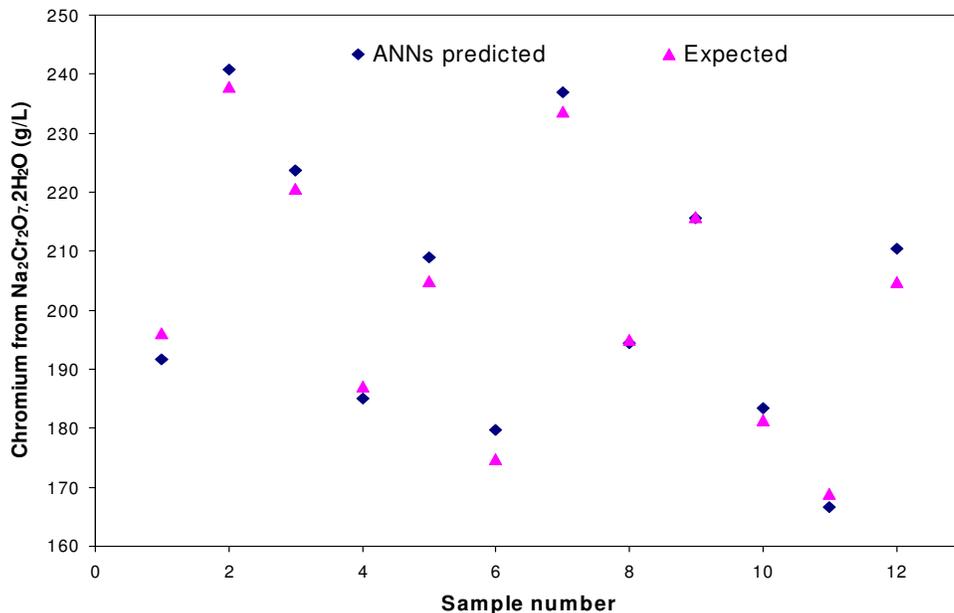


Figure A9 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from dichromate.

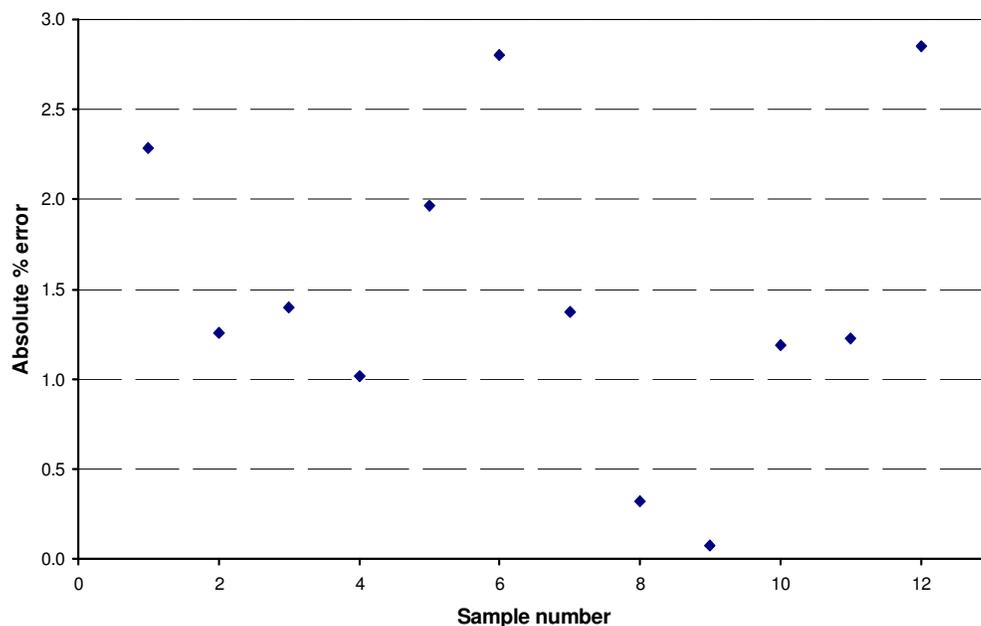


Figure A10 Variation in an absolute percentage error of chromium from dichromate. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from dichromate.

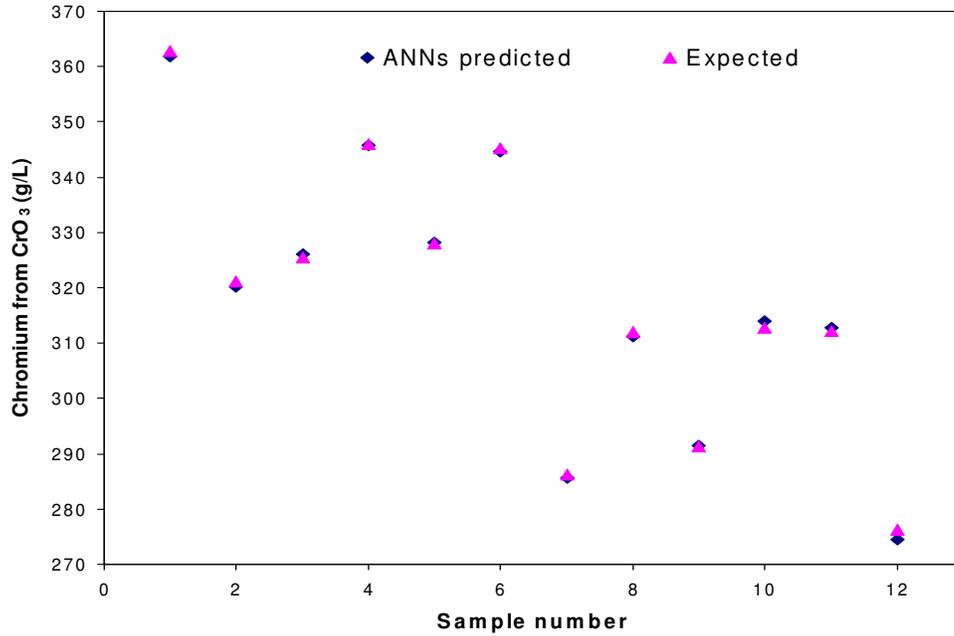


Figure A11 Test results obtained for chromium from chromic acid in the neural networks in which the first halves of the titration curves from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

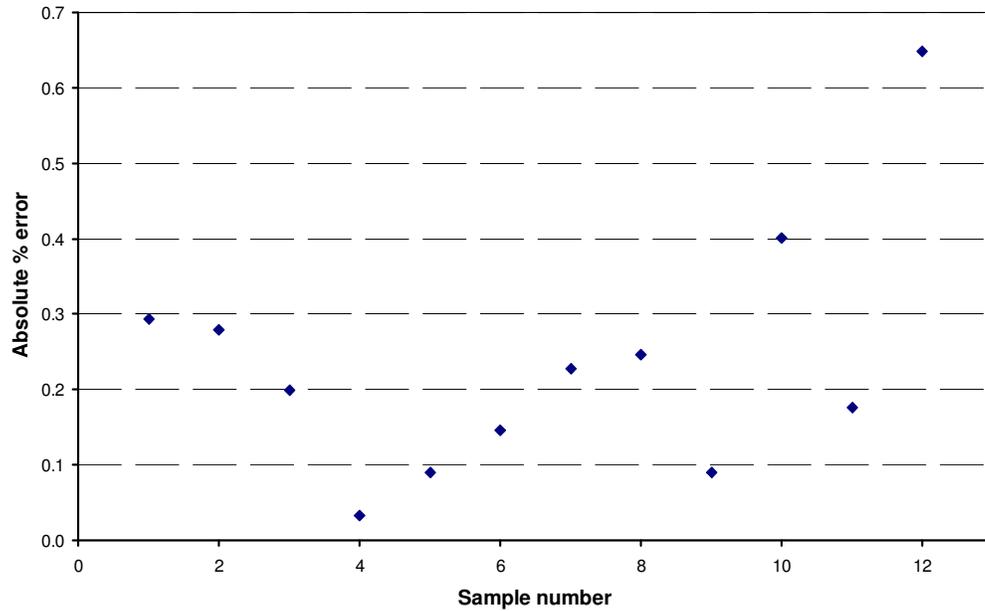


Figure A12 Variation in an absolute percentage error of chromium from chromic acid. The first halves of the titration curves from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

2. Decreased range of experimental design

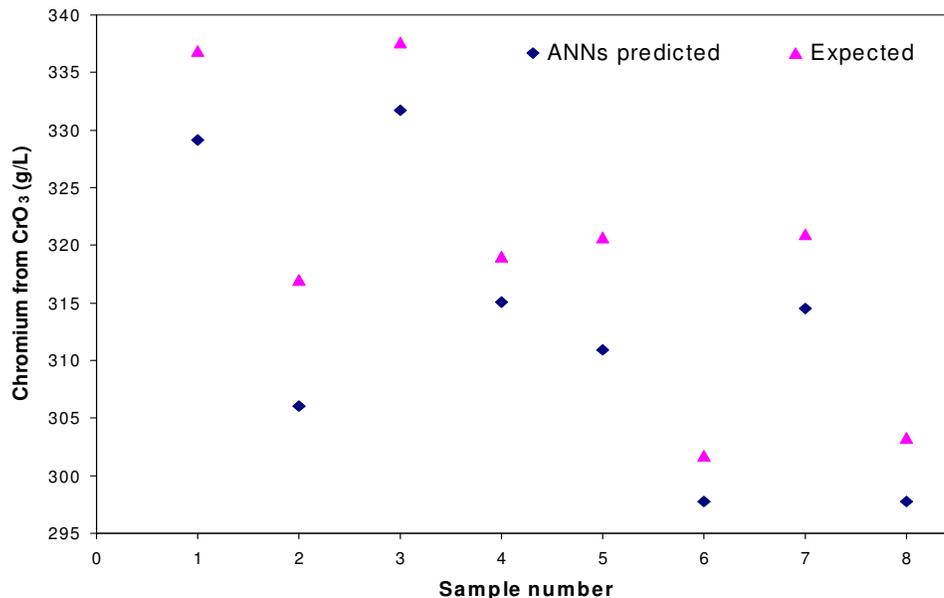


Figure A13 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium concentration.

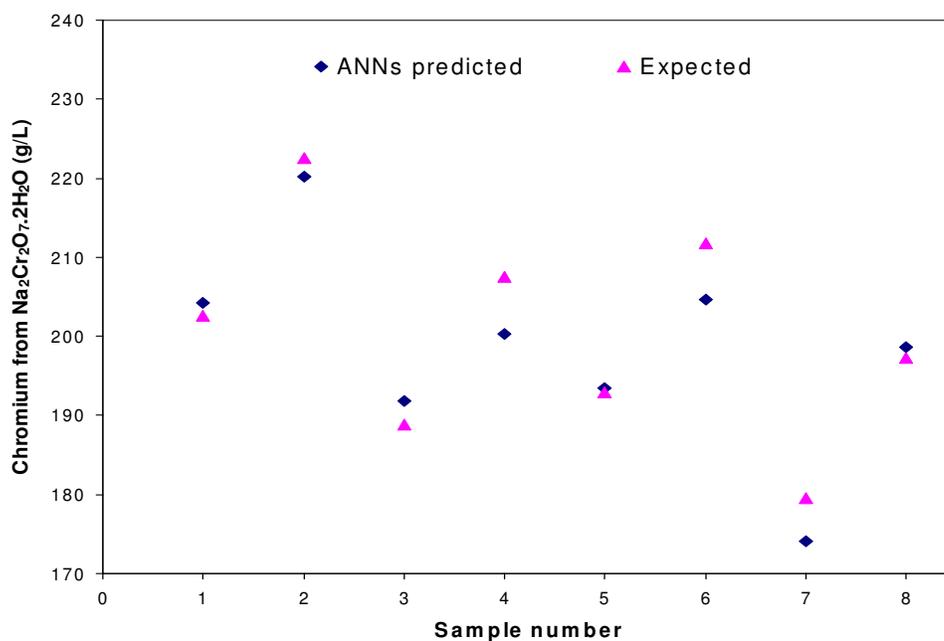


Figure A14 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium concentration.

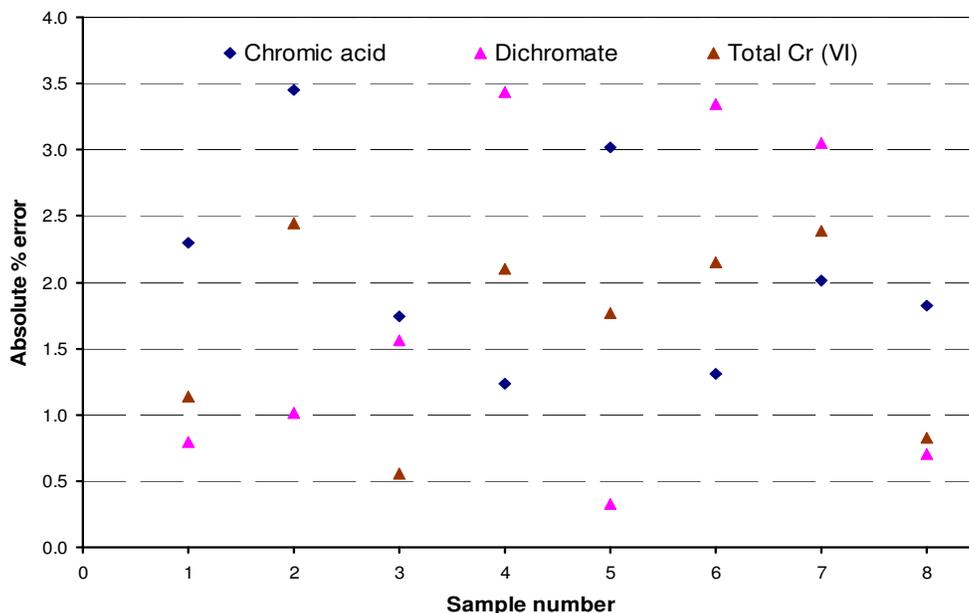


Figure A15 Variation in absolute percentage error of chromium from chromic acid, dichromate and total chromium concentration. Titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium.

3. Increased learning and test sets of the experimental design

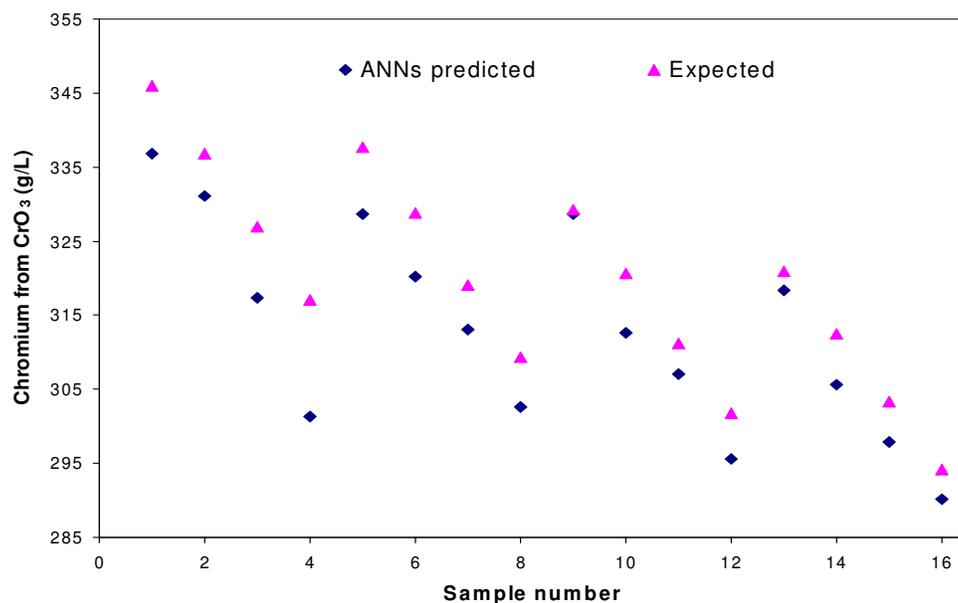


Figure A16 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium concentration.

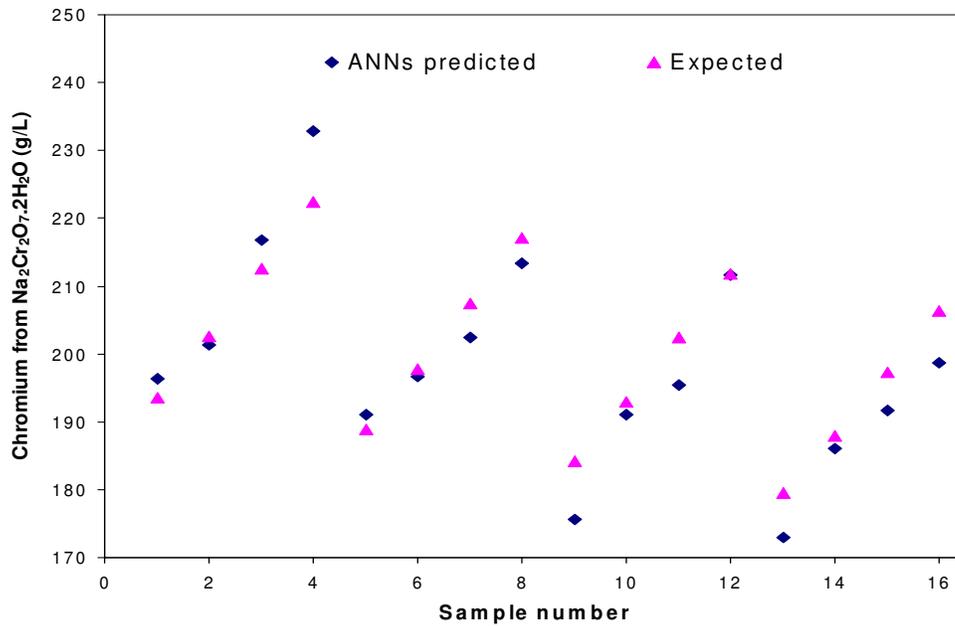


Figure A17 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

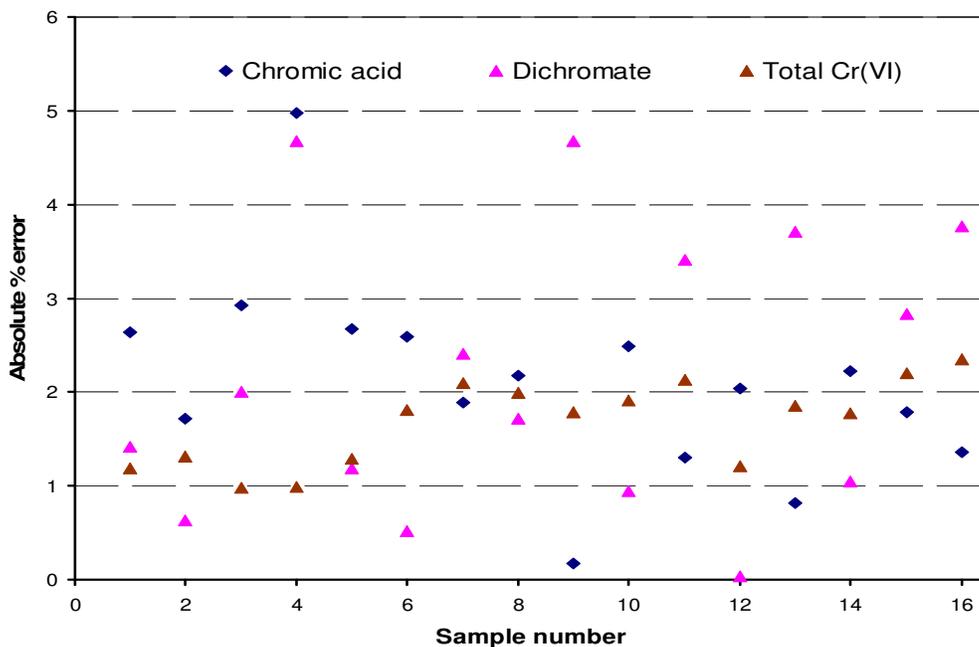


Figure A18 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium concentration. The titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium.

APPENDIX B

Experimental designs used during the preparation of chromium(VI) sample solutions ; the samples were less concentrated as compared to the samples of the 8th stage of the industrial electrolytic process used to produce chromic acid. The amount of chromium from chromic acid (CrO_3 or H_2CrO_4) was assigned to 100% chromium. It was varied by $\pm 10\%$. The concentration of chromium from dichromate was varied in a way that the total chromium would remain constant. In some cases the total chromium was not constant. These experimental designs are also shown as spreadsheet in Appendix B1 on an attached disc. Other experimental designs (for example, the initial experimental design and a decreased range of experimental design are in Appendix B2 also on a disc.

APPENDIX C

Data used to test reproducibility of acid-base procedure involving the same glass (pH) and (Ag/AgCl) reference electrodes. The test was performed with sample # 1 of learning set of data of 500 times diluted industrial chromium(VI) samples.



Titration number												
1 2 3 4 5 6 7 8 9 10												
NaOH (mL)	pH Values										Average	STDEV
39.500	12.308	12.276	12.245	12.253	12.314	12.358	12.359	12.367	12.352	12.353	12.319	0.047
39.750	12.374	12.335	12.302	12.312	12.372	12.415	12.417	12.425	12.410	12.409	12.377	0.046
40.000	12.431	12.386	12.352	12.363	12.423	12.464	12.470	12.473	12.460	12.458	12.428	0.046

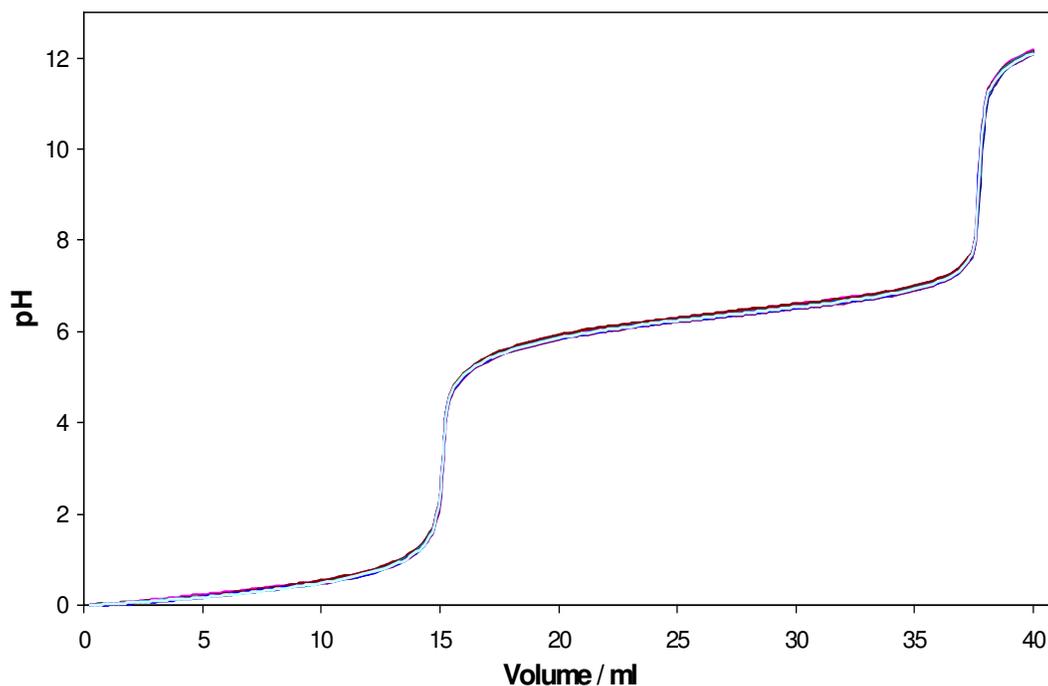


Figure C1. Normalized acid-base titration curves. Ten aliquots of chromium(VI) solution were titrated against 0.978M NaOH solution. The normalized titration curves were obtained by subtracting each and every pH reading from the initial pH value and the resulting pH values were referred to as normalized pH values.

APPENDIX D

An example of acid-base titration data obtained through automated experiment performed on solution # 1 of learning set of data of 500 times diluted industrial samples. Other acid-base titration data obtained during the experiment are in Appendix D on an attached disc

Table D1. Solution No. 1 of learning set of data

Start date&time 23-Jan-08 11:23:14 AM

PARAMETERS

 Pause time for Equilibration(s) 0
 Max. # readings to save 40
 Criterion of Stability 0.1
 Sampling Rate of pH meter(s) 1
 Max. Waiting time (min) 5

STOP CONDITIONS

 Stop pH 14
 Stop mV -500
 Stop Volume (mL) 40

Volume increment (mL)	Total volume added (mL)	Final reading (mV)	Final Std Dev	pH	Temp (°C)	Total No of readings	Elapsed Time (s)	Last readings (mV)											
0.25	0.00	375.9	0.042	0.319	0	11	11	375.9	375.9	375.9	375.9	375.9	376.0	375.9	375.9	375.9	375.9	376.0	375.9
0.25	0.25	375.6	0.000	0.326	0	11	11	375.6	375.6	375.6	375.6	375.6	375.6	375.6	375.6	375.6	375.6	375.6	375.6
0.25	0.50	375.2	0.000	0.332	0	11	11	375.2	375.2	375.2	375.2	375.2	375.2	375.2	375.2	375.2	375.2	375.2	375.2
0.25	0.75	374.8	0.000	0.340	0	11	11	374.8	374.8	374.8	374.8	374.8	374.8	374.8	374.8	374.8	374.8	374.8	374.8
0.25	1.00	374.3	0.042	0.349	0	11	11	374.3	374.4	374.3	374.3	374.4	374.3	374.3	374.3	374.3	374.3	374.3	374.3
0.25	1.25	373.9	0.032	0.356	0	11	11	373.9	373.9	373.9	373.9	373.9	373.8	373.9	373.9	373.9	373.9	373.9	373.9
0.25	1.50	373.4	0.052	0.363	0	11	11	373.4	373.5	373.5	373.4	373.5	373.5	373.4	373.4	373.4	373.4	373.4	373.4

APPENDIX D

Volume increment (mL)	Total volume added (mL)	Final reading (mV)	Final Std Dev	pH	Temp (°C)	Total No of readings	Elapsed Time (s)	Last readings (mV)											
0.25	39.50	-294.1	0.082	12.308	0	11	11	-294.0	-294.0	-294.1	-294.1	-294.1	-294.2	-294.2	-294.2	-294.2	-294.2	-294.2	-294.2
0.25	39.75	-297.8	0.067	12.374	0	11	11	-297.7	-297.7	-297.7	-297.7	-297.8	-297.8	-297.8	-297.8	-297.8	-297.8	-297.9	-297.9
0.25	40.00	-301.1	0.063	12.431	0	11	11	-301.0	-301.0	-301.0	-301.1	-301.1	-301.1	-301.1	-301.1	-301.1	-301.1	-301.2	-301.2

A Stop Condition met

End Date&Time 23-Jan-08 01:19:59 PM

APPENDIX E

An example of data loaded in the neural networks, normalized titration curves with all collected points were used as the inputs of the networks. The outputs were the total chromium and the concentration of chromium from chromic acid. Other data loaded in the networks are in Appendix E on the attached disc. The normalized titration curves were obtained by subtracting each and every pH reading from the initial pH value and the resulting pH values were referred to as normalized pH values.

