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

by

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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.

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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
^{o}C	Degree Celsius
Cr	Chromium
DC	Dichromate
DNA	De-ribose Nucleic Acid
e^-	Elementary charge of an electron (1.6021764 x 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 **For**mula **Tran**slating 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	**Mol**ecular Structure **Gen**erator 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 ($Na_2Cr_2O_7.2H_2O$)
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
$\sum$	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 ($Na_2Cr_2O_7 \cdot 2H_2O$) 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.

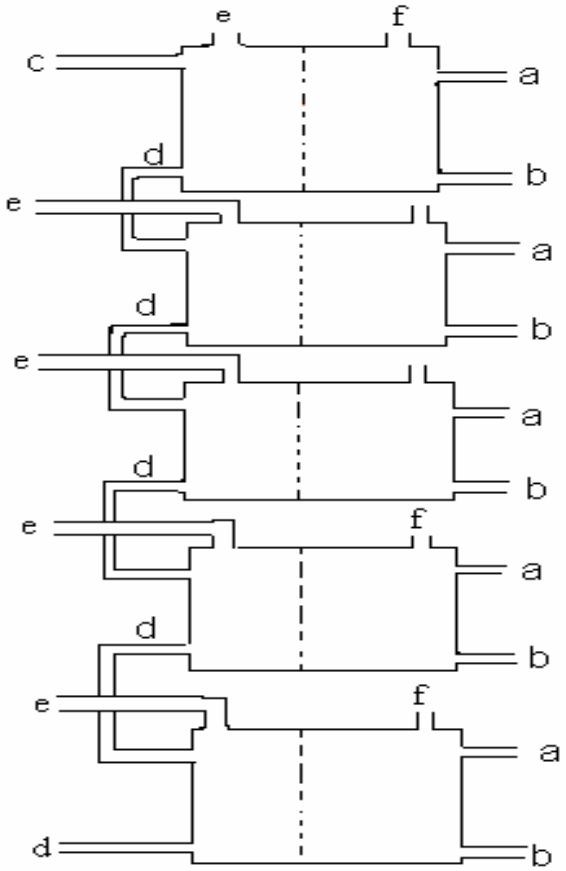

Figure 1.1 Representation of electrolytic cells arranged in series. a – inlet for catholyte feed, b – outlet for catholyte product, c – inlet for anolyte feed, d – communicating tube (for the transport of electrolyte from cell to cell), e – outlet for oxygen gas, f – outlet for hydrogen gas.

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.

$$2H_2O(\ell) + 2e^- \rightarrow H_2 \uparrow + 2OH^-(aq) \qquad \textbf{(1.1)}$$

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

$$H_2O(\ell) \rightarrow 2H^+ + \frac{1}{2}O_2 \uparrow + 2e^- \qquad \textbf{(1.2)}$$

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.

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \qquad \textbf{(1.3)}$$

$$HCrO_4^- + H^+ \leftrightarrow H_2CrO_4(aq) \qquad \textbf{(1.4)}$$

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.

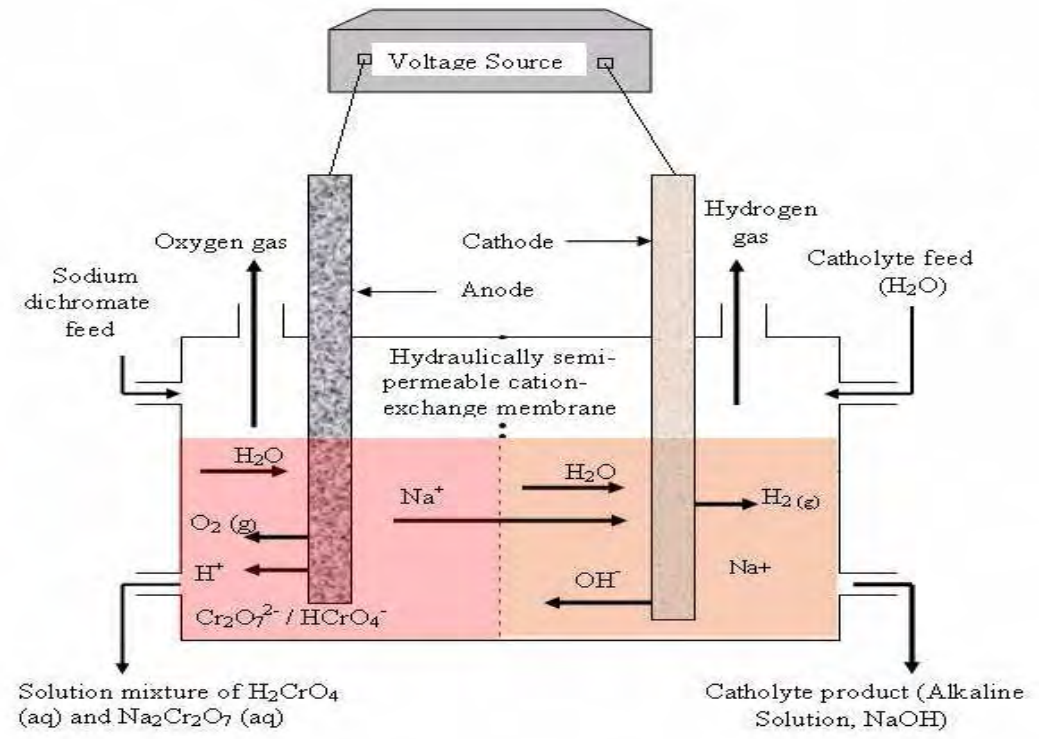

Figure 1.2 A cell used in multistage electrolytic production of chromic acid.

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^{o}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^{o}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 improves their harderability [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:

$$H_2CrO_4 \leftrightarrow 2H^+ + CrO_4^{2-} \qquad \textbf{(1.5)}$$

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:

$$H_2Cr_2O_7 \leftrightarrow 2H^+ + Cr_2O_7^{2-} \qquad \textbf{(1.6)}$$

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) transverses 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 flavor-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).

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \quad \textbf{(1.7)}$$

$$H_2CrO_4 + OH^- \leftrightarrow HCrO_4^- + H_2O \quad \textbf{(1.8)}$$

$$HCrO_4^- + OH^- \leftrightarrow CrO_4^{2-} + H_2O \quad \textbf{(1.9)}$$

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 aquoeus solution, the following equilibria must be taken into account:

$$H_2Cr_2O_4 \leftrightarrow HCr_2O_7^- + H^+ \quad \textbf{(1.10)}$$

$$HCr_2O_7^- \leftrightarrow Cr_2O_7^{2-} + H^+ \quad \textbf{(1.11)}$$

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

$$CrO_4^{2-} + H_2O \leftrightarrow HCrO_4^- + OH^- \quad \textbf{(1.12)}$$

Furthermore, dichromate salts dissolve in water and give raise 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.

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad \textbf{(1.13)}$$

$$HCrO_4^- + OH^- \leftrightarrow CrO_4^{2-} + H_2O \quad \textbf{(1.14)}$$

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 x 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 existance of bichromate ion in aquoeus 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:

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O \quad \textbf{(1.15)}$$

For that reaction, the equilibrium constant was calculated as log K = 13.77 at 20°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 β_{22} = 14.85 at 25°C and zero ionic strength. In very acidic solution, two other chromium species have been detected, namely trichromate ($Cr_3O_{10}^{2-}$) and tetrechromate ($Cr_4O_{13}^{2-}$) [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^oC 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.

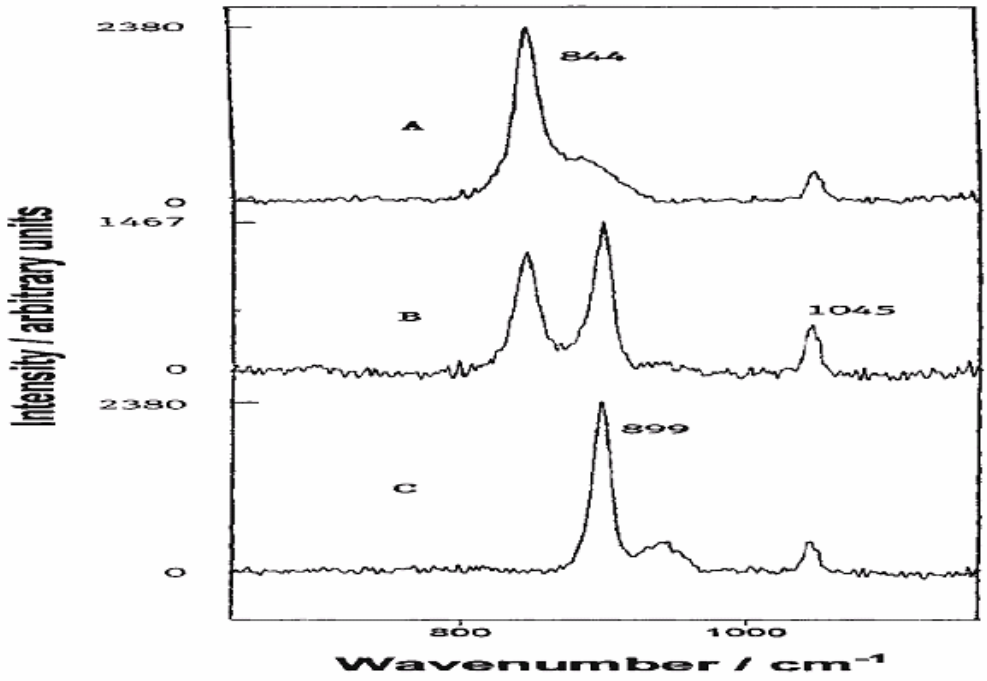

Figure 1.3 Experimental spectra (average of five exposures of 3 min each) of solution of 18 mM Cr(VI) at pH values 9.15 (A), 6.12 (B) and 3.03 (C). The peak at 1045 cm^{-1} is that of NO_3^- [33].

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.

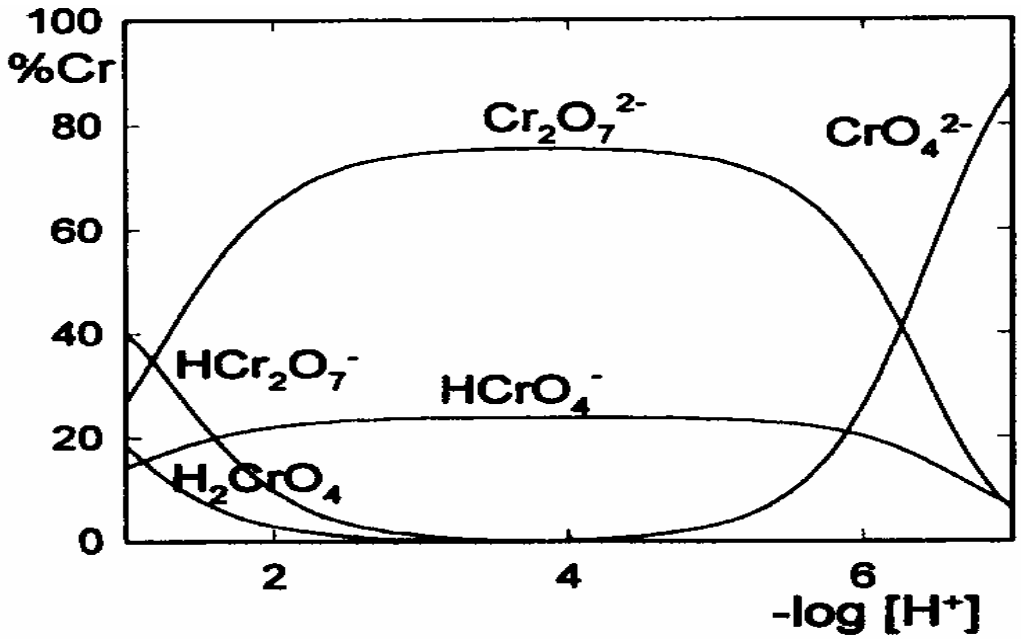

Figure 1.4 Species distribution diagram as a function of pH for total chromium(VI) concentration = 50 mM in the 3.0M KCl at 25°C [35].

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 $Na_2Cr_2O_7 \cdot 2H_2O$.

CHAPTER 2

2. EXPERIMENTAL

2.1 Reagents

Chromium trioxide (CrO_3), Formula Weight (F.W. 99.99 $gmol^{-1}$) and sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$, 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 ($FeSO_4 \cdot 7H_2O$, 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^{o}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 $Na_2Cr_2O_7 \cdot 2H_2O$ 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 $FeSO_4 \cdot 7H_2O$ 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].

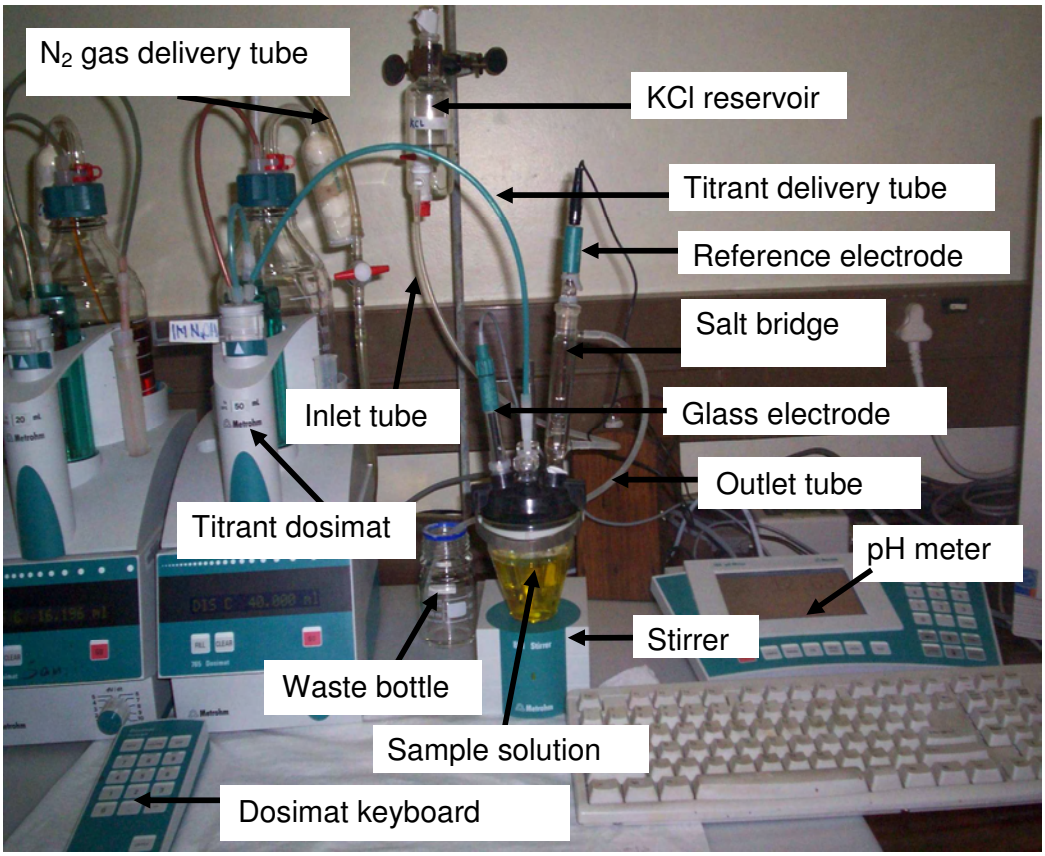

Figure 2.1 A photograph showing experimental set-up for automatic titration of chromium(VI) solutions.

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.

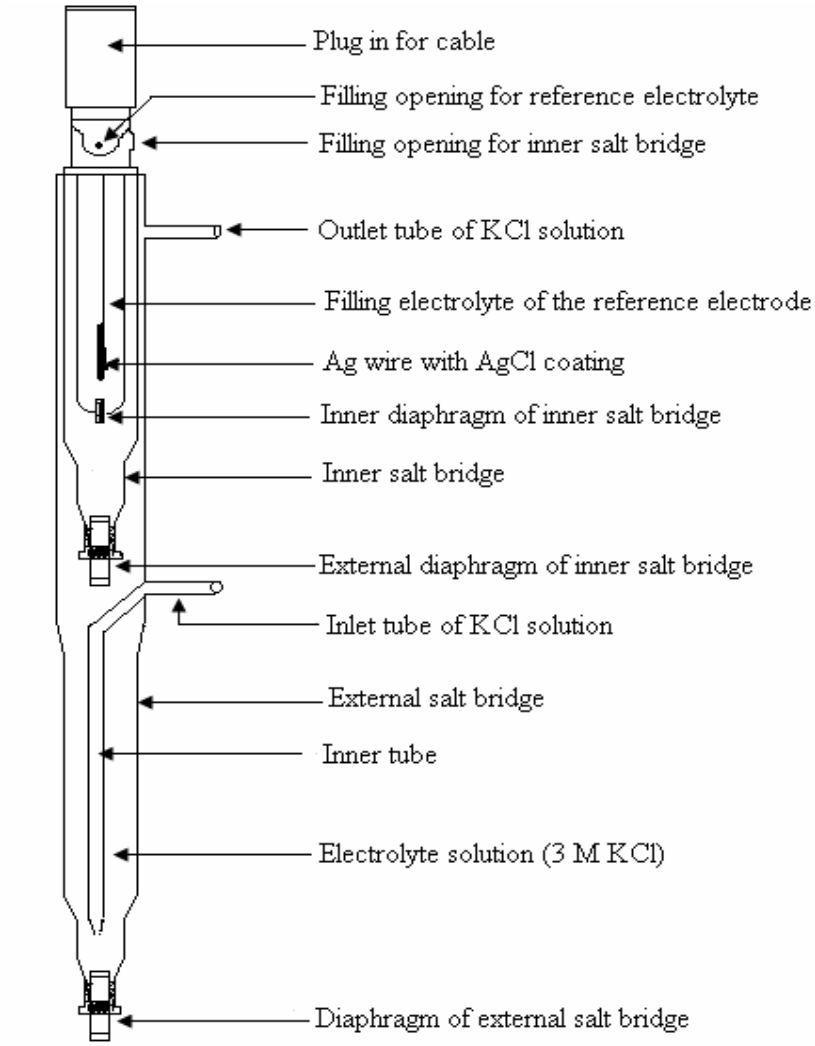

Figure 2.2 Reference electrode assembly.

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 ± 0.1°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 ± 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 ± 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.

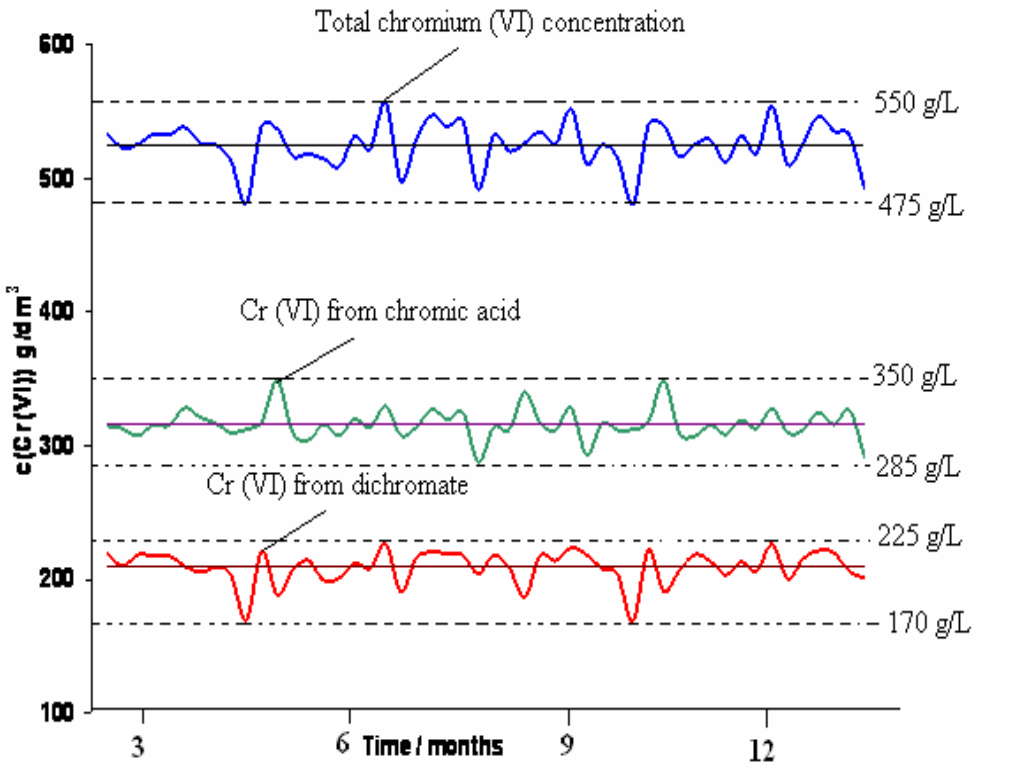

Figure 2.3 Chromium(VI) content from chromic acid and dichromate in the final stage of electrolytic process [39].

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.

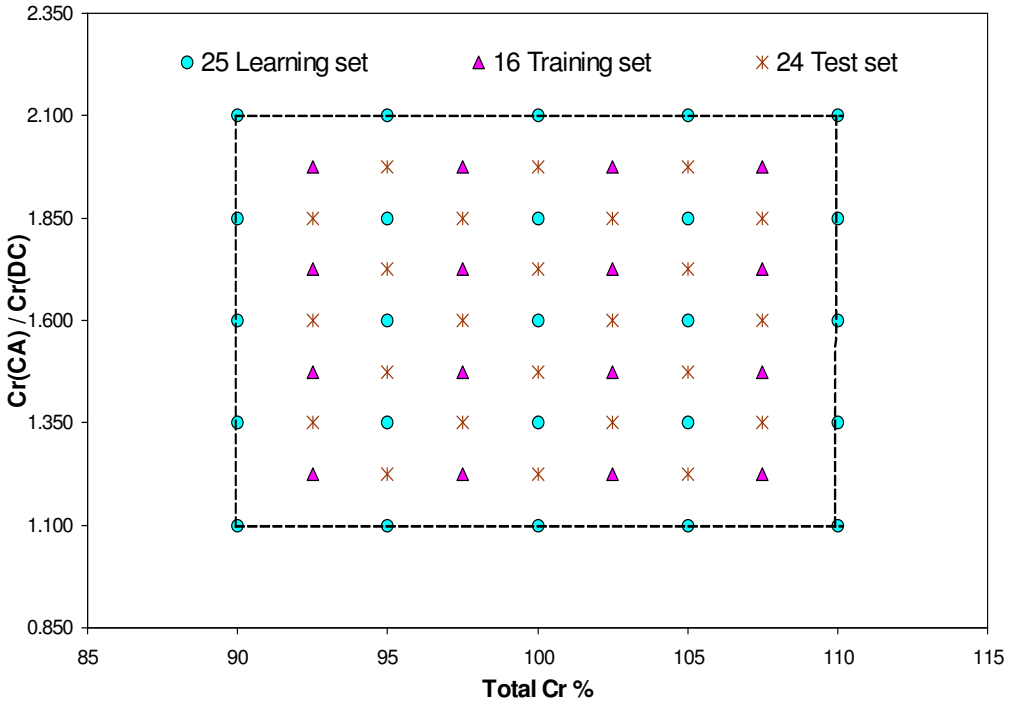

Figure 2.4 Initial experimental design

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^{o}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:

$$H_2CrO_4 + 3Fe^{2+} + 6H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \quad \textbf{(2.1)}$$

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.

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

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

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:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad \textbf{(2.4)}$$

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

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

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

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

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:

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

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.

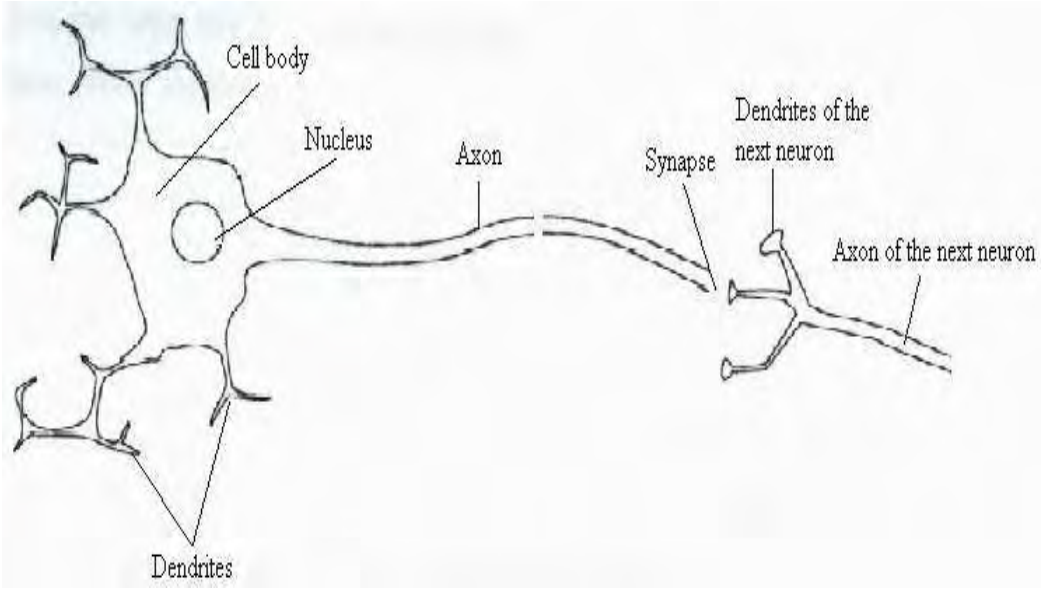

Figure 3.1 Structure of a biological neuron [44]

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 varies 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 ^{1}H 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 expect 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.

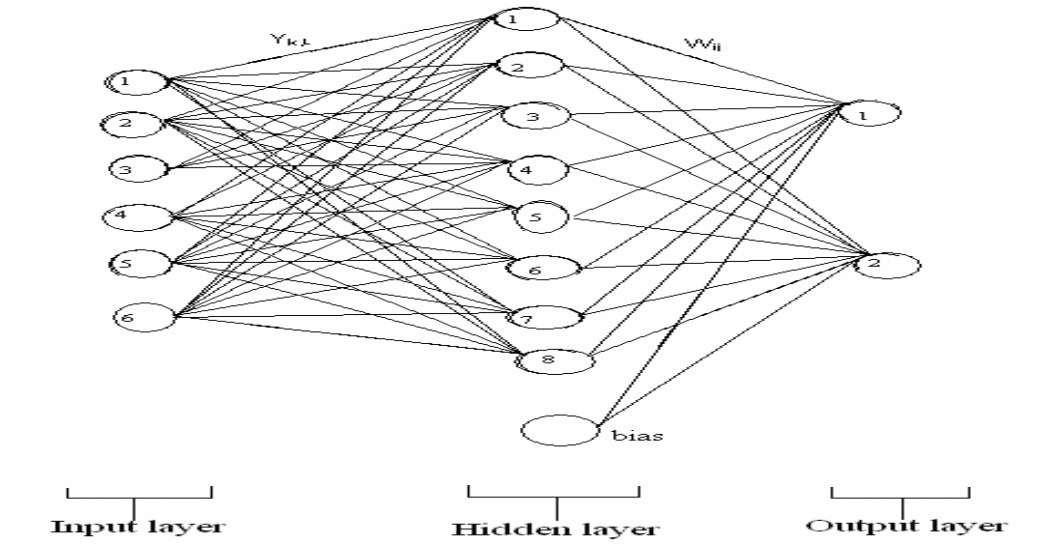

Figure 3.2 Artificial Neural Networks architecture with a single hidden layer

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.

$$\text{Weighted sum } (y_i) = \sum_{j1}^{i} x_i w_{ij} + b_j \qquad \textbf{(3.1)}$$

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.

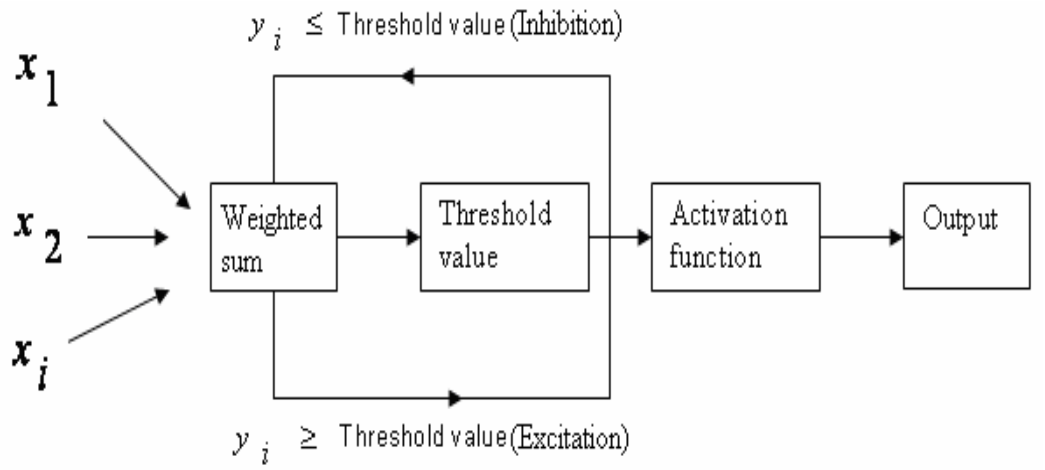

Figure 3.3 Artificial neuron [59, 60]

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

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.

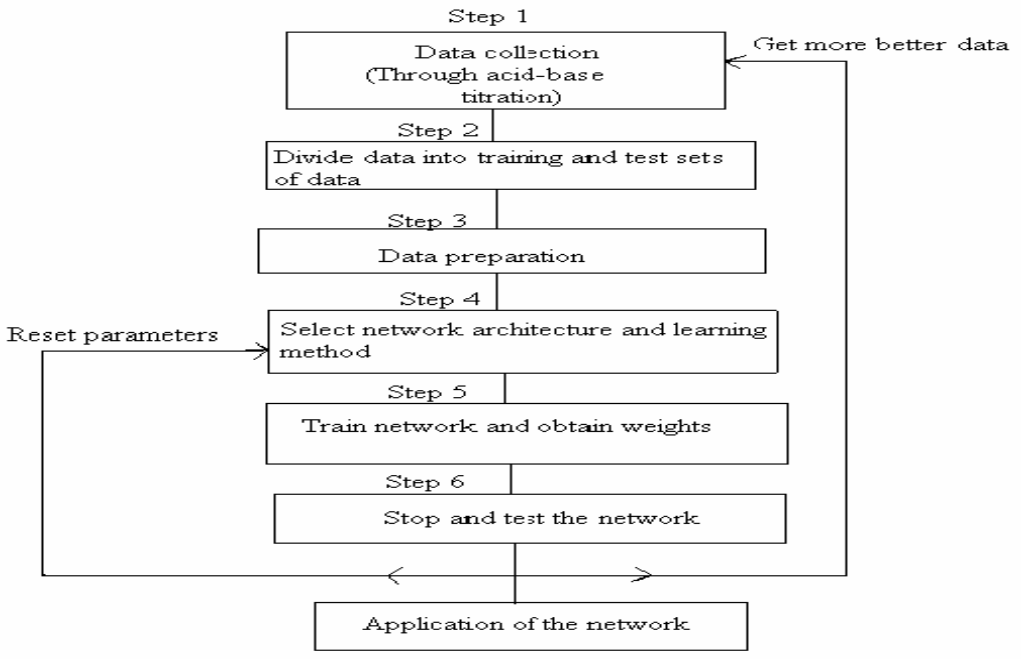

Figure 3.4 A flow chart illustrating the main steps involved during learning of ANNs.

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.

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

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.

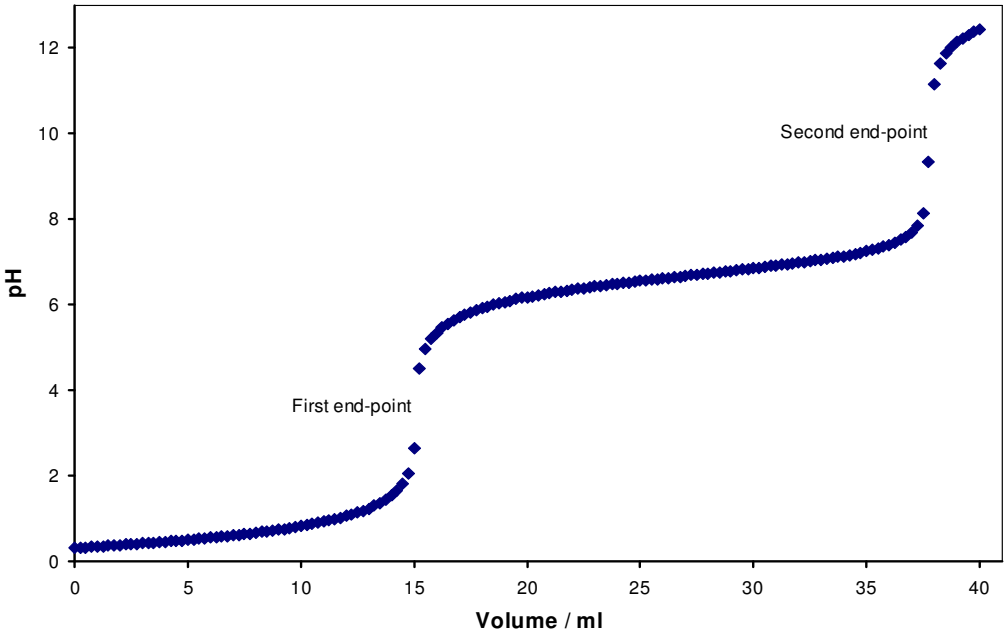

Figure 3.5 An example of acid-base titration curve fitted with modified sigmoid equation. Chromium sample contained chromic acid and dichromate was titrated against 1 M sodium hydroxide solution.

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.

$$H_2CrO_4 + OH^- \leftrightarrow HCrO_4^- + H_2O \qquad \textbf{(3.4)}$$

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

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.

$$Cr_2O_7^{2-} + 2OH^- \leftrightarrow 2CrO_4^{2-} + H_2O \quad \textbf{(3.6)}$$

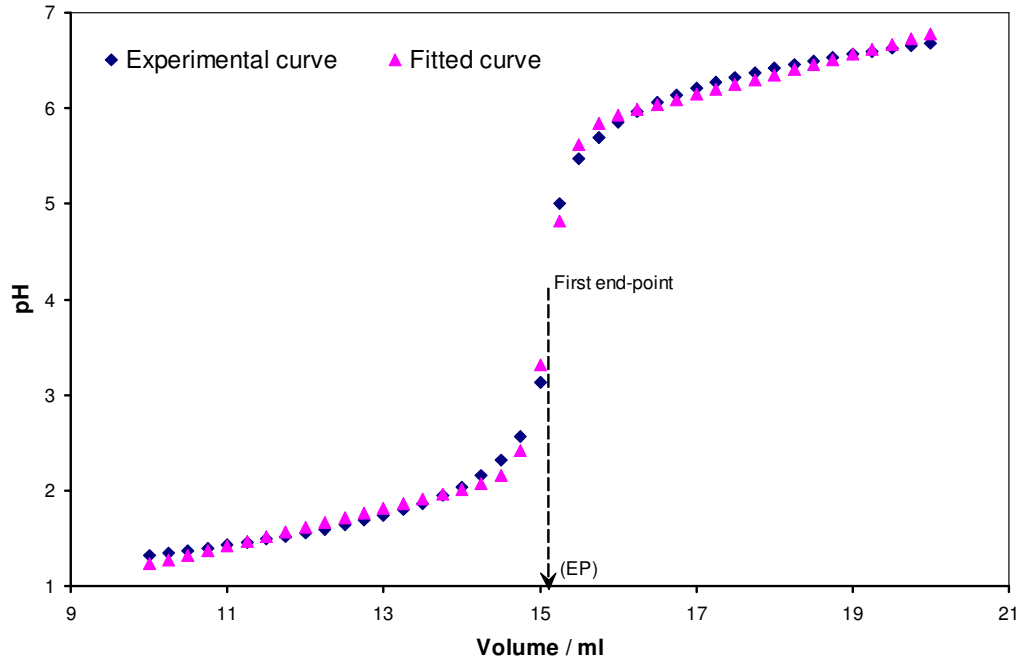

Figure 3.6 The first half of acid-base titration curve.

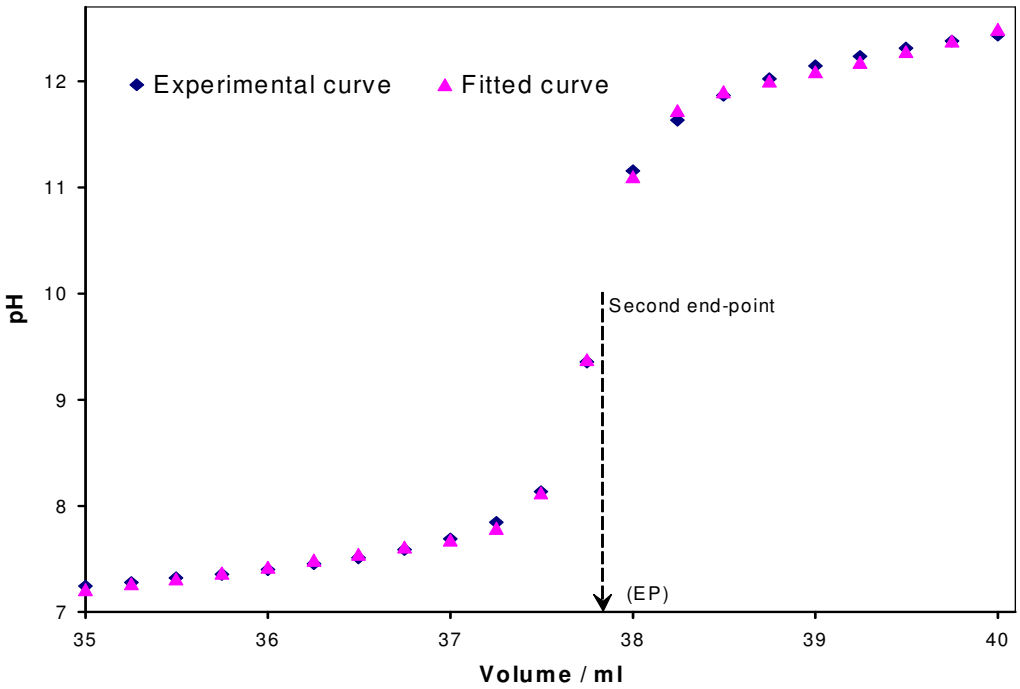

Figure 3.7 The second half of acid-base titration curve.

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

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.

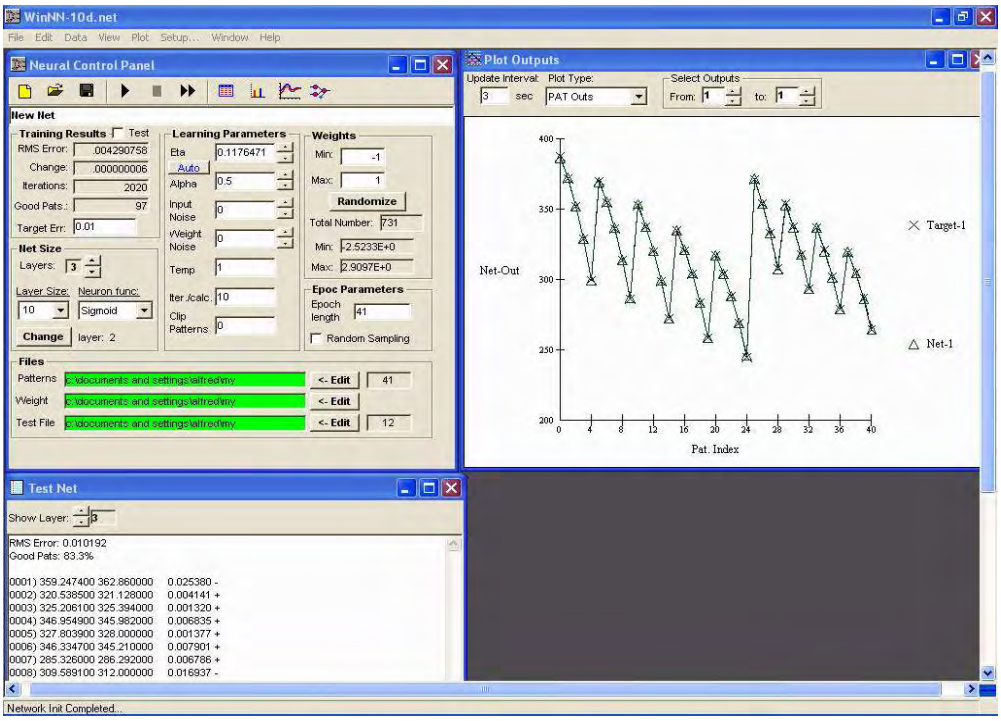

Figure 3.8 WinNNs 32 windows; the upper left-side is neural networks control window, the right one is plot outputs window and the lower one is test networks window.

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.

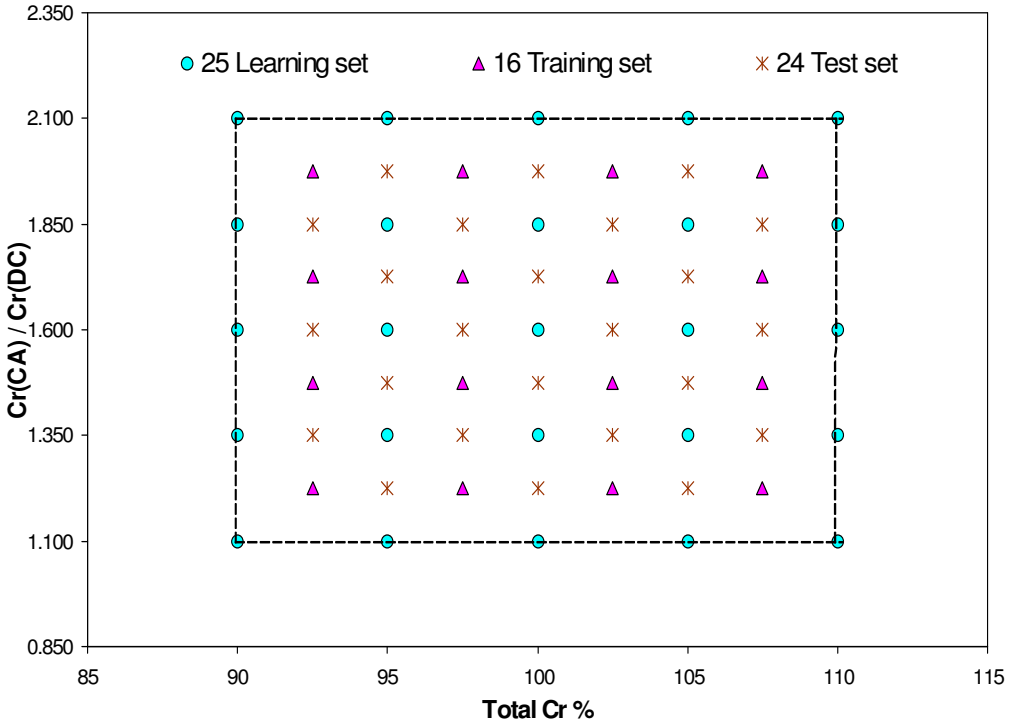

Figure 3.9 Initial experimental design

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.

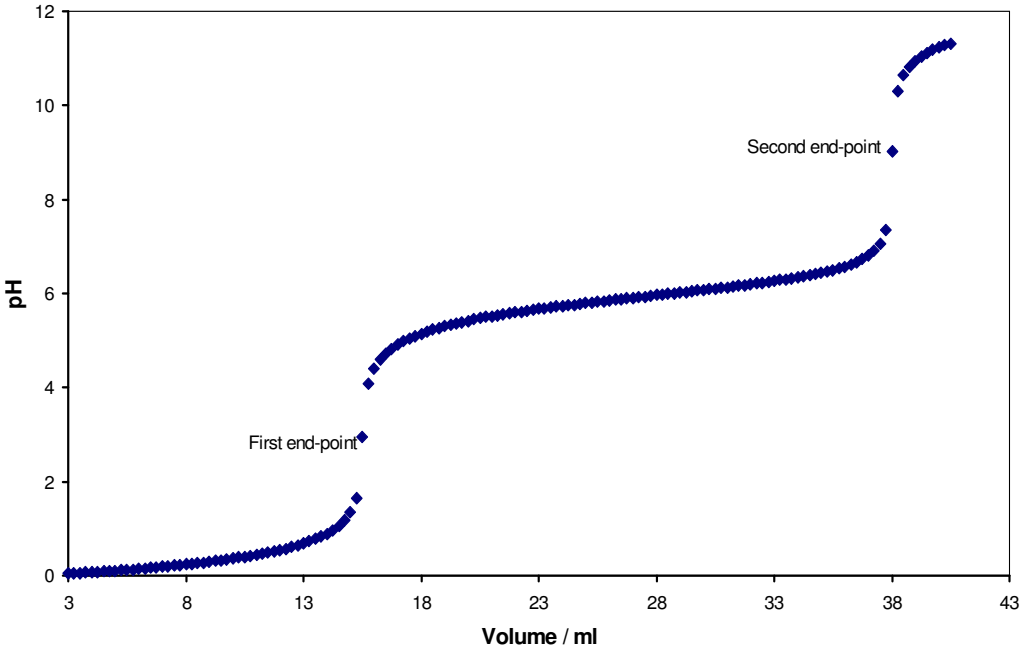

Figure 3.10 An example of acid-base titration curve with all collected points.

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.

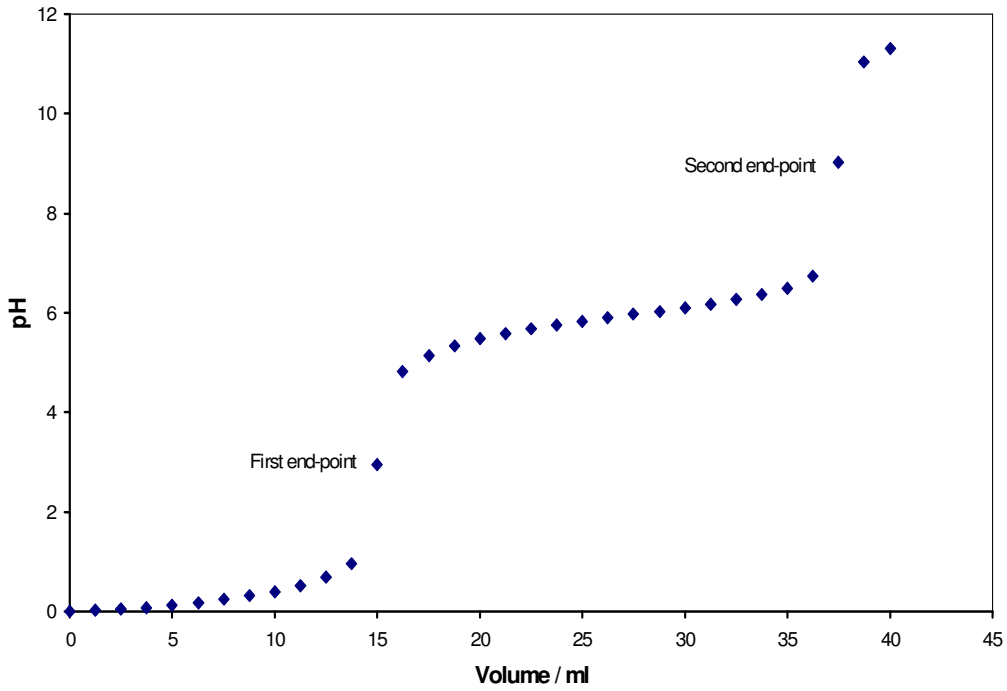

Figure 3.11 An example of acid-base titration curve with reduced or fewer points.

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.

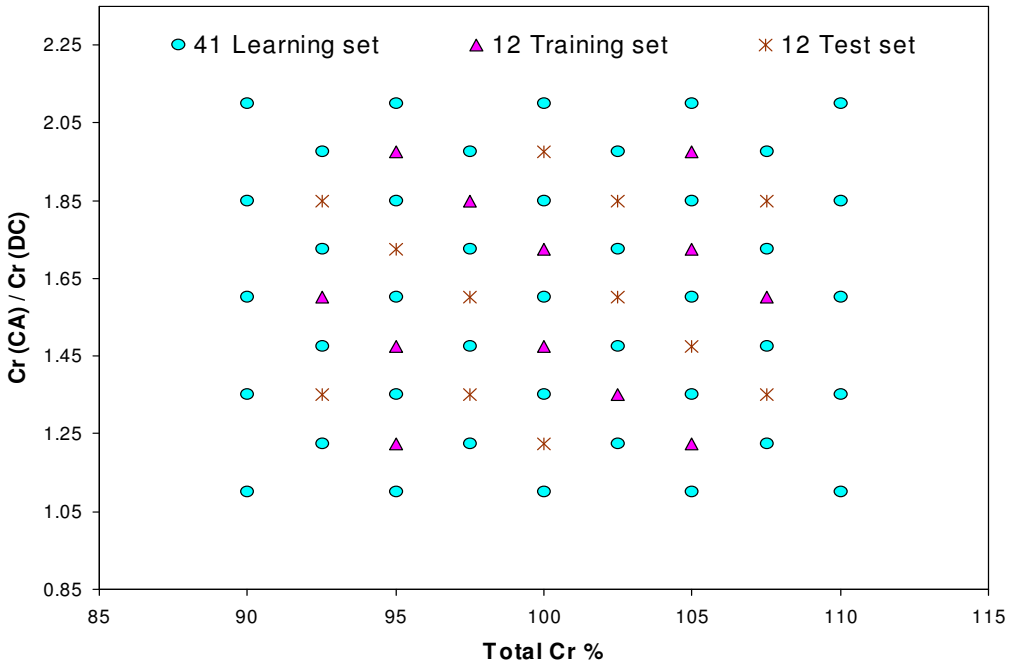

Figure 3.12 Increased learning density experimental design

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).

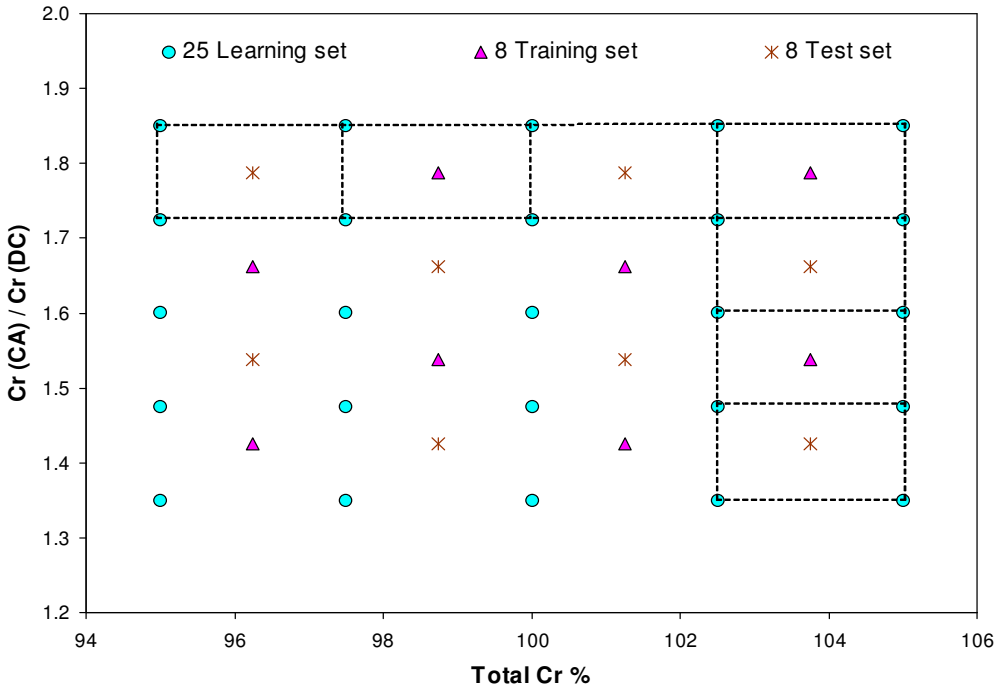

Figure 3.13 Decreased range experimental design

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.

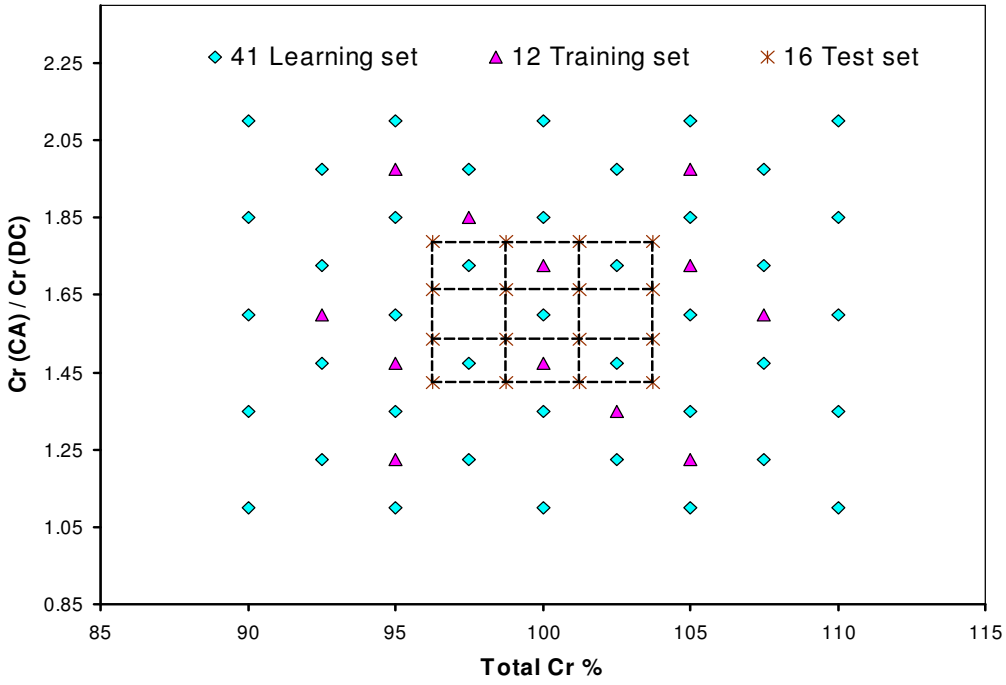

Figure 3.14 Increased learning and test sets of the experimental design

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 ($Na_2Cr_2O_7.2H_2O$). 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.

$$H_2CrO_4 + 3Fe^{2+} + 6H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad \textbf{(4.1)}$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad \textbf{(4.2)}$$

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.

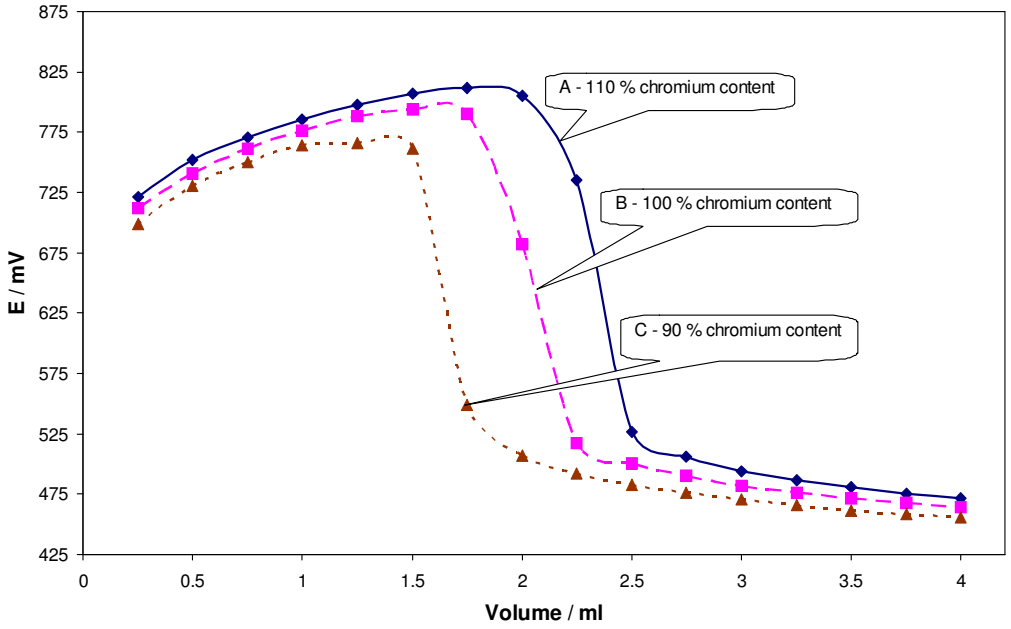

Figure 4.1 Redox titration of $Na_2Cr_2O_7 \cdot 2H_2O$ samples against 0.6 M Fe(II) solution in 1.4 M H_2SO_4 solution. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

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.

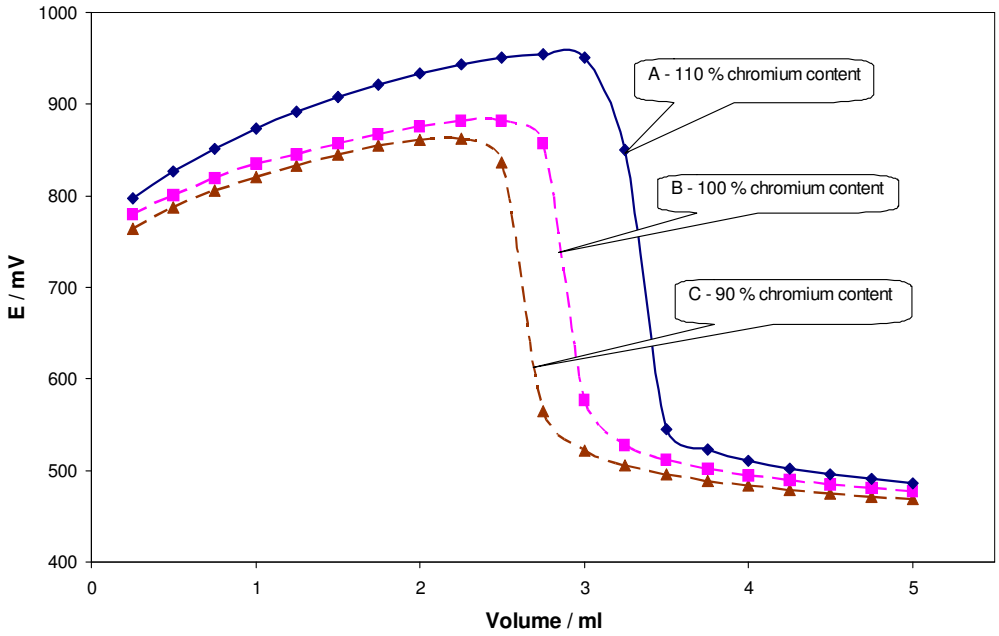

Figure 4.2 Redox titration of H_2CrO_4 samples against 0.6 M Fe(II) solution in 1.4 M H_2SO_4 solution. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

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.

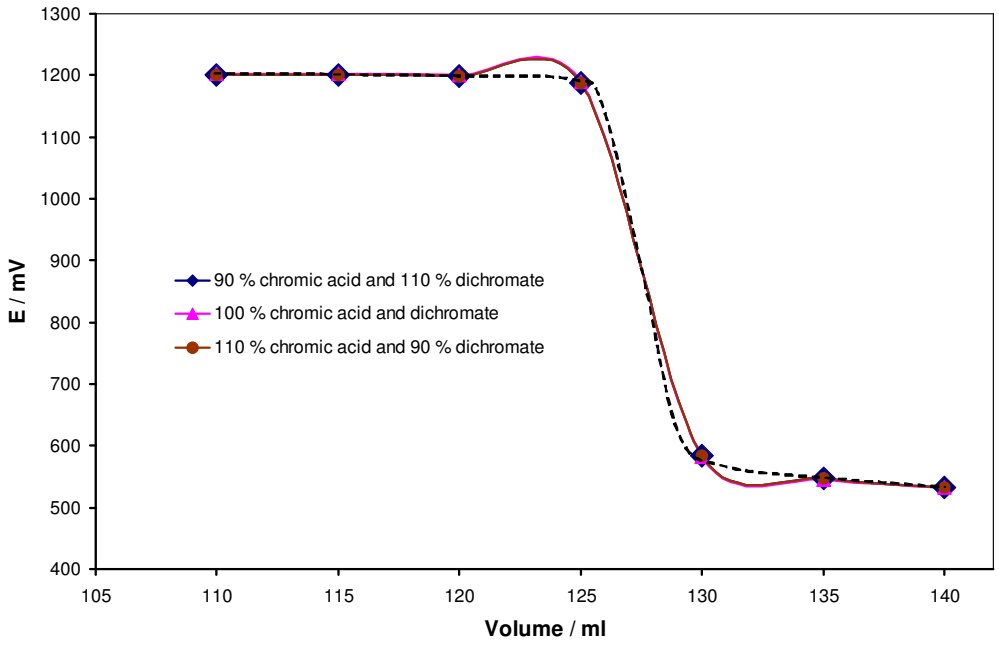

Figure 4.3 Redox titration of chromium samples against 0.6 M Fe(II) solution in 3 M H_2SO_4 solution. The total chromium concentration was equal in all three samples. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution). (Solid lines were generated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

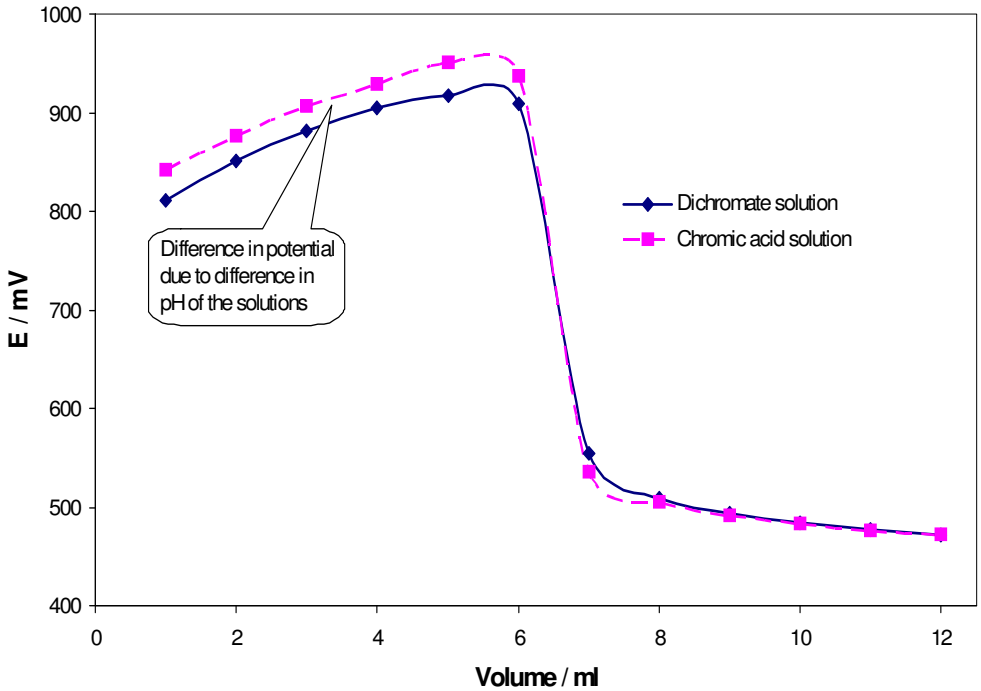

Figure 4.4 Redox titration of chromic acid and dichromate samples against 0.5 M Fe(II) solution in 1.4 M H_2SO_4 solution. Chromium concentration in chromic acid sample was equal to chromium concentration in dichromate sample. The potential of the solutions was measured with Pt electrode and Ag/AgCl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

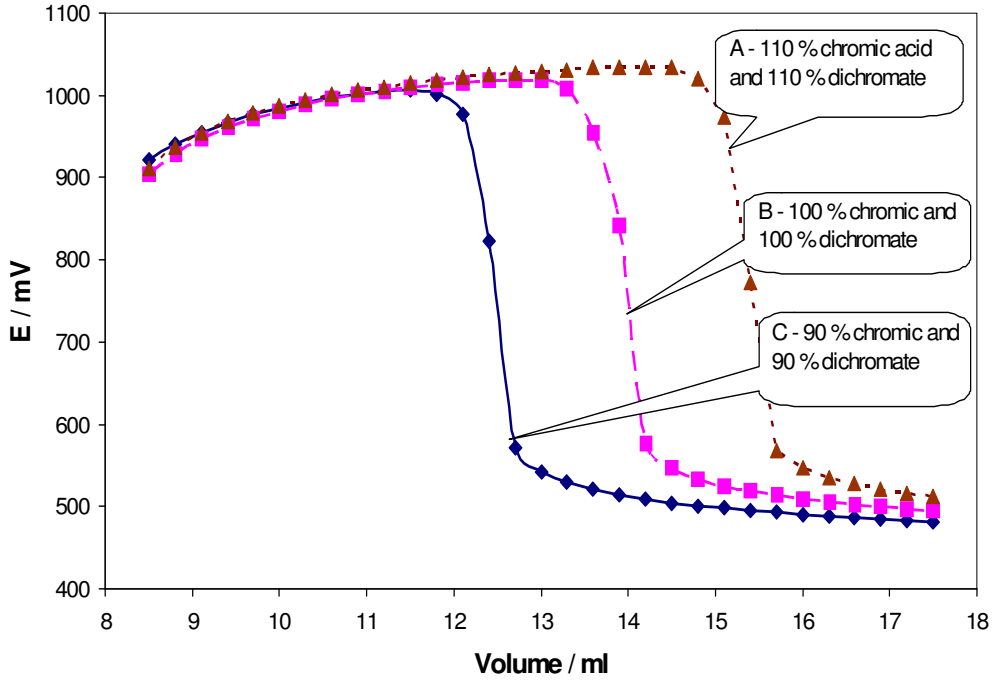

Figure 4.5 Redox titration of chromium samples against 0.5 M Fe(II) solution in 1 M H_2SO_4 solution. The total chromium concentration in all three samples was different. The potential of the solutions was measured with Pt electrode and Ag/AgCl reference electrode (3 M KCl solution).

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

Both chromium trioxide and sodium dichromate are soluble in water and give raise 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.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \quad \textbf{(4.3)}$$

$$H_2CrO_4 + OH^- \leftrightarrow HCrO_4^- + H_2O \quad \textbf{(4.4)}$$

$$HCrO_4^- + OH^- \leftrightarrow CrO_4^{2-} + H_2O \quad \textbf{(4.5)}$$

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 extend, 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.

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad \textbf{(4.6)}$$

$$HCrO_4^- + OH^- \leftrightarrow CrO_4^{2-} + H_2O \quad \textbf{(4.7)}$$

Only one jump is observed when dichromate solution is titrated with sodium hydroxide solution and it is seen as EP_3 in Figure 4.6. The initial concentration of dichromate solution was 0.0233 M.

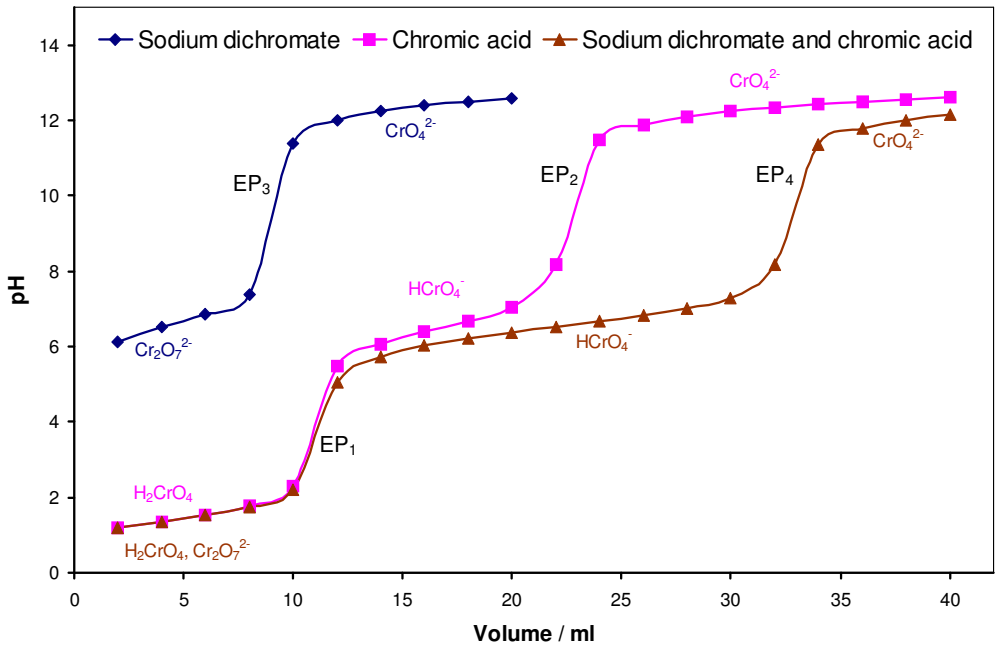

Figure 4.6 Titration of chromium(VI) solutions against 0.1 M sodium hydroxide solution as a titrant. ◊ = 0.0233 M dichromate sample and □ = 0.0554 M chromic acid sample. Δ = chromic acid and dichromate sample.

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:

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

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 ($Na_2Cr_2O_7.2H_2O$) in the training set of data of the initial experimental design.

Sample number	Concentration of $Na_2Cr_2O_7.2H_2O$/ 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 ($Na_2Cr_2O_7.2H_2O$) in the learning set of data of the initial experimental design.

Sample number	Concentration of $Na_2Cr_2O_7.2H_2O$/ 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 a shown in Table 4.5. An absolute percentage error of ≤ 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 ($Na_2Cr_2O_7.2H_2O$) in the test set of data of the initial experimental design.

Sample number	Concentration of $Na_2Cr_2O_7.2H_2O$/ 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 $Na_2Cr_2O_7.2H_2O$ are 100% reagents, they are of technical and not reagent grate purity. CrO_3 must contain $Cr_2O_7^{2-}$ and vice versa.

These two systematic errors (negative and small for CrO_3, positive and large for $Cr_2O_7^{2-}$) also indicate that CrO_3 is relatively clean. It contains small quantities of impurities. Since the presence of $Cr_2O_7^{2-}$ does not interfere in NaOH titration, it should be possible to determine CrO_3 from ANNs quite exactly. Unfortunately, large error for $Cr_2O_7^{2-}$ indicates significant impurities by CrO_3 and other forms of chromium. Because the presence of CrO_3 has influence on the $Cr_2O_7^{2-}$ 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 ≤ 1%, on average. Percentage error of ≤ 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 ≤ 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 <u>expected</u> 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 ≤ 1%, as required in the industrial electrolytic process.

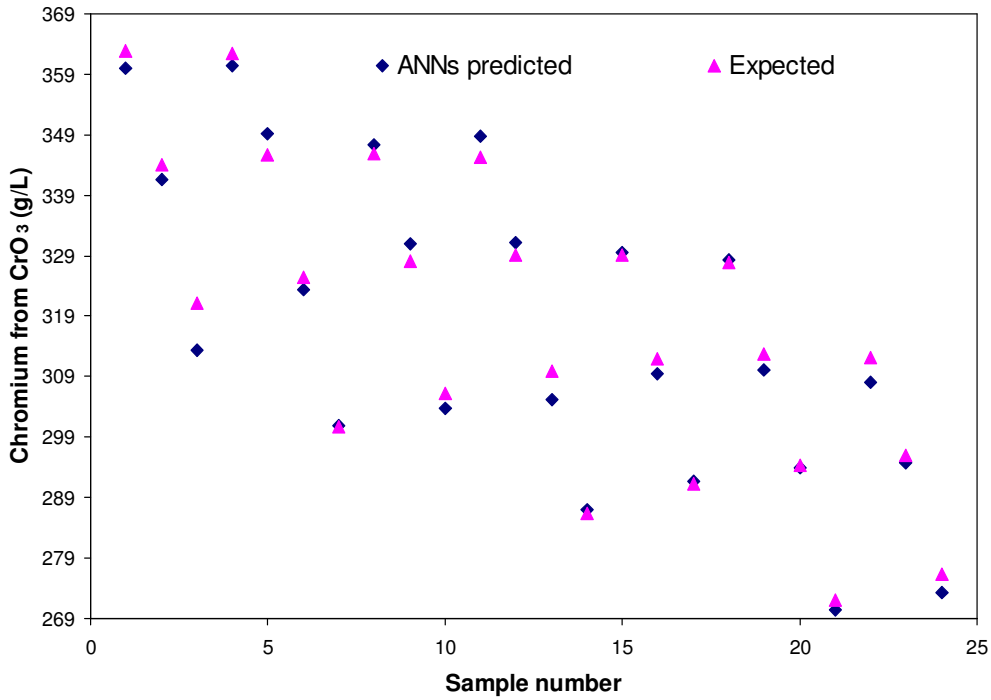

Figure 4.7 Test results obtained for chromium from chromic acid from the neural networks in which the titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the expected total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

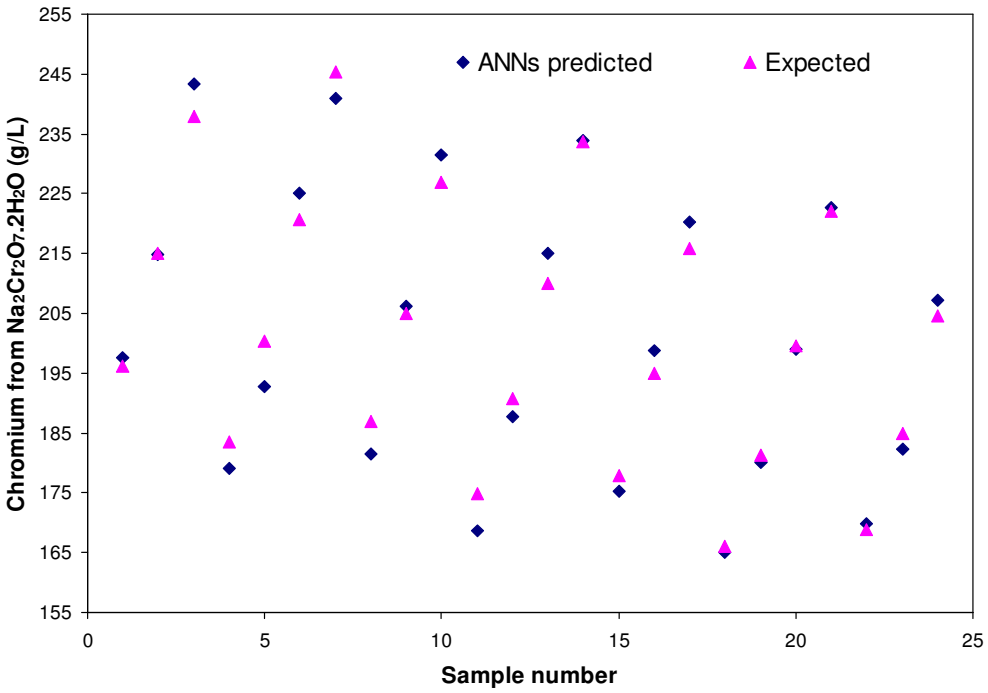

Figure 4.8 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium concentration.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

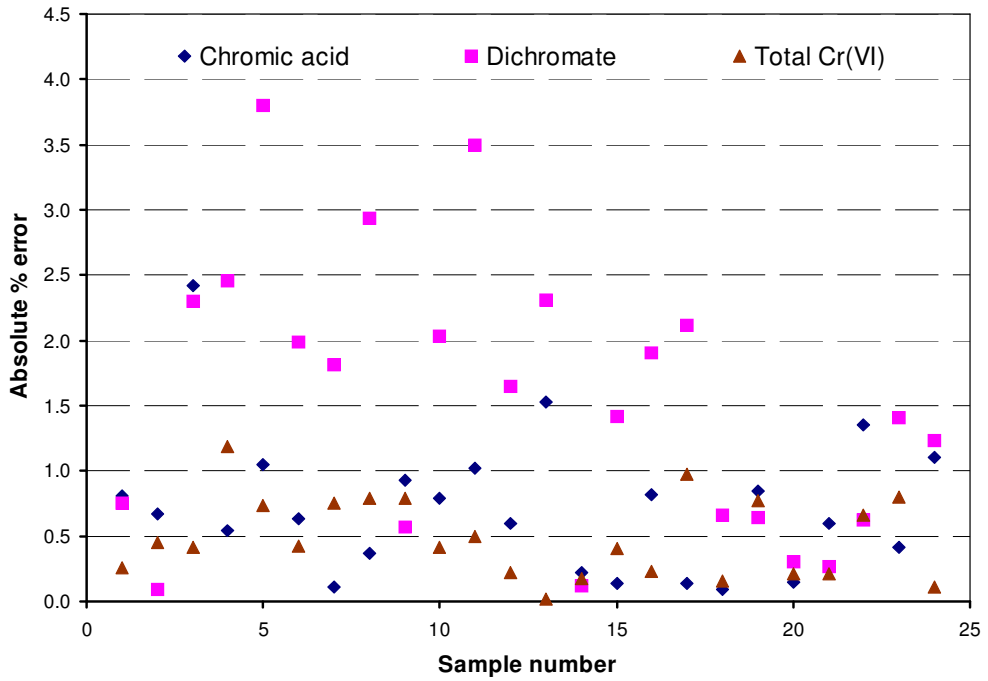

Figure 4.9 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium. The titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were the expected concentrations of chromium from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

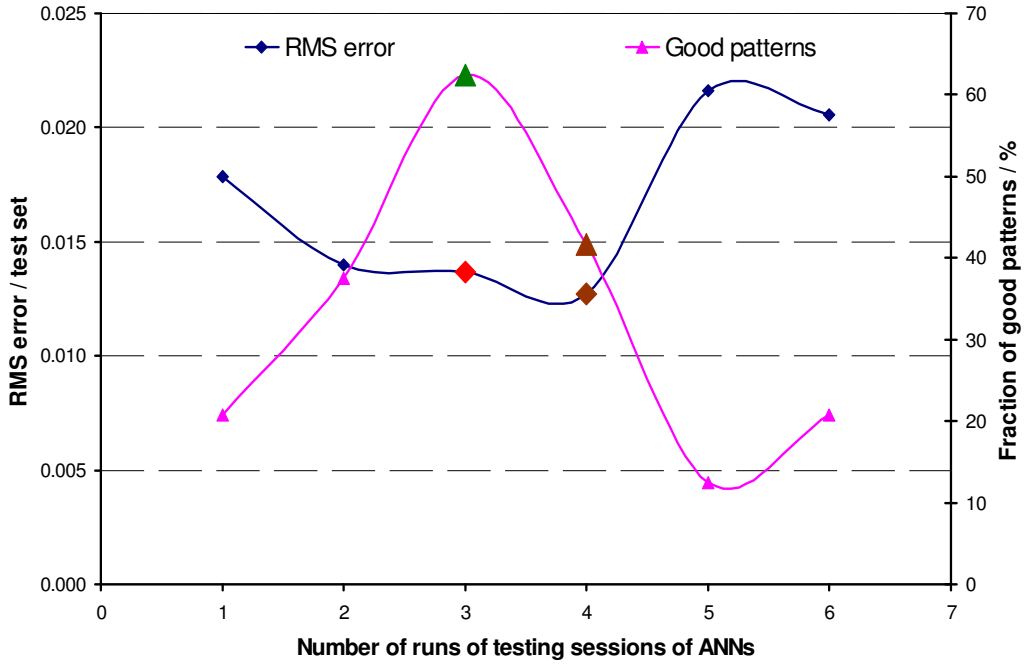

Figure 4.10 An example of variation in RMS error and number of good patterns with consecutive training/testing of ANNs. There were 10 neurons in the hidden layer. The titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were 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 ≤ 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.

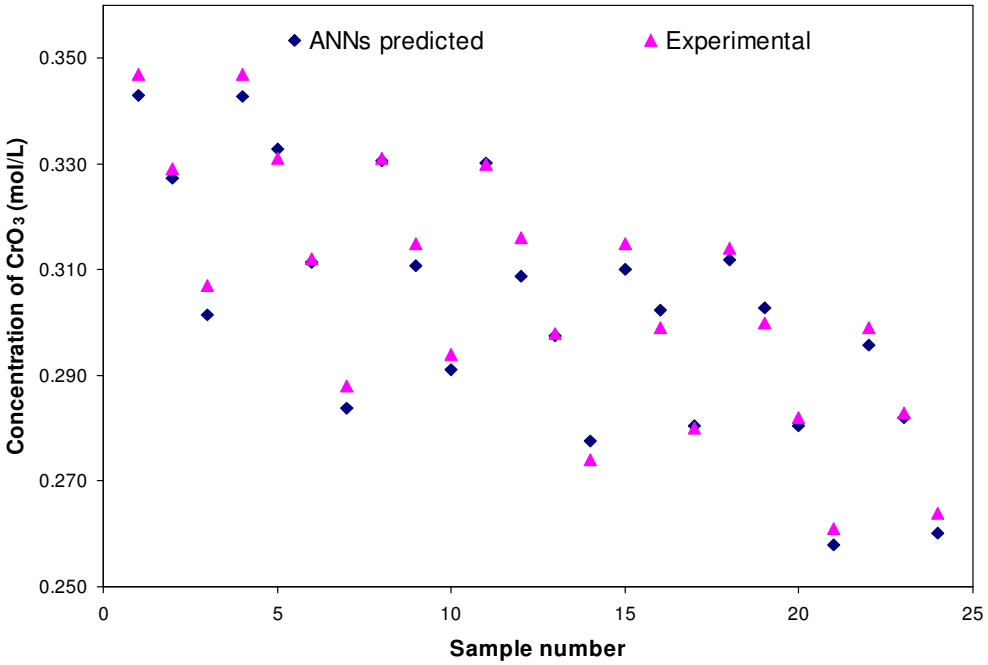

Figure 4.11 Test results obtained for chromic acid in the neural networks in which titration curves with all collected points from the initial experimental design were used as the inputs. The outputs were the concentrations of chromic acid and dichromate obtained by fitting titration curves (experimental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

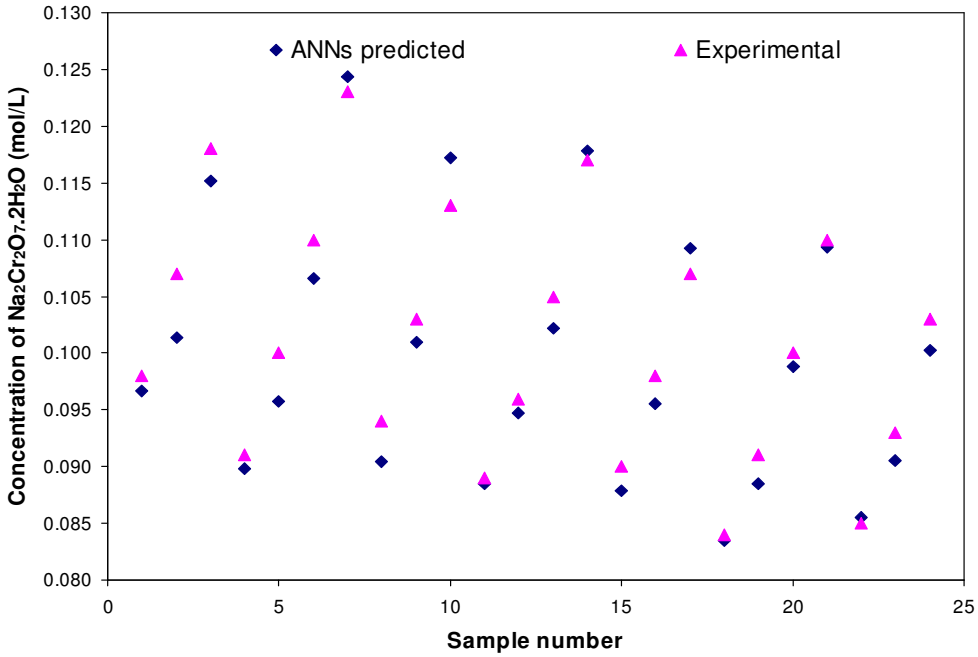

Figure 4.12 Test results obtained for dichromate concentration in the neural networks in which titration curves with all collected points from the initial experimental design were provided as the inputs. The outputs were the concentrations of chromic acid and dichromate obtained by fitting titration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

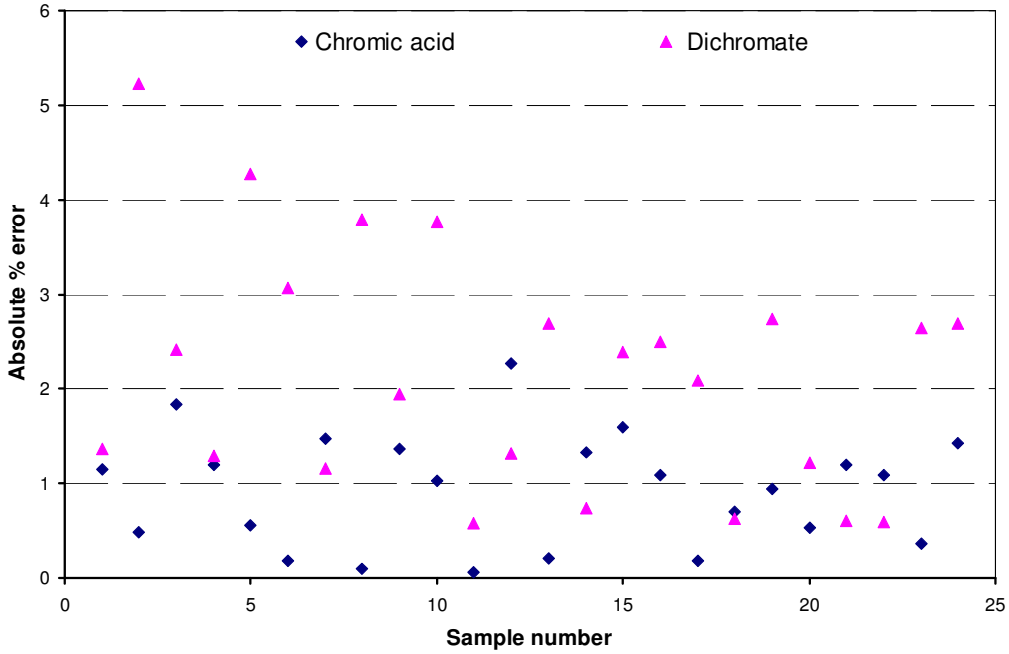

Figure 4.13 Variation in absolute percentage error of chromic acid and dichromate concentration. Titration curves with all collected points from the initial experimental design were the inputs of the neural networks. The outputs were the concentrations of chromic acid and dichromate obtained by fitting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

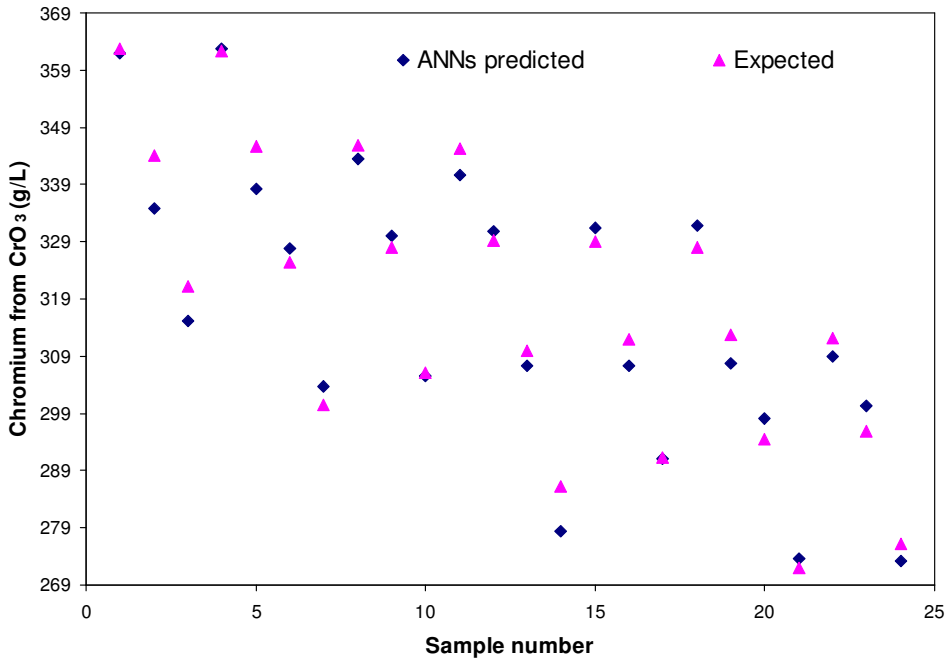

Figure 4.14 Test results obtained for chromium from chromic acid in the neural networks in which titration curves with fewer points from the initial experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium.

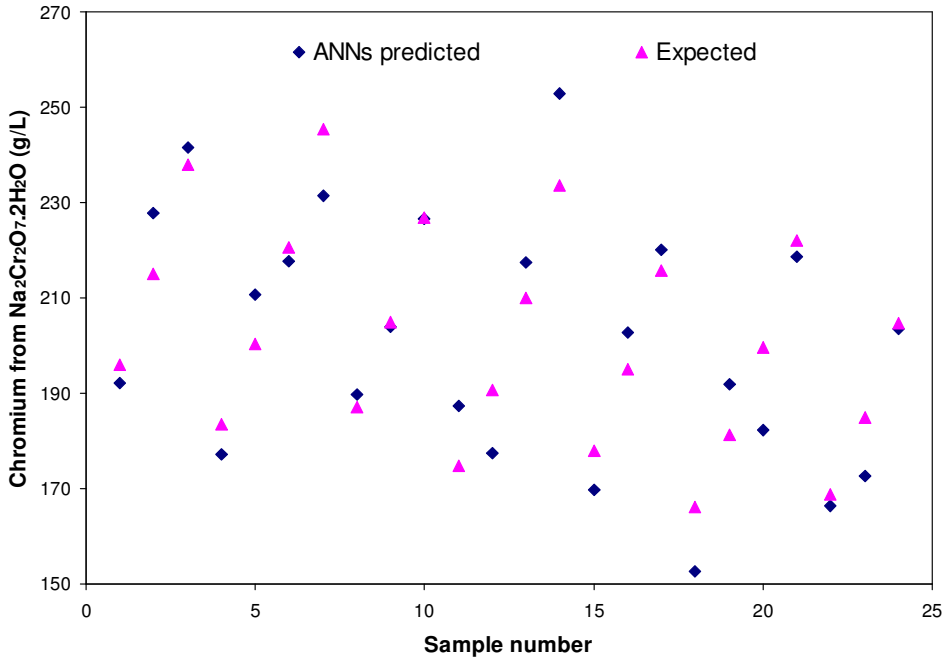

Figure 4.15 Test results obtained for chromium from dichromate in the neural networks in which titration curves with fewer points from the initial experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and total chromium. The concentration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

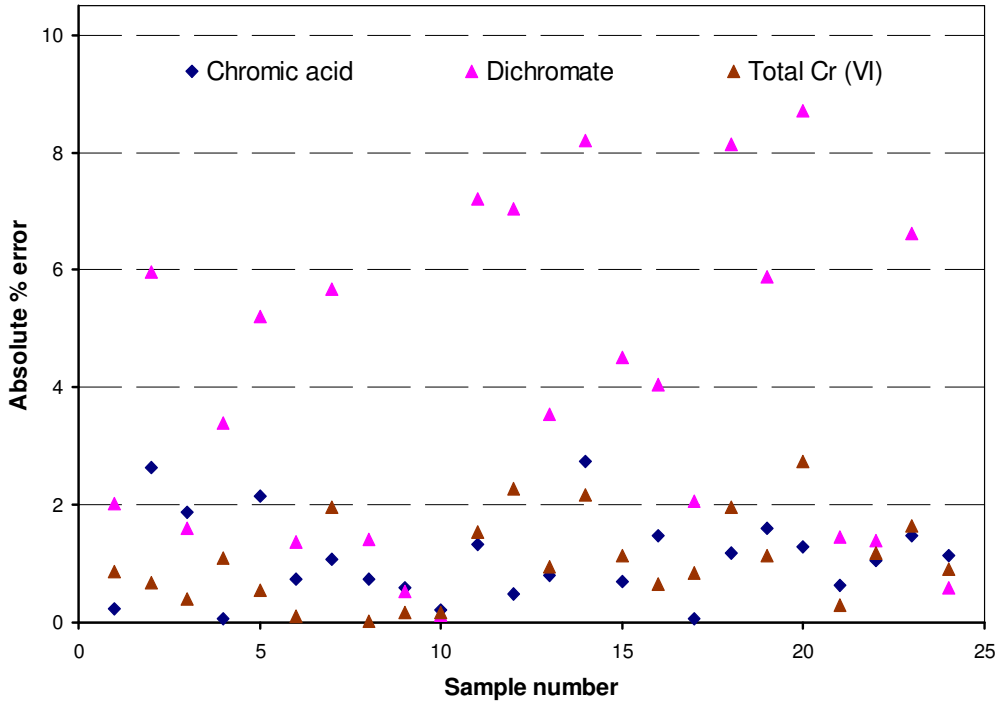

Figure 4.16 Variation in percentage error of chromium from chromic acid, dichromate concentration and total chromium concentration. Titration curves with fewer points from the initial experimental design were the inputs of the neural networks. The outputs were the expected concentrations of chromium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

Absolute percentage error of ≤ 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 ≤ 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%.

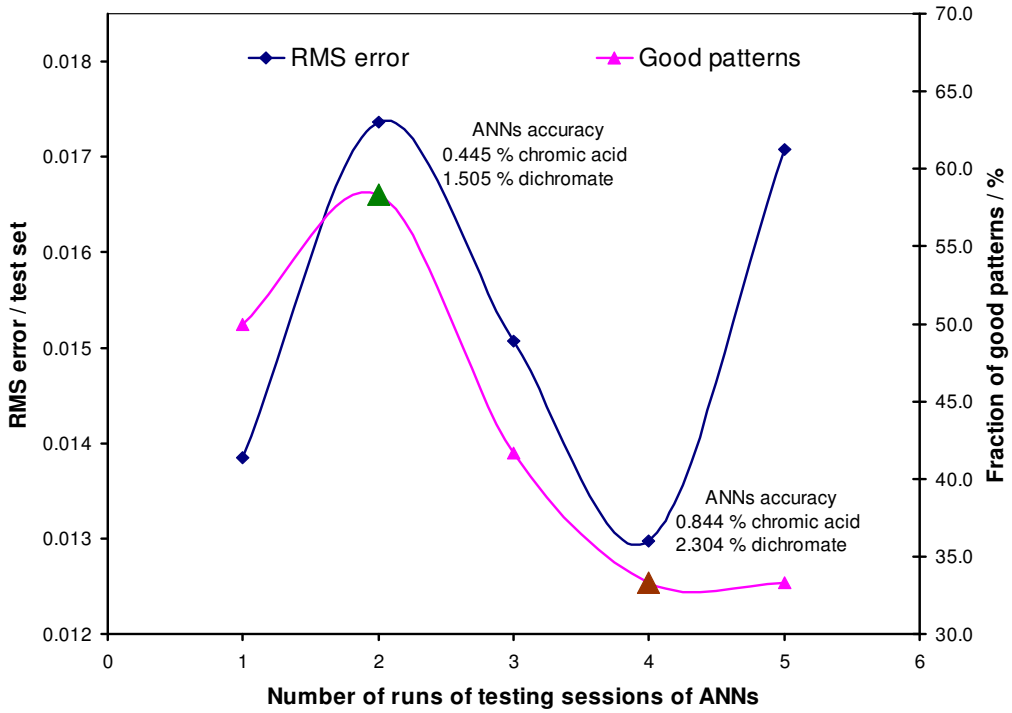

Figure 4.17 An example of variation in an RMS error and number of good patterns with consecutive training/testing of ANNs. There were 18 neurons in the hidden layer. Titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs 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 form 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 halve 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 / CrO_3; No. = number; NaDC = Sodium dichromate ($Na_2Cr_2O_7.2H_2O$).

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 $H_2Cr_2O_7$. 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 8^{th} 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 ± 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.

1 Increased learning data set in the experimental design

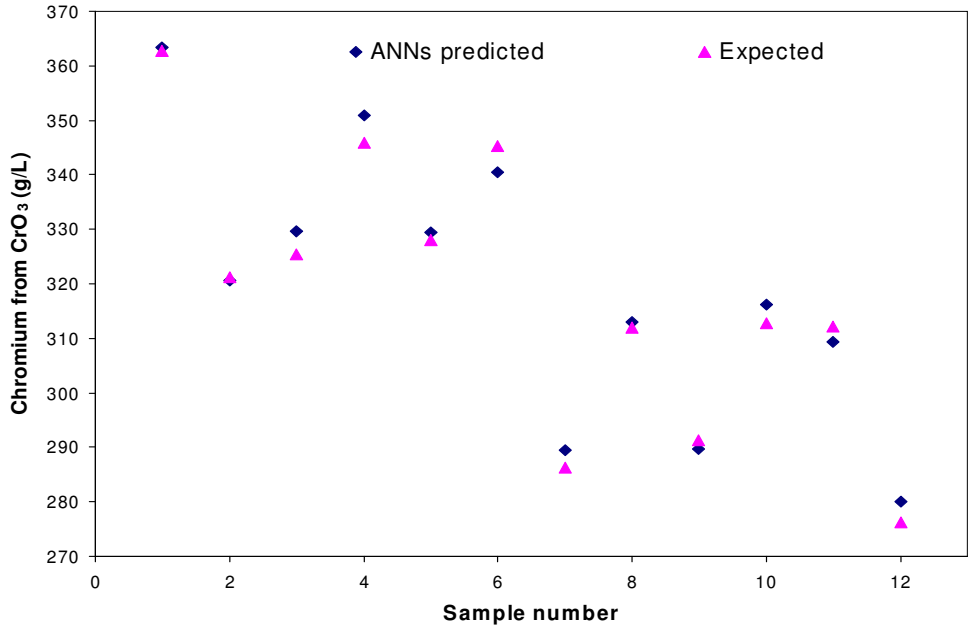

Figure A1 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

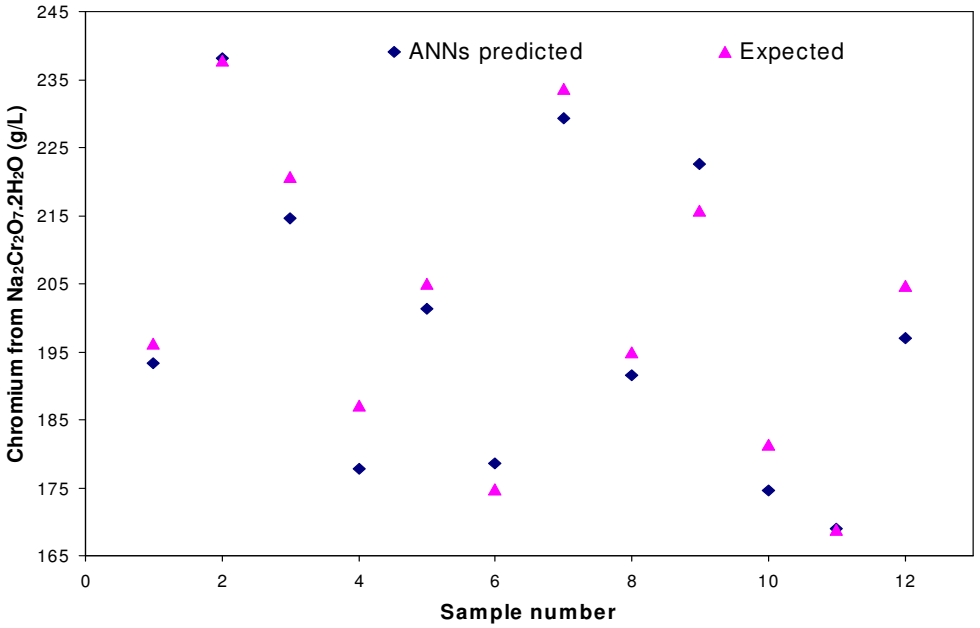

Figure A2 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

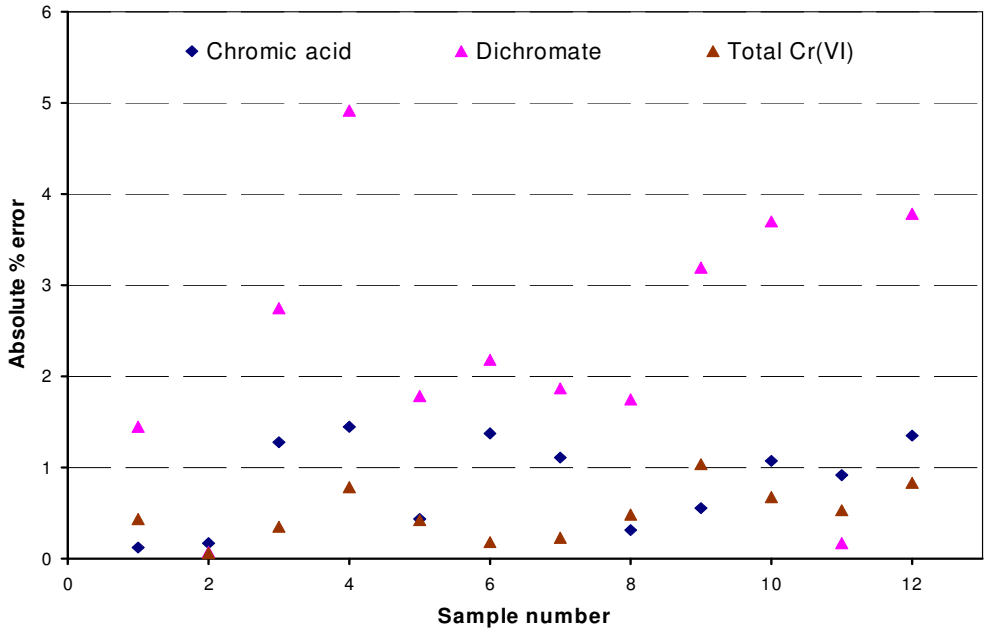

Figure A3 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium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

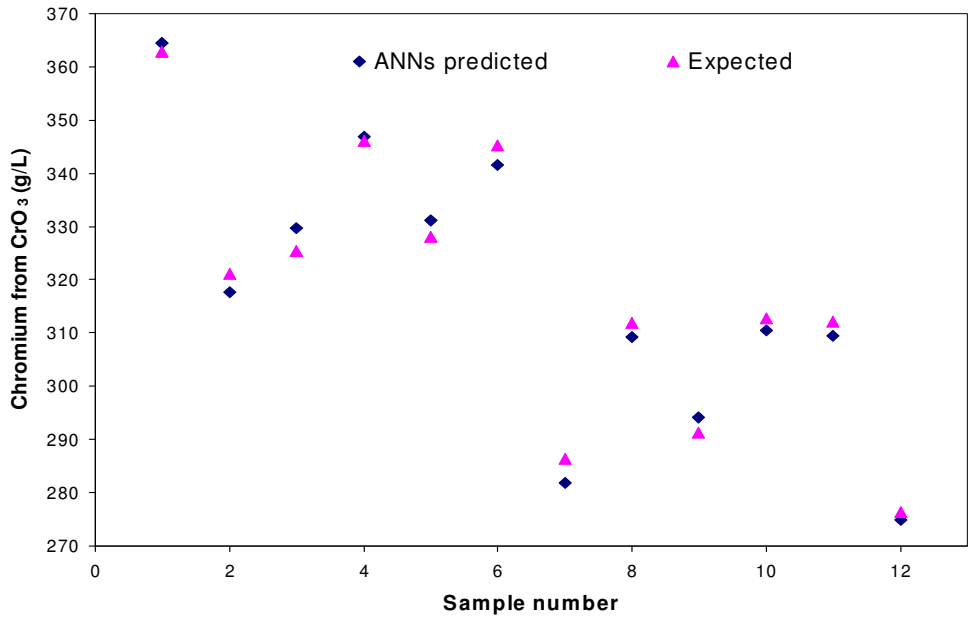

Figure A4 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with fewer or reduced points from increased learning data set in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid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

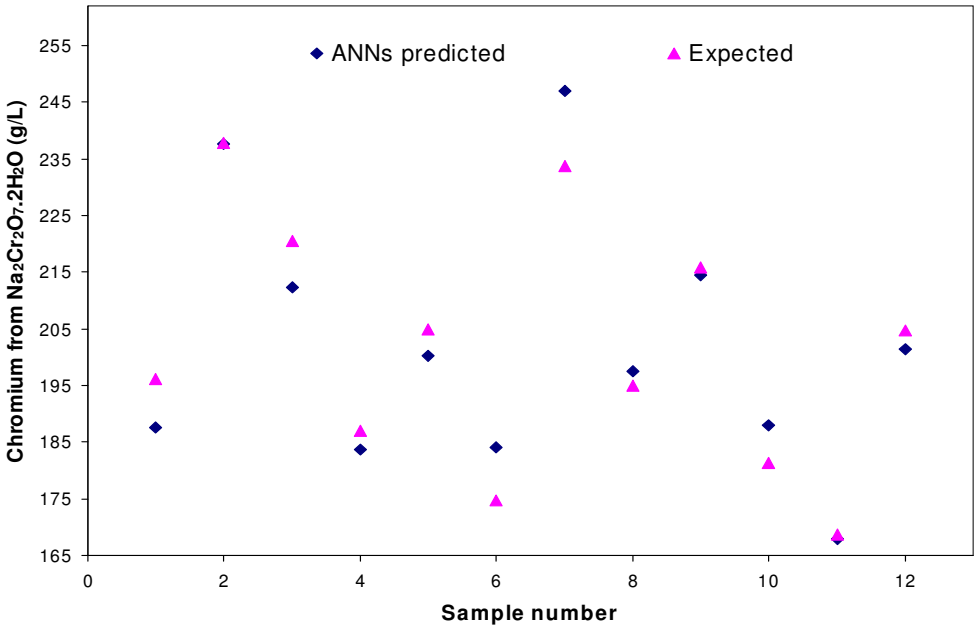

Figure A5 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with fewer or reduced points from increased learning data set in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium. The concentration of chromium from dichromate was calculated as the difference between the total chromium and chromium from chromic acid.

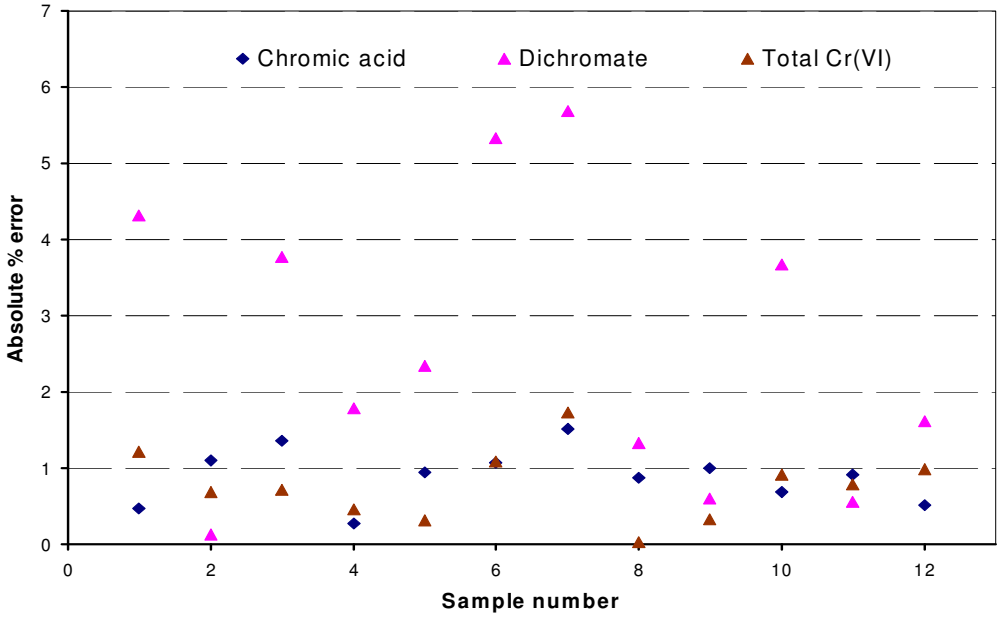

Figure A6 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium. The titration curves with fewer or reduced points from increased learning data in the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic acid and the total chromium.

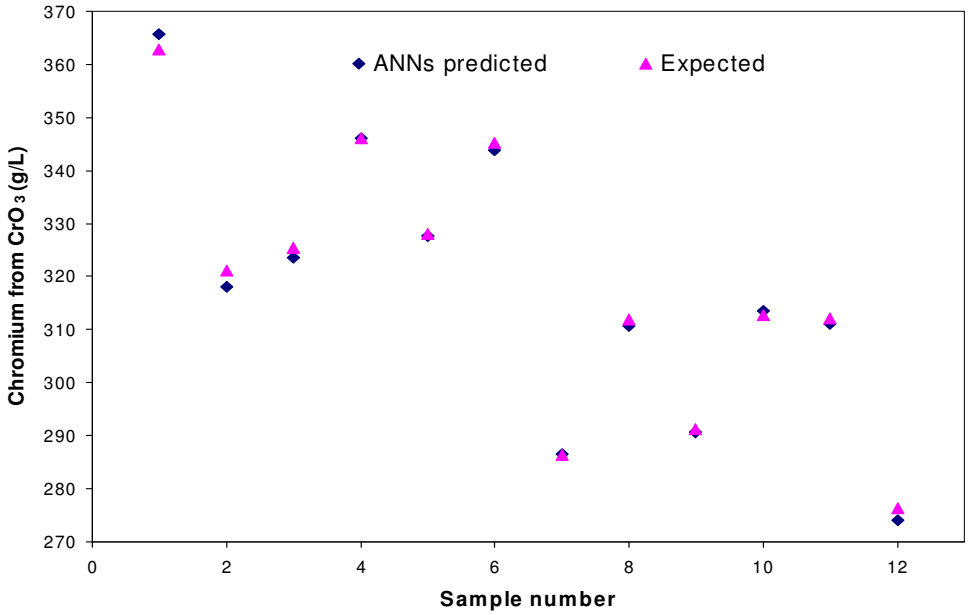

Figure A7 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

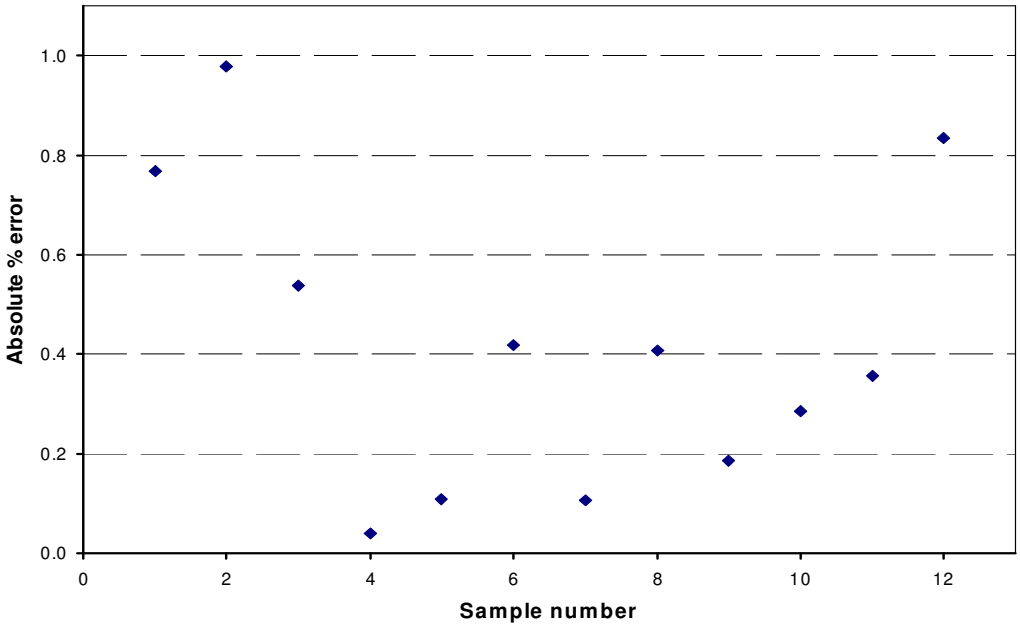

Figure A8 Variation in an absolute percentage error of chromium from chromic acid. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

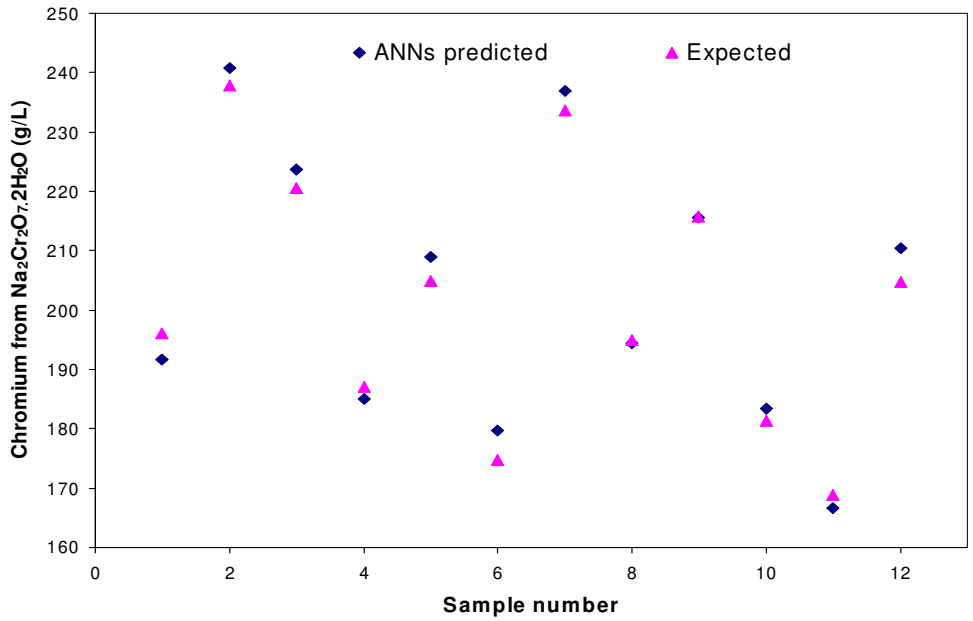

Figure A9 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from dichromate.

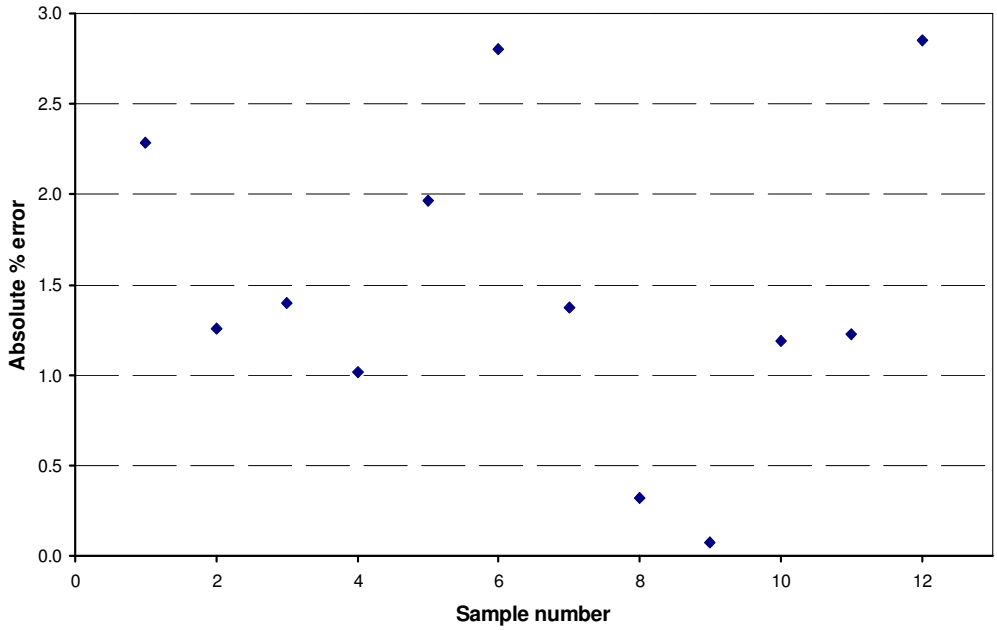

Figure A10 Variation in an absolute percentage error of chromium from dichromate. The titration curves with all collected points from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from dichromate.

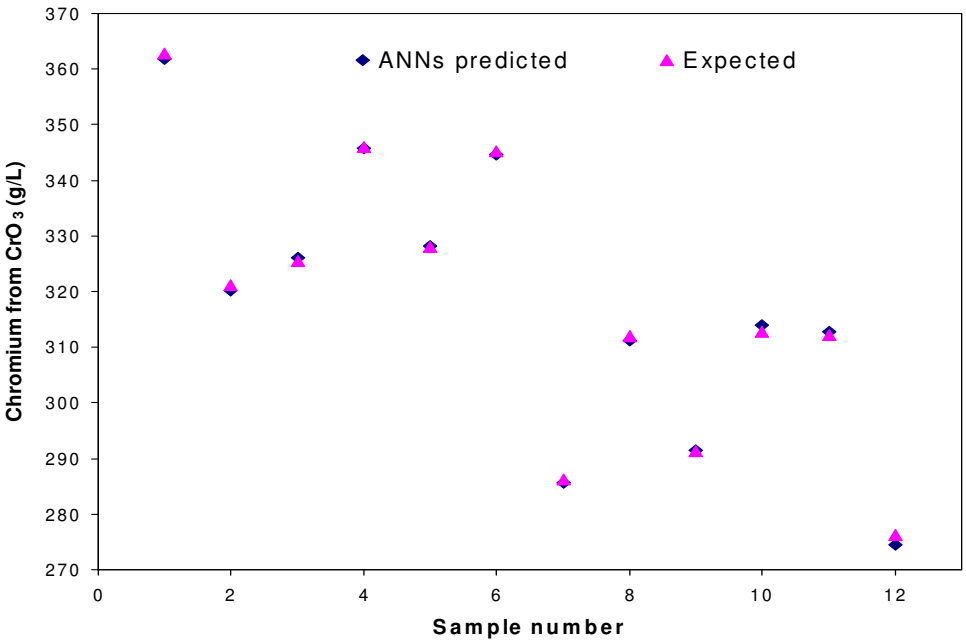

Figure A11 Test results obtained for chromium from chromic acid in the neural networks in which the first halves of the titration curves from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

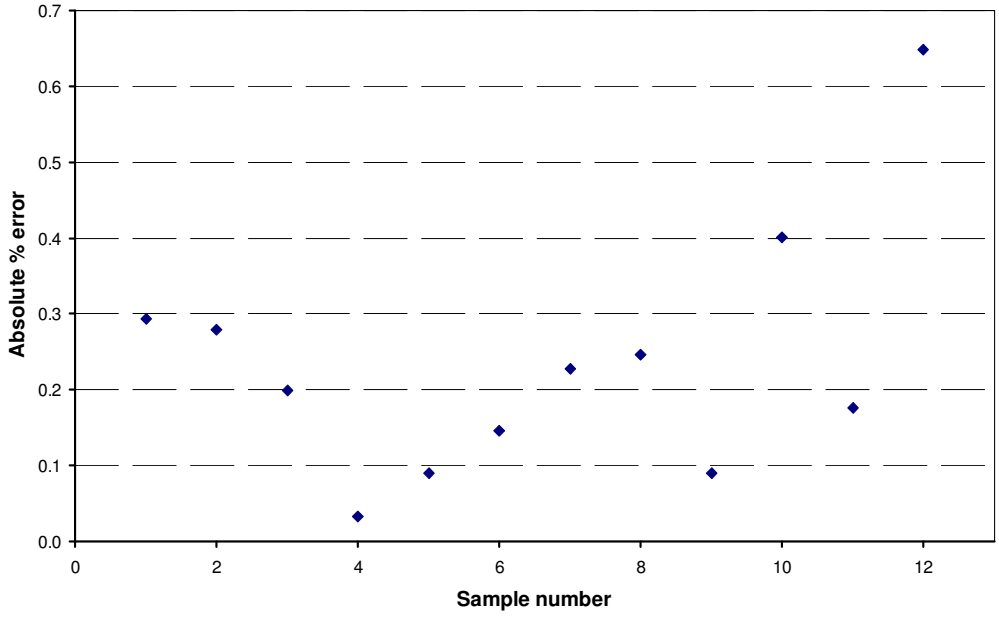

Figure A12 Variation in an absolute percentage error of chromium from chromic acid. The first halves of the titration curves from increased learning data in the experimental design were used as the inputs. The output was the expected concentration of chromium from chromic acid.

2. Decreased range of experimental design

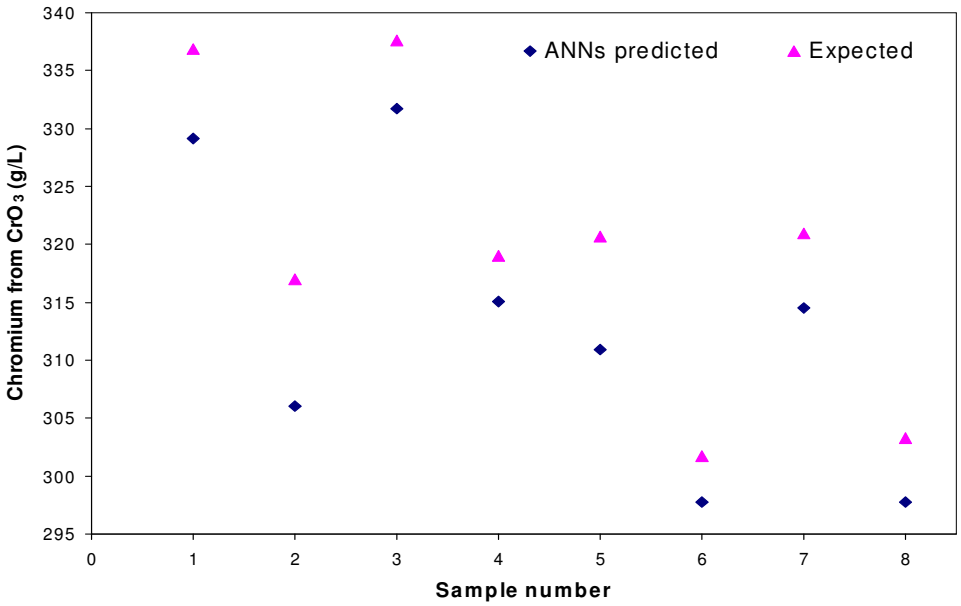

Figure A13 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total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

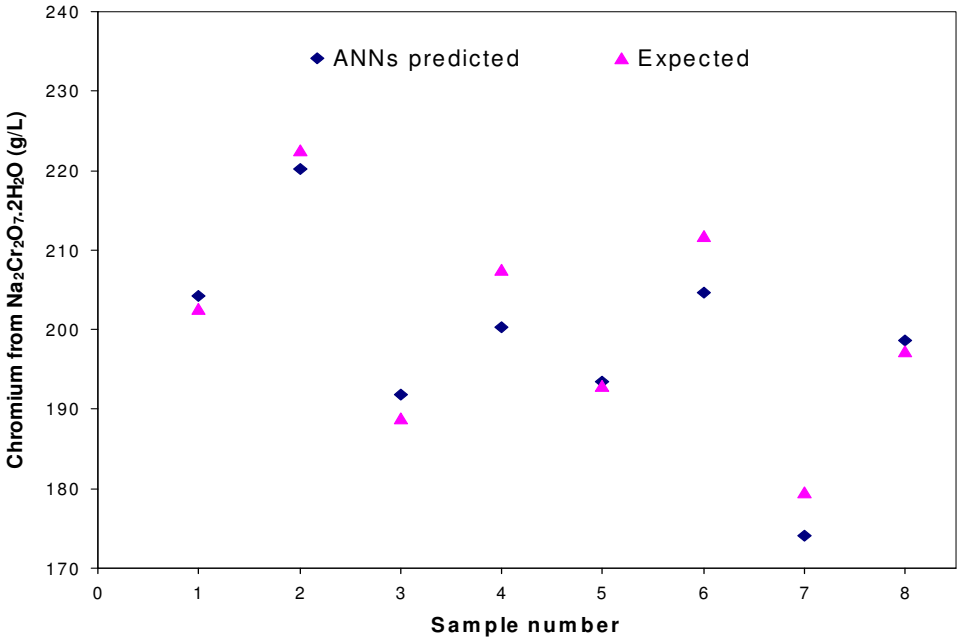

Figure A14 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic acid and the total chromium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

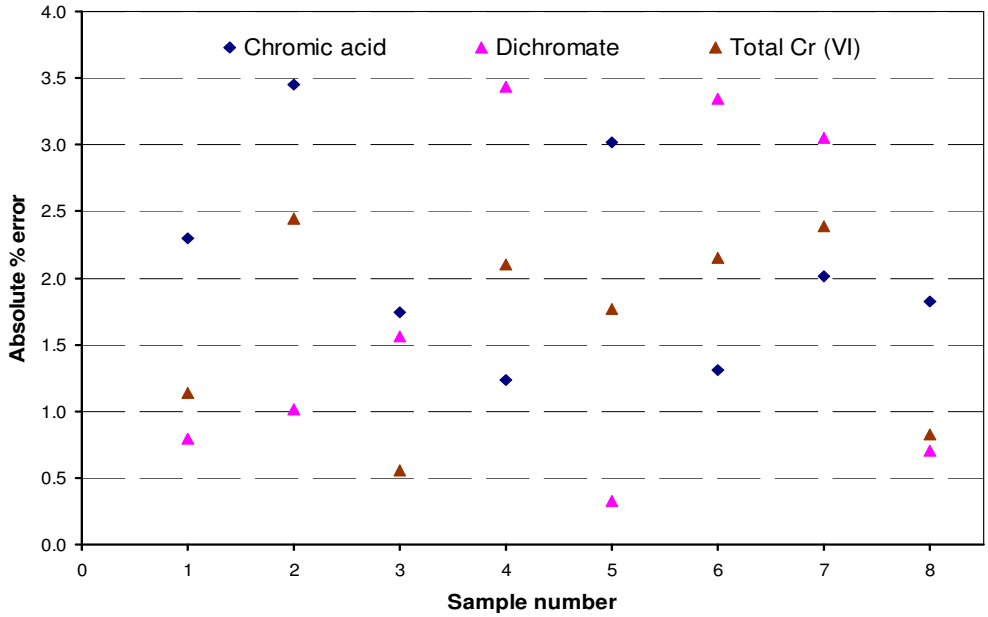

Figure A15 Variation in absolute percentage error of chromium from chromic acid, dichromate and total chromium concentration. Titration curves with all collected points from a decreased range of experimental design were used as the inputs. The outputs were the expected concentrations of chromium from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

3. Increased learning and test sets of the experimental design

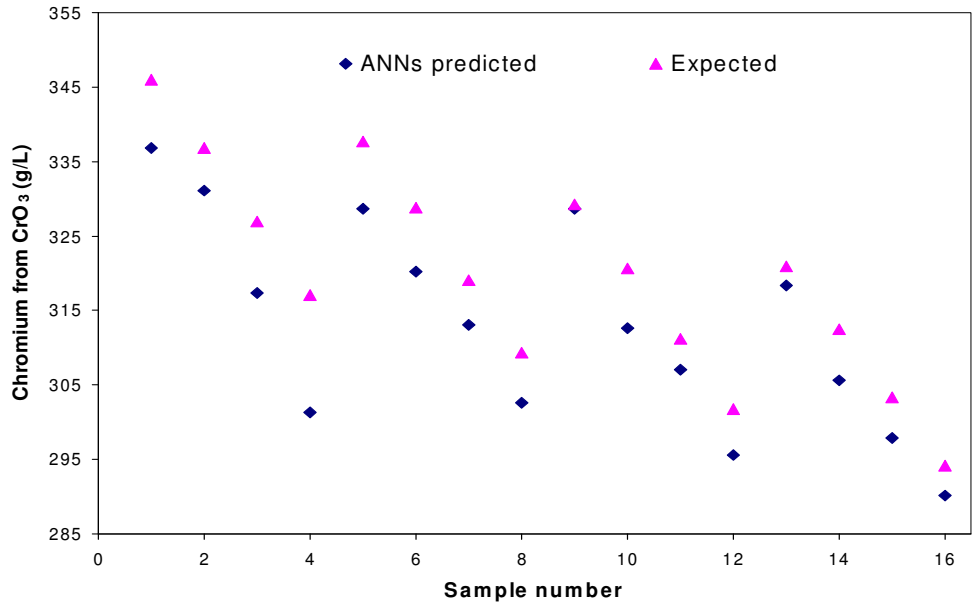

Figure A16 Test results obtained for chromium from chromic acid in the neural networks in which the titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentration of chromium from chromic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

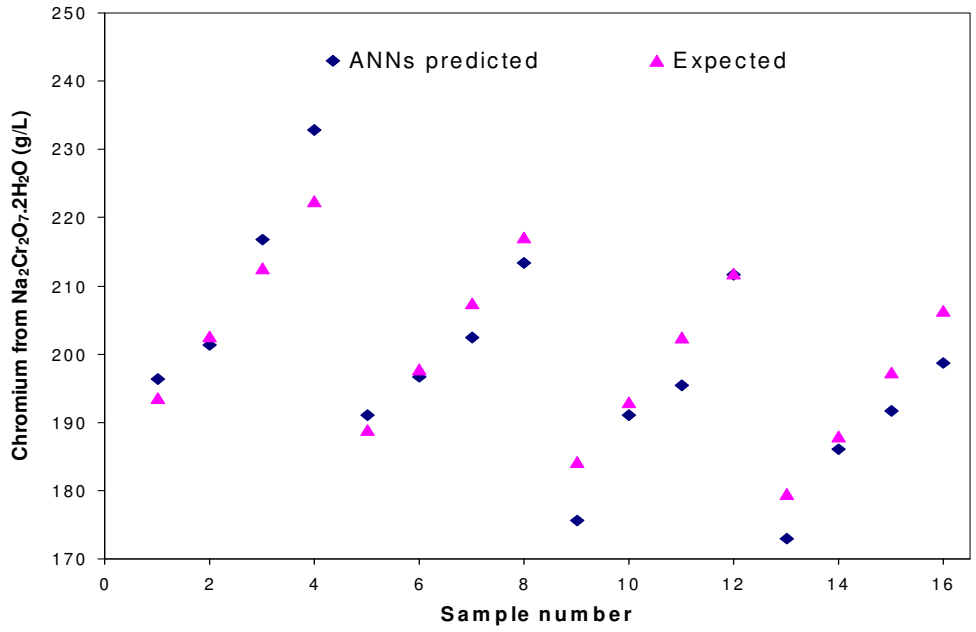

Figure A17 Test results obtained for chromium from dichromate in the neural networks in which the titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentrations of chromium from chromic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

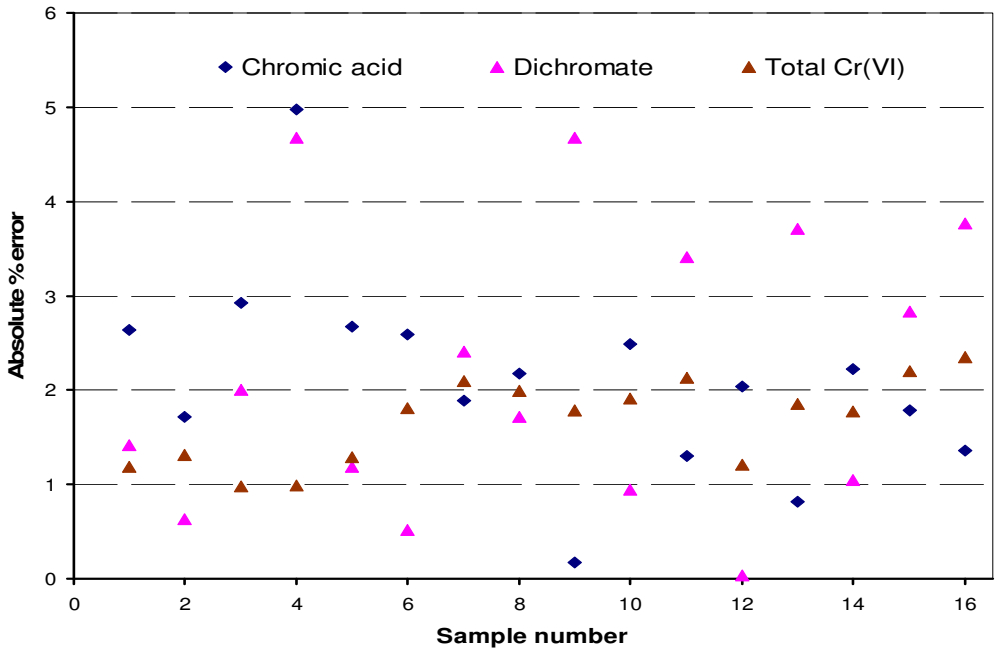

Figure A18 Variation in an absolute percentage error of chromium from chromic acid, dichromate and the total chromium concentration. The titration curves with all collected points from increased learning and test sets of the experimental design were used as the inputs. The outputs were the expected concentration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

Table B1. Preparation of 20 times diluted chromium samples, as compared to the samples in the 8th stage of the industrial electrolytic process. The total chromium concentration was constant.

Chromium trioxide (CrO_3)	Volume of flask (mL) 200	Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	Volume of flask (mL) 200
mole	100	mole	298
mass (g)	12.3063	mass (g)	12.9494
[CrO_3] mol/L	0.6153	[NaDC] mol/L	0.2173
Mass (g) Cr	6.3993	Mass (g) Cr	2.2596

Sample Number	%	needed (g) Cr from CrO_3	needed (g) CrO_3	needed (vol) mL CrO_3	needed (g) Total Cr	needed (g) Cr from NaDC	needed (g) NaDC	needed (vol) mL NaDC	Vol (mL) CrO_3 & NaDC	Required Total Vol (mL)	Volume (H_2O) needed (mL)	Concentration (g/L) of chromium (VI) solutions		
												Cr from CrO_3	Cr from NaDC	Total chromium (VI)
1	110	0.3520	0.6769	11.001	0.5300	0.1780	0.5100	7.877	18.879	20.000	1.121	17.600	8.900	26.500
2	107.50	0.3440	0.6615	10.751	0.5300	0.1860	0.5330	8.231	18.983	20.000	1.017	17.200	9.300	26.500
3	105	0.3360	0.6462	10.501	0.5300	0.1940	0.5559	8.585	19.087	20.000	0.913	16.800	9.700	26.500
4	102.50	0.3280	0.6308	10.251	0.5300	0.2020	0.5788	8.940	19.191	20.000	0.809	16.400	10.100	26.500
5	100	0.3200	0.6154	10.001	0.5300	0.2100	0.6017	9.294	19.295	20.000	0.705	16.000	10.500	26.500
6	97.50	0.3120	0.6000	9.751	0.5300	0.2180	0.6247	9.648	19.399	20.000	0.601	15.600	10.900	26.500
7	95	0.3040	0.5846	9.501	0.5300	0.2260	0.6476	10.002	19.503	20.000	0.497	15.200	11.300	26.500
8	92.50	0.2960	0.5692	9.251	0.5300	0.2340	0.6705	10.356	19.607	20.000	0.393	14.800	11.700	26.500
9	90	0.2880	0.5538	9.001	0.5300	0.2420	0.6934	10.710	19.711	20.000	0.289	14.400	12.100	26.500

APPENDIX B

Table B2. Preparation of 100 times diluted chromium samples, as compared to the samples in the 8th stage of the industrial electrolytic process. The total chromium concentration was constant.

Chromium trioxide (CrO_3)	Volume of flask (mL) 250	Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	Volume of flask (mL) 250
mole	100	mole	298
mass (g)	15.3845	mass (g)	16.1865
[CrO_3] mol/L	0.6154	[NaDC] mol/L	0.2173
Mass (g) Cr	7.9999	Mass (g) Cr	5.6490

Sample Number	%	needed (g) Cr from CrO_3	needed (g) CrO_3	needed (vol) mL CrO_3	needed (g) Total Cr	needed (g) Cr from NaDC	needed (g) NaDC	needed (vol) mL NaDC	Vol (mL) CrO_3 & NaDC	Required Total Vol (mL)	Volume (H_2O) needed (mL)	Concentration (g/L) of chromium (VI) solutions		
												Cr from CrO_3	Cr from NaDC	Total chromium (VI)
1	110	0.0704	0.1354	2.200	0.1060	0.0356	0.1020	1.576	3.776	20.000	16.224	3.5200	1.7800	5.3000
2	107.50	0.0688	0.1323	2.150	0.1060	0.0372	0.1066	1.646	3.796	20.000	16.204	3.4400	1.8600	5.3000
3	105	0.0672	0.1292	2.100	0.1060	0.0388	0.1112	1.717	3.817	20.000	16.183	3.3600	1.9400	5.3000
4	102.50	0.0656	0.1262	2.050	0.1060	0.0404	0.1158	1.788	3.838	20.000	16.162	3.2800	2.0200	5.3000
5	100	0.064	0.1231	2.000	0.1060	0.042	0.1203	1.859	3.859	20.000	16.141	3.2000	2.1000	5.3000
6	97.50	0.0624	0.1200	1.950	0.1060	0.0436	0.1249	1.788	3.838	20.000	16.162	3.1200	2.1800	5.3000
7	95	0.0608	0.1169	1.900	0.1060	0.0452	0.1295	1.717	3.817	20.000	16.183	3.0400	2.2600	5.3000
8	92.50	0.0592	0.1138	1.850	0.1060	0.0468	0.1341	2.071	3.921	20.000	16.079	2.960	2.3400	5.3000
9	90	0.0576	0.1108	1.800	0.1060	0.0484	0.1387	2.142	3.942	20.000	16.058	2.880	2.4200	5.3000

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Table B3. Preparation of 100 times diluted chromium samples, as compared to the samples in the 8th stage of the industrial electrolytic process. The total chromium concentration was not constant.

Chromium trioxide (CrO_3)	Volume of flask (mL)	Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	Volume of flask (mL)
	250		250
mole	100	mole	298
mass (g)	15.3845	mass (g)	16.1865
[CrO_3] mol/L	0.6154	[NaDC] mol/L	0.2173
Mass (g) Cr	7.9999	Mass (g) Cr	5.6490

Sample Number	%	needed (g) Cr from CrO_3	needed (g) CrO_3	needed (vol) mL CrO_3	needed (g) Total Cr	needed (g) Cr from NaDC	needed (g) NaDC	needed (vol) mL NaDC	Vol (mL) CrO_3 & NaDC	Required Total Vol (mL)	Volume (H_2O) needed (mL)	Concentration (g/L) of chromium (VI) solutions		
												Cr from CrO_3	Cr from NaDC	Total chromium (VI)
1	110	0.0704	0.1354	2.200	0.1302	0.0598	0.1714	2.646	4.847	20.000	15.153	3.5200	2.9900	6.5100
2	107.50	0.0688	0.1323	2.150	0.1270	0.0582	0.1668	2.576	4.726	20.000	15.274	3.4400	2.9100	6.3500
3	105	0.0672	0.1292	2.100	0.1238	0.0566	0.1622	2.505	4.605	20.000	15.395	3.3600	2.8300	6.1900
4	102.50	0.0656	0.1262	2.050	0.1206	0.0550	0.1576	2.434	4.484	20.000	15.516	3.2800	2.7500	6.0300
5	100	0.0640	0.1231	2.000	0.1174	0.0534	0.1530	2.363	4.363	20.000	15.637	3.2000	2.6700	5.8700
6	97.50	0.0624	0.1200	1.950	0.1142	0.0518	0.1484	2.292	4.242	20.000	15.758	3.1200	2.5900	5.7100
7	95	0.0608	0.1169	1.900	0.1110	0.0502	0.1438	2.222	4.122	20.000	15.878	3.0400	2.5100	5.5500
8	92.50	0.0592	0.1138	1.850	0.1078	0.0486	0.1393	2.151	4.001	20.000	15.999	2.9600	2.4300	5.3900
9	90	0.0576	0.1108	1.800	0.1046	0.0470	0.1347	2.080	3.880	20.000	16.120	2.8800	2.3500	5.2300

APPENDIX B

Table B4.1. Learning set of data used to train Artificial Neural Networks. Chromium samples were 500 times diluted as compared to the samples in the 8th stage of the industrial electrolytic process.

EXPERIMENTAL DESIGN

Total chromium in g:	520	set to 100%									Chromic acid STOCK solution (CrO_3)			Dichromate STOCK aolution ($Na_2Cr_2O_7.2H_2O$)										
Chromium from CA:	320	Ratio	1.6								volume of vol. flask			volume of vol. flask										
Chromium from $Na_2Cr_2O_7.2H_2O$	200										1000 ml			1000 ml										
		molar mass CrO_3	100								[CA]	0.8		[NaD]	0.4									
		molar mass NaDC	298								CA mass	80.0000 g		NaD mass	119.2000 g									
		molar mass Cr	52								Cr (g)	41.6000		Cr (g)	41.6000									

LAST STAGE OF ELECTROLYTIC CA PRODUCTION

Assumed [NaOH] 1 M

	LEARNING SET FACTORIAL DESIGN 5^2	Industrial samples composition								Required in a titration cell			Volume of STOCK solution required (ml)								Expected volume of titrant to react with			
	Total Chromium (normalised) in %	Cr(CA) / Cr(NaD)	Total Cr (g/l)	Cr from CA (g/l)	Cr from NaD (g/l)	No of CA moles/l	Na of NaD moles/l	Mass of CA (g/l)	Mass of NaD.2H2O (g/l)	Total Cr (g)	Cr from CA (g)	Cr from NaD (g)	CA	NaD.2H2O	Total Volume (ml)	Water required (ml)	Equivalent Cr g/l	[CA] in titration cell	[NaD] in titration cell	CA (1st EP)	NaD	NaD from CA	Total vol. (2nd EP) (ml)
solution #											500					40							
1	110.000	2.100	572.0000	387.4839	184.5161	7.4516	1.7742	745.1613	528.7097	1.1440	0.7750	0.3690	18.629	8.871	27.500	12.500	28.6000	0.3726	0.0887	14.903	7.0968	14.9032	36.903
2	110.000	1.850	572.0000	371.2982	200.7018	7.1404	1.9298	714.0351	575.0877	1.1440	0.7426	0.4014	17.851	9.649	27.500	12.500	28.6000	0.3570	0.0965	14.281	7.7193	14.2807	36.281
3	110.000	1.600	572.0000	352.0000	220.0000	6.7692	2.1154	676.9231	630.3846	1.1440	0.7040	0.4400	16.923	10.577	27.500	12.500	28.6000	0.3385	0.1058	13.538	8.4615	13.5385	35.538
4	110.000	1.350	572.0000	328.5957	243.4043	6.3191	2.3404	631.9149	697.4468	1.1440	0.6572	0.4868	15.798	11.702	27.500	12.500	28.6000	0.3160	0.1170	12.638	9.3617	12.6383	34.638
5	110.000	1.100	572.0000	299.6190	272.3810	5.7619	2.6190	576.1905	780.4762	1.1440	0.5992	0.5448	14.405	13.095	27.500	12.500	28.6000	0.2881	0.1310	11.524	10.4762	11.5238	33.524
6	105.000	2.100	546.0000	369.8710	176.1290	7.1129	1.6935	711.2903	504.6774	1.0920	0.7397	0.3523	17.782	8.468	26.250	13.750	27.3000	0.3556	0.0847	14.226	6.7742	14.2258	35.226
7	105.000	1.850	546.0000	354.4211	191.5789	6.8158	1.8421	681.5789	548.9474	1.0920	0.7088	0.3832	17.039	9.211	26.250	13.750	27.3000	0.3408	0.0921	13.632	7.3684	13.6316	34.632
8	105.000	1.600	546.0000	336.0000	210.0000	6.4615	2.0192	646.1538	601.7308	1.0920	0.6720	0.4200	16.154	10.096	26.250	13.750	27.3000	0.3231	0.1010	12.923	8.0769	12.9231	33.923
9	105.000	1.350	546.0000	313.6596	232.3404	6.0319	2.2340	603.1915	665.7447	1.0920	0.6273	0.4647	15.080	11.170	26.250	13.750	27.3000	0.3016	0.1117	12.064	8.9362	12.0638	33.064
10	105.000	1.100	546.0000	286.0000	260.0000	5.5000	2.5000	550.0000	745.0000	1.0920	0.5720	0.5200	13.750	12.500	26.250	13.750	27.3000	0.2750	0.1250	11.000	10.0000	11.0000	32.000
11	100.000	2.100	520.0000	352.2581	167.7419	6.7742	1.6129	677.4194	480.6452	1.0400	0.7045	0.3355	16.935	8.065	25.000	15.000	26.0000	0.3387	0.0806	13.548	6.4516	13.5484	33.548
12	100.000	1.850	520.0000	337.5439	182.4561	6.4912	1.7544	649.1228	522.8070	1.0400	0.6751	0.3649	16.228	8.772	25.000	15.000	26.0000	0.3246	0.0877	12.982	7.0175	12.9825	32.982
13	100.000	1.600	520.0000	320.0000	200.0000	6.1538	1.9231	615.3846	573.0769	1.0400	0.6400	0.4000	15.385	9.615	25.000	15.000	26.0000	0.3077	0.0962	12.308	7.6923	12.3077	32.308
14	100.000	1.350	520.0000	298.7234	221.2766	5.7447	2.1277	574.4681	634.0426	1.0400	0.5974	0.4426	14.362	10.638	25.000	15.000	26.0000	0.2872	0.1064	11.489	8.5106	11.4894	31.489
15	100.000	1.100	520.0000	272.3810	247.6190	5.2381	2.3810	523.8095	709.5238	1.0400	0.5448	0.4952	13.095	11.905	25.000	15.000	26.0000	0.2619	0.1190	10.476	9.5238	10.4762	30.476
16	95.000	2.100	494.0000	334.6452	159.3548	6.4355	1.5323	643.5484	456.6129	0.9880	0.6693	0.3187	16.089	7.661	23.750	16.250	24.7000	0.3218	0.0766	12.871	6.1290	12.8710	31.871
17	95.000	1.850	494.0000	320.6667	173.3333	6.1667	1.6667	616.6667	496.6667	0.9880	0.6413	0.3467	15.417	8.333	23.750	16.250	24.7000	0.3083	0.0833	12.333	6.6667	12.3333	31.333
18	95.000	1.600	494.0000	304.0000	190.0000	5.8462	1.8269	584.6154	544.4231	0.9880	0.6080	0.3800	14.615	9.135	23.750	16.250	24.7000	0.2923	0.0913	11.692	7.3077	11.6923	30.692
19	95.000	1.350	494.0000	283.7872	210.2128	5.4574	2.0213	545.7447	602.3404	0.9880	0.5676	0.4204	13.644	10.106	23.750	16.250	24.7000	0.2729	0.1011	10.915	8.0851	10.9149	29.915
20	95.000	1.100	494.0000	258.7619	235.2381	4.9762	2.2619	497.6190	674.0476	0.9880	0.5175	0.4705	12.440	11.310	23.750	16.250	24.7000	0.2488	0.1131	9.952	9.0476	9.9524	28.952
21	90.000	2.100	468.0000	317.0323	150.9677	6.0968	1.4516	609.6774	432.5806	0.9360	0.6341	0.3019	15.242	7.258	22.500	17.500	23.4000	0.3048	0.0726	12.194	5.8065	12.1935	30.194
22	90.000	1.850	468.0000	303.7895	164.2105	5.8421	1.5789	584.2105	470.5263	0.9360	0.6076	0.3284	14.605	7.895	22.500	17.500	23.4000	0.2921	0.0789	11.684	6.3158	11.6842	29.684
23	90.000	1.600	468.0000	288.0000	180.0000	5.5385	1.7308	553.8462	515.7692	0.9360	0.5760	0.3600	13.846	8.654	22.500	17.500	23.4000	0.2769	0.0865	11.077	6.9231	11.0769	29.077
24	90.000	1.350	468.0000	268.8511	199.1489	5.1702	1.9149	517.0213	570.6383	0.9360	0.5377	0.3983	12.926	9.574	22.500	17.500	23.4000	0.2585	0.0957	10.340	7.6596	10.3404	28.340
25	90.000	1.100	468.0000	245.1429	222.8571	4.7143	2.1429	471.4286	638.5714	0.9360	0.4903	0.4457	11.786	10.714	22.500	17.500	23.4000	0.2357	0.1071	9.429	8.5714	9.4286	27.429

Table B4.2. Training set of data used to train Artificial Neural Networks. Chromium samples were 500 times diluted as compared to the samples in the 8th stage of the industrial electrolytic process.

	LAST STAGE OF ELECTROLYTIC CA PRODUCTION																		Assumed [NaOH]	1 M				
	Industrial samples composition									Required in a titration cell			Volume of STOCK solution required (ml)								Expected volume of titrant to react with			
	Total Chromium (normalised) in %	Cr(CA) / Cr(NaD)	Total Cr (g/l)	Cr from CA (g/l)	Cr from NaD (g/l)	No of CA moles/l	No of NaD moles/l	Mass of CA (g/l)	Mass of NaD.2H2O (g/l)	Total Cr (g)	Cr from CA (g)	Cr from NaD (g)	CA	$NaD.2H_2O$	Total Volume (ml)	Water required (ml)	Equivalent Cr g/l	[CA] in titration cell	[NaD] in titration cell	CA (1st EP)	NaD	NaD from CA	Total vol. (2nd EP) (ml)
solution #	TRAINING SET										500					50								
1	107.500	1.975	559.0000	371.1008	187.8992	7.137	1.807	713.6555	538.4034	1.1180	0.7422	0.3758	17.841	9.034	26.875	13.125	27.950	0.357	0.090	14.273	7.227	14.273	35.773
2	107.500	1.725	559.0000	353.8624	205.1376	6.805	1.972	680.5046	587.7982	1.1180	0.7077	0.4103	17.013	9.862	26.875	13.125	27.950	0.340	0.099	13.610	7.890	13.610	35.110
3	107.500	1.475	559.0000	333.1414	225.8586	6.407	2.172	640.6566	647.1717	1.1180	0.6663	0.4517	16.016	10.859	26.875	13.125	27.950	0.320	0.109	12.813	8.687	12.813	34.313
4	107.500	1.225	559.0000	307.7640	251.2360	5.919	2.416	591.8539	719.8876	1.1180	0.6155	0.5025	14.796	12.079	26.875	13.125	27.950	0.296	0.121	11.837	9.663	11.837	33.337
5	102.500	1.975	533.0000	353.8403	179.1597	6.805	1.723	680.4622	513.3613	1.0660	0.7077	0.3583	17.012	8.613	25.625	14.375	26.650	0.340	0.086	13.609	6.891	13.609	34.109
6	102.500	1.725	533.0000	337.4037	195.5963	6.489	1.881	648.8532	560.4587	1.0660	0.6748	0.3912	16.221	9.404	25.625	14.375	26.650	0.324	0.094	12.977	7.523	12.977	33.477
7	102.500	1.475	533.0000	317.6465	215.3535	6.109	2.071	610.8586	617.0707	1.0660	0.6353	0.4307	15.271	10.354	25.625	14.375	26.650	0.305	0.104	12.217	8.283	12.217	32.717
8	102.500	1.225	533.0000	293.4494	239.5506	5.643	2.303	564.3258	686.4045	1.0660	0.5869	0.4791	14.108	11.517	25.625	14.375	26.650	0.282	0.115	11.287	9.213	11.287	31.787
9	97.500	1.975	507.0000	336.5798	170.4202	6.473	1.639	647.2689	488.3193	1.0140	0.6732	0.3408	16.182	8.193	24.375	15.625	25.350	0.324	0.082	12.945	6.555	12.945	32.445
10	97.500	1.725	507.0000	320.9450	186.0550	6.172	1.789	617.2018	533.1193	1.0140	0.6419	0.3721	15.430	8.945	24.375	15.625	25.350	0.309	0.089	12.344	7.156	12.344	31.844
11	97.500	1.475	507.0000	302.1515	204.8485	5.811	1.970	581.0606	586.9697	1.0140	0.6043	0.4097	14.527	9.848	24.375	15.625	25.350	0.291	0.098	11.621	7.879	11.621	31.121
12	97.500	1.225	507.0000	279.1348	227.8652	5.368	2.191	536.7978	652.9213	1.0140	0.5583	0.4557	13.420	10.955	24.375	15.625	25.350	0.268	0.110	10.736	8.764	10.736	30.236
13	92.500	1.975	481.0000	319.3193	161.6807	6.141	1.555	614.0756	463.2773	0.9620	0.6386	0.3234	15.352	7.773	23.125	16.875	24.050	0.307	0.078	12.282	6.218	12.282	30.782
14	92.500	1.725	481.0000	304.4862	176.5138	5.856	1.697	585.5505	505.7798	0.9620	0.6090	0.3530	14.639	8.486	23.125	16.875	24.050	0.293	0.085	11.711	6.789	11.711	30.211
15	92.500	1.475	481.0000	286.6566	194.3434	5.513	1.869	551.2626	556.8687	0.9620	0.5733	0.3887	13.782	9.343	23.125	16.875	24.050	0.276	0.093	11.025	7.475	11.025	29.525
16	92.500	1.225	481.0000	264.8202	216.1798	5.093	2.079	509.2697	619.4382	0.9620	0.5296	0.4324	12.732	10.393	23.125	16.875	24.050	0.255	0.104	10.185	8.315	10.185	28.685

APPENDIX B

Table B4.3. Test set of data used to validate Artificial Neural Networks. Chromium samples were 500 times diluted as compared to the samples in the 8th stage of the industrial electrolytic process.

LAST STAGE OF ELECTROLYTIC CA PRODUCTION — Assumed [NaOH] 1 M

	Industrial samples composition									Required in a titration cell			Volume of STOCK solution required (ml)							Expected volume of titrant to react with				
	Total Chromium (normalised) in %	Cr(CA) / Cr(NaD)	Total Cr (g/l)	Cr from CA (g/l)	Cr from NaD (g/l)	No of CA moles/l	No of NaD moles/l	Mass of CA (g/l)	Mass of NaD.2H2O (g/l)	Total Cr (g)	Cr from CA (g)	Cr from NaD (g)	CA	$NaD.2H_2O$	Total Volume (ml)	Water required (ml)	Equivalent Cr g/l	[CA] in titration cell	[NaD] in titration cell	CA (1st EP)	NaD	NaD from CA	Total vol. (2nd EP) (ml)
solution #	TEST SET										500					50							
1	107.500	1.850	559.0000	362.8596	196.1404	6.978	1.886	697.8070	562.0175	1.1180	0.7257	0.3923	17.445	9.430	26.875	13.125	27.950	0.349	0.094	13.956	7.544	13.956	35.456
2	107.500	1.600	559.0000	344.0000	215.0000	6.615	2.067	661.5385	616.0577	1.1180	0.6880	0.4300	16.538	10.337	26.875	13.125	27.950	0.331	0.103	13.231	8.269	13.231	34.731
3	107.500	1.350	559.0000	321.1277	237.8723	6.176	2.287	617.5532	681.5957	1.1180	0.6423	0.4757	15.439	11.436	26.875	13.125	27.950	0.309	0.114	12.351	9.149	12.351	33.851
4	105.000	1.975	546.0000	362.4706	183.5294	6.971	1.765	697.0588	525.8824	1.0920	0.7249	0.3671	17.426	8.824	26.250	13.750	27.300	0.349	0.088	13.941	7.059	13.941	34.941
5	105.000	1.725	546.0000	345.6330	200.3670	6.647	1.927	664.6789	574.1284	1.0920	0.6913	0.4007	16.617	9.633	26.250	13.750	27.300	0.332	0.096	13.294	7.706	13.294	34.294
6	105.000	1.475	546.0000	325.3939	220.6061	6.258	2.121	625.7576	632.1212	1.0920	0.6508	0.4412	15.644	10.606	26.250	13.750	27.300	0.313	0.106	12.515	8.485	12.515	33.515
7	105.000	1.225	546.0000	300.6067	245.3933	5.781	2.360	578.0899	703.1461	1.0920	0.6012	0.4908	14.452	11.798	26.250	13.750	27.300	0.289	0.118	11.562	9.438	11.562	32.562
8	102.500	1.850	533.0000	345.9825	187.0175	6.654	1.798	665.3509	535.8772	1.0660	0.6920	0.3740	16.634	8.991	25.625	14.375	26.650	0.333	0.090	13.307	7.193	13.307	33.807
9	102.500	1.600	533.0000	328.0000	205.0000	6.308	1.971	630.7692	587.4038	1.0660	0.6560	0.4100	15.769	9.856	25.625	14.375	26.650	0.315	0.099	12.615	7.885	12.615	33.115
10	102.500	1.350	533.0000	306.1915	226.8085	5.888	2.181	588.8298	649.8936	1.0660	0.6124	0.4536	14.721	10.904	25.625	14.375	26.650	0.294	0.109	11.777	8.723	11.777	32.277
11	100.000	1.975	520.0000	345.2101	174.7899	6.639	1.681	663.8655	500.8403	1.0400	0.6904	0.3496	16.597	8.403	25.000	15.000	26.000	0.332	0.084	13.277	6.723	13.277	33.277
12	100.000	1.725	520.0000	329.1743	190.8257	6.330	1.835	633.0275	546.7890	1.0400	0.6583	0.3817	15.826	9.174	25.000	15.000	26.000	0.317	0.092	12.661	7.339	12.661	32.661
13	100.000	1.475	520.0000	309.8990	210.1010	5.960	2.020	595.9596	602.0202	1.0400	0.6198	0.4202	14.899	10.101	25.000	15.000	26.000	0.298	0.101	11.919	8.081	11.919	31.919
14	100.000	1.225	520.0000	286.2921	233.7079	5.506	2.247	550.5618	669.6629	1.0400	0.5726	0.4674	13.764	11.236	25.000	15.000	26.000	0.275	0.112	11.011	8.989	11.011	31.011
15	97.500	1.850	507.0000	329.1053	177.8947	6.329	1.711	632.8947	509.7368	1.0140	0.6582	0.3558	15.822	8.553	24.375	15.625	25.350	0.316	0.086	12.658	6.842	12.658	32.158
16	97.500	1.600	507.0000	312.0000	195.0000	6.000	1.875	600.0000	558.7500	1.0140	0.6240	0.3900	15.000	9.375	24.375	15.625	25.350	0.300	0.094	12.000	7.500	12.000	31.500
17	97.500	1.350	507.0000	291.2553	215.7447	5.601	2.074	560.1064	618.1915	1.0140	0.5825	0.4315	14.003	10.372	24.375	15.625	25.350	0.280	0.104	11.202	8.298	11.202	30.702
18	95.000	1.975	494.0000	327.9496	166.0504	6.307	1.597	630.6723	475.7983	0.9880	0.6559	0.3321	15.767	7.983	23.750	16.250	24.700	0.315	0.080	12.613	6.387	12.613	31.613
19	95.000	1.725	494.0000	312.7156	181.2844	6.014	1.743	601.3761	519.4495	0.9880	0.6254	0.3626	15.034	8.716	23.750	16.250	24.700	0.301	0.087	12.028	6.972	12.028	31.028
20	95.000	1.475	494.0000	294.4040	199.5960	5.662	1.919	566.1616	571.9192	0.9880	0.5888	0.3992	14.154	9.596	23.750	16.250	24.700	0.283	0.096	11.323	7.677	11.323	30.323
21	95.000	1.225	494.0000	271.9775	222.0225	5.230	2.135	523.0337	636.1798	0.9880	0.5440	0.4440	13.076	10.674	23.750	16.250	24.700	0.262	0.107	10.461	8.539	10.461	29.461
22	92.500	1.850	481.0000	312.2281	168.7719	6.004	1.623	600.4386	483.5965	0.9620	0.6245	0.3375	15.011	8.114	23.125	16.875	24.050	0.300	0.081	12.009	6.491	12.009	30.509
23	92.500	1.600	481.0000	296.0000	185.0000	5.692	1.779	569.2308	530.0962	0.9620	0.5920	0.3700	14.231	8.894	23.125	16.875	24.050	0.285	0.089	11.385	7.115	11.385	29.885
24	92.500	1.350	481.0000	276.3191	204.6809	5.314	1.968	531.3830	586.4894	0.9620	0.5526	0.4094	13.285	9.840	23.125	16.875	24.050	0.266	0.098	10.628	7.872	10.628	29.128

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.

Table C1. Data used to test reproducibility of acid-base titration procedure involving the same glass and reference electrodes.

	Titration number											
	1	2	3	4	5	6	7	8	9	10		
NaOH (mL)	pH Values										Average	STDEV
0.000	0.319	0.208	0.201	0.275	0.339	0.318	0.310	0.376	0.359	0.336	0.304	0.059
0.250	0.326	0.212	0.207	0.286	0.343	0.321	0.314	0.380	0.362	0.340	0.309	0.058
0.500	0.332	0.218	0.215	0.296	0.348	0.326	0.319	0.385	0.366	0.346	0.315	0.057
0.750	0.340	0.225	0.224	0.305	0.354	0.331	0.326	0.389	0.374	0.352	0.322	0.057
1.000	0.349	0.233	0.233	0.314	0.359	0.338	0.334	0.395	0.381	0.360	0.330	0.056
1.250	0.356	0.243	0.240	0.322	0.365	0.345	0.342	0.402	0.390	0.367	0.337	0.055
1.500	0.363	0.253	0.248	0.332	0.372	0.356	0.350	0.409	0.398	0.375	0.346	0.055
1.750	0.372	0.264	0.256	0.342	0.380	0.365	0.358	0.416	0.406	0.381	0.354	0.054
2.000	0.381	0.276	0.265	0.353	0.389	0.374	0.367	0.424	0.414	0.389	0.363	0.053
2.250	0.389	0.288	0.274	0.364	0.397	0.381	0.376	0.432	0.422	0.397	0.372	0.052
2.500	0.399	0.300	0.283	0.375	0.407	0.387	0.385	0.440	0.431	0.405	0.381	0.051
2.750	0.408	0.314	0.293	0.386	0.416	0.395	0.394	0.448	0.440	0.415	0.391	0.050
3.000	0.417	0.328	0.303	0.396	0.427	0.403	0.403	0.457	0.449	0.424	0.401	0.049
3.250	0.426	0.342	0.313	0.408	0.437	0.415	0.413	0.468	0.459	0.434	0.412	0.049
3.500	0.437	0.357	0.325	0.418	0.449	0.429	0.423	0.479	0.468	0.445	0.423	0.048
3.750	0.447	0.372	0.336	0.428	0.460	0.442	0.433	0.490	0.477	0.455	0.434	0.047
4.000	0.457	0.385	0.349	0.439	0.472	0.453	0.443	0.501	0.487	0.465	0.445	0.046
4.250	0.468	0.400	0.362	0.449	0.484	0.465	0.454	0.513	0.497	0.475	0.457	0.045
4.500	0.479	0.414	0.375	0.460	0.497	0.477	0.465	0.525	0.506	0.485	0.468	0.044
4.750	0.490	0.427	0.388	0.470	0.510	0.488	0.476	0.537	0.516	0.496	0.480	0.044
5.000	0.502	0.439	0.401	0.480	0.523	0.500	0.487	0.550	0.526	0.507	0.492	0.044
5.250	0.513	0.452	0.415	0.491	0.536	0.512	0.499	0.563	0.537	0.518	0.504	0.043
5.500	0.526	0.465	0.429	0.502	0.549	0.524	0.511	0.576	0.550	0.529	0.516	0.043
5.750	0.539	0.479	0.443	0.512	0.562	0.537	0.524	0.591	0.563	0.541	0.529	0.043
6.000	0.551	0.491	0.458	0.524	0.575	0.550	0.537	0.605	0.576	0.553	0.542	0.043
6.250	0.565	0.505	0.474	0.535	0.588	0.563	0.550	0.619	0.589	0.566	0.555	0.042
6.500	0.578	0.518	0.490	0.547	0.602	0.576	0.563	0.633	0.603	0.579	0.569	0.042
6.750	0.592	0.532	0.506	0.559	0.615	0.590	0.577	0.648	0.617	0.592	0.583	0.042
7.000	0.606	0.546	0.523	0.571	0.629	0.604	0.592	0.663	0.632	0.605	0.597	0.042
7.250	0.621	0.559	0.540	0.584	0.643	0.619	0.606	0.677	0.648	0.619	0.612	0.041
7.500	0.636	0.574	0.558	0.597	0.657	0.634	0.622	0.693	0.664	0.633	0.627	0.041
7.750	0.652	0.590	0.576	0.611	0.671	0.649	0.638	0.708	0.680	0.648	0.642	0.041
8.000	0.668	0.604	0.594	0.625	0.687	0.666	0.654	0.724	0.697	0.662	0.658	0.041
8.250	0.685	0.620	0.612	0.640	0.702	0.682	0.671	0.740	0.715	0.678	0.675	0.041
8.500	0.703	0.636	0.630	0.655	0.718	0.700	0.689	0.756	0.733	0.695	0.692	0.041
8.750	0.722	0.652	0.649	0.671	0.734	0.718	0.708	0.773	0.751	0.711	0.709	0.041
9.000	0.740	0.670	0.668	0.688	0.751	0.737	0.727	0.790	0.770	0.728	0.727	0.041
9.250	0.760	0.688	0.687	0.705	0.769	0.757	0.747	0.808	0.790	0.746	0.746	0.041

	Titration number											
	1	2	3	4	5	6	7	8	9	10		
NaOH (mL)	pH Values										Average	STDEV
9.500	0.781	0.706	0.707	0.723	0.787	0.778	0.768	0.827	0.809	0.765	0.765	0.041
9.750	0.802	0.725	0.728	0.742	0.806	0.799	0.789	0.847	0.829	0.786	0.785	0.041
10.000	0.826	0.746	0.750	0.762	0.826	0.822	0.812	0.867	0.851	0.806	0.807	0.042
10.250	0.849	0.767	0.772	0.784	0.847	0.845	0.836	0.888	0.873	0.828	0.829	0.042
10.500	0.874	0.790	0.796	0.805	0.870	0.870	0.861	0.910	0.896	0.851	0.852	0.042
10.750	0.900	0.813	0.820	0.829	0.893	0.897	0.887	0.935	0.920	0.874	0.877	0.042
11.000	0.927	0.838	0.845	0.854	0.918	0.924	0.915	0.960	0.946	0.900	0.903	0.043
11.250	0.957	0.866	0.873	0.880	0.944	0.954	0.945	0.986	0.973	0.927	0.931	0.043
11.500	0.988	0.894	0.902	0.909	0.971	0.985	0.976	1.014	1.002	0.956	0.960	0.043
11.750	1.022	0.925	0.933	0.939	1.002	1.018	1.010	1.045	1.033	0.986	0.991	0.044
12.000	1.058	0.959	0.967	0.972	1.035	1.054	1.046	1.077	1.066	1.020	1.025	0.044
12.250	1.097	0.995	1.004	1.008	1.071	1.094	1.086	1.113	1.102	1.057	1.063	0.045
12.500	1.139	1.034	1.043	1.047	1.109	1.136	1.128	1.154	1.142	1.097	1.103	0.046
12.750	1.186	1.079	1.088	1.090	1.152	1.184	1.175	1.197	1.186	1.141	1.148	0.046
13.000	1.239	1.129	1.137	1.139	1.200	1.237	1.228	1.247	1.236	1.190	1.198	0.047
13.250	1.297	1.185	1.193	1.195	1.255	1.296	1.288	1.303	1.291	1.247	1.255	0.048
13.500	1.365	1.249	1.257	1.258	1.318	1.365	1.357	1.368	1.355	1.311	1.320	0.049
13.750	1.444	1.326	1.332	1.333	1.393	1.446	1.437	1.443	1.432	1.389	1.398	0.051
14.000	1.539	1.419	1.423	1.424	1.483	1.543	1.534	1.536	1.524	1.482	1.491	0.052
14.250	1.658	1.535	1.538	1.539	1.598	1.666	1.656	1.655	1.641	1.603	1.609	0.054
14.500	1.818	1.694	1.694	1.695	1.752	1.833	1.821	1.818	1.801	1.767	1.769	0.057
14.750	2.068	1.949	1.940	1.939	1.997	2.100	2.085	2.075	2.058	2.042	2.025	0.063
15.000	2.633	2.564	2.574	2.497	2.567	2.785	2.752	2.762	2.730	2.873	2.674	0.123
15.250	4.508	4.438	4.445	4.373	4.467	4.607	4.592	4.615	4.581	4.620	4.525	0.090
15.500	4.967	4.877	4.892	4.855	4.931	5.020	5.011	5.027	5.010	5.014	4.960	0.066
15.750	5.198	5.105	5.123	5.101	5.171	5.240	5.235	5.249	5.241	5.233	5.190	0.060
16.000	5.352	5.263	5.281	5.267	5.332	5.392	5.387	5.403	5.396	5.384	5.346	0.056
16.250	5.468	5.383	5.399	5.390	5.453	5.504	5.499	5.520	5.512	5.499	5.463	0.054
16.500	5.562	5.482	5.495	5.490	5.550	5.596	5.591	5.615	5.608	5.594	5.558	0.052
16.750	5.642	5.565	5.576	5.573	5.633	5.673	5.668	5.694	5.687	5.674	5.639	0.050
17.000	5.710	5.635	5.646	5.644	5.702	5.739	5.734	5.763	5.755	5.743	5.707	0.049
17.250	5.771	5.697	5.707	5.705	5.763	5.797	5.793	5.823	5.815	5.804	5.768	0.048
17.500	5.825	5.753	5.763	5.760	5.818	5.849	5.846	5.877	5.868	5.859	5.822	0.047
17.750	5.874	5.803	5.812	5.809	5.866	5.895	5.893	5.925	5.917	5.908	5.870	0.046
18.000	5.920	5.848	5.857	5.854	5.910	5.937	5.936	5.970	5.961	5.953	5.915	0.046
18.250	5.960	5.891	5.899	5.896	5.952	5.975	5.977	6.011	6.001	5.994	5.956	0.045
18.500	5.999	5.930	5.938	5.934	5.990	6.011	6.014	6.049	6.040	6.034	5.994	0.045
18.750	6.035	5.967	5.975	5.970	6.025	6.044	6.050	6.084	6.075	6.070	6.030	0.044
19.000	6.068	6.001	6.009	6.003	6.059	6.075	6.082	6.117	6.109	6.103	6.063	0.044
19.250	6.098	6.033	6.041	6.035	6.090	6.103	6.112	6.148	6.139	6.135	6.093	0.044

	Titration number											
	1	2	3	4	5	6	7	8	9	10		
NaOH (mL)	pH Values										Average	STDEV
19.500	6.127	6.063	6.071	6.064	6.120	6.131	6.142	6.177	6.169	6.165	6.123	0.044
19.750	6.154	6.091	6.101	6.092	6.148	6.157	6.170	6.205	6.197	6.194	6.151	0.043
20.000	6.179	6.117	6.127	6.118	6.174	6.181	6.196	6.232	6.224	6.221	6.177	0.044
20.250	6.204	6.143	6.154	6.143	6.200	6.205	6.221	6.257	6.249	6.246	6.202	0.043
20.500	6.226	6.168	6.182	6.167	6.224	6.227	6.245	6.281	6.272	6.272	6.226	0.043
20.750	6.248	6.191	6.209	6.189	6.247	6.249	6.268	6.304	6.295	6.295	6.250	0.042
21.000	6.270	6.214	6.235	6.211	6.269	6.270	6.291	6.326	6.317	6.318	6.272	0.042
21.250	6.291	6.237	6.257	6.233	6.289	6.290	6.312	6.347	6.338	6.340	6.293	0.042
21.500	6.311	6.258	6.277	6.253	6.310	6.310	6.332	6.367	6.359	6.361	6.314	0.042
21.750	6.331	6.280	6.296	6.272	6.330	6.329	6.353	6.387	6.378	6.382	6.334	0.042
22.000	6.350	6.300	6.313	6.291	6.348	6.347	6.372	6.406	6.398	6.401	6.353	0.042
22.250	6.369	6.318	6.330	6.310	6.367	6.366	6.391	6.425	6.417	6.418	6.371	0.042
22.500	6.387	6.331	6.346	6.328	6.386	6.384	6.410	6.443	6.435	6.436	6.389	0.043
22.750	6.405	6.345	6.362	6.346	6.403	6.402	6.428	6.461	6.453	6.453	6.406	0.044
23.000	6.423	6.361	6.378	6.364	6.421	6.419	6.446	6.479	6.470	6.470	6.423	0.044
23.250	6.441	6.379	6.394	6.382	6.438	6.436	6.464	6.496	6.488	6.488	6.441	0.044
23.500	6.459	6.397	6.410	6.399	6.456	6.454	6.481	6.513	6.505	6.503	6.458	0.044
23.750	6.475	6.415	6.426	6.416	6.473	6.470	6.499	6.530	6.522	6.519	6.475	0.044
24.000	6.492	6.433	6.442	6.433	6.489	6.486	6.516	6.546	6.538	6.534	6.491	0.043
24.250	6.508	6.451	6.459	6.449	6.505	6.502	6.533	6.562	6.554	6.550	6.507	0.043
24.500	6.523	6.469	6.474	6.465	6.521	6.518	6.549	6.578	6.570	6.566	6.523	0.043
24.750	6.539	6.486	6.491	6.481	6.536	6.534	6.565	6.594	6.586	6.581	6.539	0.042
25.000	6.554	6.503	6.507	6.496	6.552	6.550	6.581	6.609	6.601	6.597	6.555	0.042
25.250	6.570	6.520	6.523	6.512	6.567	6.565	6.596	6.624	6.617	6.612	6.571	0.042
25.500	6.585	6.535	6.540	6.527	6.582	6.580	6.610	6.639	6.632	6.627	6.586	0.041
25.750	6.601	6.550	6.555	6.542	6.597	6.596	6.625	6.654	6.647	6.641	6.601	0.041
26.000	6.616	6.566	6.571	6.557	6.612	6.611	6.640	6.668	6.662	6.656	6.616	0.041
26.250	6.631	6.581	6.587	6.572	6.626	6.626	6.654	6.683	6.676	6.671	6.631	0.041
26.500	6.646	6.597	6.603	6.586	6.641	6.640	6.668	6.698	6.691	6.686	6.646	0.040
26.750	6.660	6.612	6.618	6.600	6.655	6.654	6.683	6.712	6.706	6.699	6.660	0.040
27.000	6.674	6.628	6.633	6.615	6.669	6.669	6.697	6.727	6.720	6.714	6.675	0.040
27.250	6.688	6.642	6.648	6.630	6.684	6.690	6.711	6.741	6.735	6.729	6.690	0.040
27.500	6.702	6.657	6.663	6.644	6.698	6.714	6.725	6.756	6.749	6.743	6.705	0.040
27.750	6.717	6.672	6.679	6.658	6.712	6.741	6.739	6.771	6.764	6.757	6.721	0.040
28.000	6.732	6.687	6.694	6.673	6.727	6.755	6.753	6.784	6.778	6.772	6.736	0.040
28.250	6.746	6.702	6.708	6.688	6.741	6.768	6.768	6.799	6.792	6.786	6.750	0.040
28.500	6.762	6.717	6.722	6.703	6.756	6.780	6.782	6.814	6.807	6.801	6.764	0.040
28.750	6.777	6.733	6.736	6.718	6.771	6.795	6.797	6.828	6.822	6.816	6.779	0.039
29.000	6.793	6.749	6.750	6.732	6.785	6.809	6.812	6.843	6.836	6.830	6.794	0.039
29.250	6.808	6.764	6.764	6.747	6.800	6.823	6.827	6.858	6.851	6.845	6.809	0.039

	Titration number											
	1	2	3	4	5	6	7	8	9	10		
NaOH (mL)	pH Values										Average	STDEV
29.500	6.825	6.779	6.777	6.762	6.814	6.838	6.841	6.873	6.866	6.860	6.824	0.040
29.750	6.841	6.795	6.792	6.777	6.830	6.853	6.856	6.888	6.881	6.875	6.839	0.039
30.000	6.857	6.811	6.806	6.792	6.845	6.868	6.872	6.903	6.896	6.891	6.854	0.040
30.250	6.873	6.827	6.820	6.807	6.860	6.884	6.887	6.918	6.911	6.906	6.869	0.040
30.500	6.889	6.843	6.835	6.823	6.875	6.899	6.902	6.933	6.927	6.921	6.885	0.040
30.750	6.906	6.859	6.851	6.839	6.891	6.915	6.919	6.949	6.943	6.937	6.901	0.040
31.000	6.921	6.874	6.866	6.855	6.907	6.931	6.934	6.965	6.959	6.953	6.917	0.040
31.250	6.935	6.891	6.882	6.871	6.923	6.947	6.950	6.981	6.975	6.969	6.932	0.040
31.500	6.950	6.908	6.897	6.887	6.939	6.964	6.967	6.997	6.991	6.985	6.949	0.040
31.750	6.965	6.924	6.914	6.904	6.956	6.980	6.984	7.014	7.008	7.002	6.965	0.040
32.000	6.981	6.941	6.931	6.921	6.972	6.998	7.002	7.031	7.025	7.021	6.982	0.040
32.250	6.998	6.959	6.948	6.939	6.990	7.015	7.019	7.049	7.043	7.038	7.000	0.040
32.500	7.015	6.977	6.966	6.958	7.008	7.034	7.038	7.068	7.062	7.057	7.018	0.040
32.750	7.034	6.996	6.985	6.976	7.027	7.053	7.056	7.086	7.081	7.076	7.037	0.040
33.000	7.053	7.016	7.004	6.996	7.046	7.073	7.076	7.106	7.100	7.095	7.057	0.040
33.250	7.073	7.036	7.023	7.016	7.067	7.094	7.096	7.127	7.121	7.116	7.077	0.041
33.500	7.094	7.058	7.046	7.038	7.088	7.115	7.118	7.148	7.143	7.137	7.099	0.040
33.750	7.116	7.077	7.068	7.060	7.111	7.138	7.140	7.170	7.164	7.160	7.120	0.041
34.000	7.139	7.095	7.092	7.083	7.134	7.161	7.164	7.194	7.189	7.184	7.144	0.042
34.250	7.164	7.115	7.117	7.108	7.159	7.186	7.189	7.219	7.213	7.210	7.168	0.043
34.500	7.191	7.140	7.144	7.134	7.185	7.213	7.215	7.245	7.240	7.236	7.194	0.043
34.750	7.218	7.168	7.172	7.163	7.213	7.242	7.244	7.273	7.269	7.265	7.223	0.043
35.000	7.248	7.200	7.203	7.193	7.243	7.272	7.274	7.304	7.299	7.296	7.253	0.043
35.250	7.281	7.236	7.237	7.226	7.276	7.306	7.308	7.337	7.332	7.329	7.287	0.042
35.500	7.318	7.275	7.275	7.262	7.313	7.343	7.344	7.373	7.369	7.367	7.324	0.042
35.750	7.358	7.318	7.315	7.303	7.352	7.384	7.385	7.414	7.410	7.408	7.365	0.042
36.000	7.403	7.366	7.361	7.348	7.398	7.430	7.430	7.460	7.456	7.454	7.411	0.042
36.250	7.455	7.421	7.415	7.401	7.451	7.484	7.484	7.513	7.510	7.510	7.464	0.042
36.500	7.516	7.487	7.480	7.466	7.515	7.550	7.548	7.577	7.575	7.575	7.529	0.042
36.750	7.592	7.564	7.559	7.545	7.593	7.632	7.628	7.659	7.655	7.657	7.608	0.043
37.000	7.693	7.669	7.663	7.651	7.698	7.743	7.737	7.769	7.764	7.772	7.716	0.047
37.250	7.843	7.830	7.820	7.813	7.860	7.919	7.905	7.938	7.933	7.951	7.881	0.053
37.500	8.132	8.174	8.143	8.129	8.191	8.307	8.260	8.302	8.291	8.354	8.228	0.084
37.750	9.354	9.831	9.655	9.548	9.743	10.133	9.943	9.986	9.841	10.155	9.819	0.253
38.000	11.153	11.294	11.259	11.209	11.323	11.435	11.390	11.405	11.371	11.431	11.327	0.097
38.250	11.636	11.672	11.644	11.634	11.717	11.781	11.763	11.777	11.756	11.783	11.716	0.064
38.500	11.868	11.876	11.849	11.852	11.924	11.976	11.965	11.980	11.963	11.973	11.923	0.055
38.750	12.022	12.016	11.988	11.994	12.061	12.109	12.103	12.117	12.099	12.104	12.061	0.051
39.000	12.140	12.123	12.094	12.101	12.166	12.210	12.207	12.218	12.204	12.206	12.167	0.049
39.250	12.232	12.206	12.177	12.185	12.248	12.292	12.290	12.299	12.285	12.286	12.250	0.047

	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

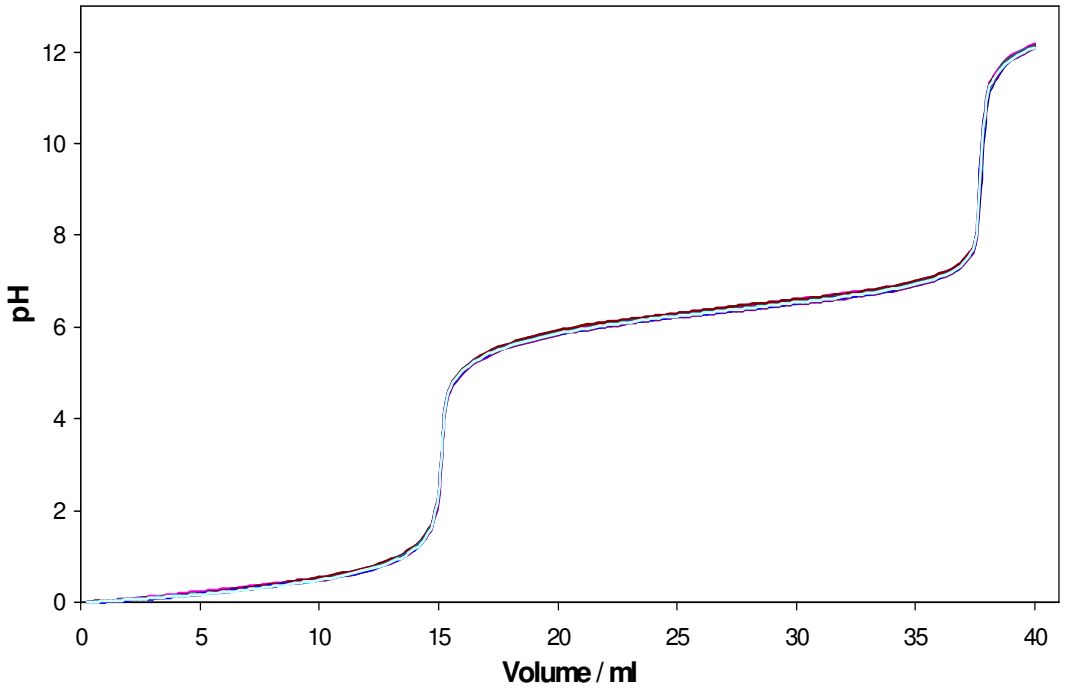

Figure C1. Normalized acid-base titration curves. Ten aliquots of chromium(VI) solution were titrated against 0.978M NaOH solution. The normalized titration curves were obtained by subtracting each and every pH reading from the initial pH value and the resulting pH values were referred to as normalized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

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	1.75	373.0	0.000	0.372	0	11	11	373.0	373.0	373.0	373.0	373.0	373.0	373.0	373.0	373.0	373.0	373.0
0.25	2.00	372.5	0.000	0.381	0	11	11	372.5	372.5	372.5	372.5	372.5	372.5	372.5	372.5	372.5	372.5	372.5
0.25	2.25	372.0	0.000	0.389	0	11	11	372.0	372.0	372.0	372.0	372.0	372.0	372.0	372.0	372.0	372.0	372.0
0.25	2.50	371.5	0.032	0.399	0	11	11	371.6	371.5	371.5	371.5	371.5	371.5	371.5	371.5	371.5	371.5	371.5
0.25	2.75	371.0	0.000	0.408	0	11	11	371.0	371.0	371.0	371.0	371.0	371.0	371.0	371.0	371.0	371.0	371.0
0.25	3.00	370.5	0.032	0.417	0	11	11	370.5	370.5	370.5	370.5	370.5	370.5	370.5	370.5	370.4	370.5	370.5
0.25	3.25	369.9	0.032	0.426	0	11	11	370.0	369.9	369.9	369.9	369.9	369.9	369.9	369.9	369.9	369.9	369.9
0.25	3.50	369.4	0.000	0.437	0	11	11	369.4	369.4	369.4	369.4	369.4	369.4	369.4	369.4	369.4	369.4	369.4
0.25	3.75	368.8	0.000	0.447	0	11	11	368.8	368.8	368.8	368.8	368.8	368.8	368.8	368.8	368.8	368.8	368.8
0.25	4.00	368.2	0.000	0.457	0	11	11	368.2	368.2	368.2	368.2	368.2	368.2	368.2	368.2	368.2	368.2	368.2
0.25	4.25	367.6	0.053	0.468	0	11	11	367.7	367.7	367.7	367.7	367.6	367.7	367.6	367.6	367.6	367.6	367.6
0.25	4.50	367.0	0.000	0.479	0	11	11	367.0	367.0	367.0	367.0	367.0	367.0	367.0	367.0	367.0	367.0	367.0
0.25	4.75	366.4	0.000	0.490	0	11	11	366.4	366.4	366.4	366.4	366.4	366.4	366.4	366.4	366.4	366.4	366.4
0.25	5.00	365.8	0.042	0.502	0	11	11	365.8	365.8	365.8	365.8	365.8	365.8	365.8	365.8	365.7	365.7	365.7
0.25	5.25	365.1	0.000	0.513	0	11	11	365.1	365.1	365.1	365.1	365.1	365.1	365.1	365.1	365.1	365.1	365.1
0.25	5.50	364.4	0.042	0.526	0	11	11	364.4	364.4	364.4	364.4	364.4	364.4	364.4	364.3	364.4	364.3	364.4
0.25	5.75	363.7	0.000	0.539	0	11	11	363.7	363.7	363.7	363.7	363.7	363.7	363.7	363.7	363.7	363.7	363.7
0.25	6.00	363.0	0.042	0.551	0	11	11	363.0	363.0	363.0	363.0	363.0	363.0	362.9	363.0	363.0	362.9	362.9
0.25	6.25	362.2	0.000	0.565	0	11	11	362.2	362.2	362.2	362.2	362.2	362.2	362.2	362.2	362.2	362.2	362.2
0.25	6.50	361.5	0.042	0.578	0	11	11	361.5	361.5	361.5	361.5	361.5	361.5	361.5	361.5	361.4	361.4	361.4
0.25	6.75	360.7	0.000	0.592	0	11	11	360.7	360.7	360.7	360.7	360.7	360.7	360.7	360.7	360.7	360.7	360.7

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	7.00	359.9	0.000	0.606	0	11	11	359.9	359.9	359.9	359.9	359.9	359.9	359.9	359.9	359.9	359.9	359.9
0.25	7.25	359.1	0.000	0.621	0	11	11	359.1	359.1	359.1	359.1	359.1	359.1	359.1	359.1	359.1	359.1	359.1
0.25	7.50	358.2	0.052	0.636	0	11	11	358.3	358.2	358.3	358.2	358.2	358.3	358.2	358.2	358.3	358.2	358.2
0.25	7.75	357.4	0.042	0.652	0	11	11	357.4	357.4	357.4	357.4	357.4	357.4	357.4	357.3	357.3	357.4	357.3
0.25	8.00	356.4	0.052	0.668	0	11	11	356.5	356.5	356.5	356.4	356.4	356.4	356.4	356.4	356.5	356.4	356.4
0.25	8.25	355.5	0.000	0.685	0	11	11	355.5	355.5	355.5	355.5	355.5	355.5	355.5	355.5	355.5	355.5	355.5
0.25	8.50	354.5	0.000	0.703	0	11	11	354.5	354.5	354.5	354.5	354.5	354.5	354.5	354.5	354.5	354.5	354.5
0.25	8.75	353.5	0.032	0.722	0	11	11	353.5	353.5	353.5	353.5	353.5	353.5	353.5	353.5	353.5	353.4	353.5
0.25	9.00	352.4	0.032	0.740	0	11	11	352.5	352.4	352.4	352.4	352.4	352.4	352.4	352.4	352.4	352.4	352.4
0.25	9.25	351.3	0.000	0.760	0	11	11	351.3	351.3	351.3	351.3	351.3	351.3	351.3	351.3	351.3	351.3	351.3
0.25	9.50	350.1	0.048	0.781	0	11	11	350.2	350.2	350.2	350.1	350.1	350.1	350.1	350.1	350.1	350.1	350.1
0.25	9.75	348.9	0.052	0.802	0	11	11	349.0	348.9	349.0	348.9	348.9	348.9	348.9	348.9	349.0	349.0	348.9
0.25	10.00	347.7	0.048	0.826	0	11	11	347.7	347.7	347.7	347.7	347.7	347.7	347.7	347.6	347.6	347.6	347.7
0.25	10.25	346.3	0.042	0.849	0	11	11	346.3	346.3	346.4	346.3	346.3	346.4	346.3	346.3	346.3	346.3	346.3
0.25	10.50	344.9	0.052	0.874	0	11	11	345.0	345.0	345.0	345.0	344.9	344.9	344.9	344.9	344.9	344.9	344.9
0.25	10.75	343.5	0.000	0.900	0	11	11	343.5	343.5	343.5	343.5	343.5	343.5	343.5	343.5	343.5	343.5	343.5
0.25	11.00	341.9	0.052	0.927	0	11	11	342.0	342.0	342.0	342.0	341.9	341.9	341.9	341.9	341.9	341.9	341.9
0.25	11.25	340.3	0.000	0.957	0	11	11	340.3	340.3	340.3	340.3	340.3	340.3	340.3	340.3	340.3	340.3	340.3
0.25	11.50	338.6	0.000	0.988	0	11	11	338.6	338.6	338.6	338.6	338.6	338.6	338.6	338.6	338.6	338.6	338.6
0.25	11.75	336.7	0.032	1.022	0	11	11	336.8	336.7	336.7	336.7	336.7	336.7	336.7	336.7	336.7	336.7	336.7
0.25	12.00	334.7	0.000	1.058	0	11	11	334.7	334.7	334.7	334.7	334.7	334.7	334.7	334.7	334.7	334.7	334.6

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	12.25	332.5	0.000	1.097	0	11	11	332.5	332.5	332.5	332.5	332.5	332.5	332.5	332.5	332.5	332.5	332.5
0.25	12.50	330.2	0.052	1.139	0	11	11	330.2	330.2	330.2	330.2	330.2	330.1	330.1	330.2	330.1	330.1	330.1
0.25	12.75	327.5	0.042	1.186	0	11	11	327.6	327.6	327.5	327.5	327.5	327.5	327.5	327.5	327.5	327.5	327.5
0.25	13.00	324.6	0.032	1.239	0	11	11	324.6	324.6	324.6	324.6	324.6	324.6	324.6	324.6	324.6	324.5	324.6
0.25	13.25	321.3	0.032	1.297	0	11	11	321.4	321.3	321.3	321.3	321.3	321.3	321.3	321.3	321.3	321.3	321.3
0.25	13.50	317.6	0.053	1.365	0	11	11	317.6	317.6	317.6	317.6	317.6	317.5	317.5	317.5	317.5	317.5	317.5
0.25	13.75	313.1	0.032	1.444	0	11	11	313.1	313.1	313.2	313.1	313.1	313.1	313.1	313.1	313.1	313.1	313.1
0.25	14.00	307.8	0.042	1.539	0	11	11	307.9	307.9	307.8	307.8	307.8	307.8	307.8	307.8	307.8	307.8	307.7
0.25	14.25	301.2	0.063	1.658	0	11	11	301.2	301.3	301.2	301.2	301.2	301.2	301.2	301.1	301.1	301.1	301.1
0.25	14.50	292.3	0.070	1.818	0	11	11	292.4	292.3	292.3	292.3	292.3	292.2	292.2	292.2	292.2	292.2	292.2
0.25	14.75	278.5	0.097	2.068	0	11	11	278.6	278.6	278.5	278.5	278.5	278.4	278.4	278.4	278.4	278.3	278.3
0.25	15.00	246.9	0.099	2.633	0	27	27	247.8	247.8	247.7	247.7	247.7	247.6	247.5	247.6	247.5	247.3	247.4
								247.3	247.3	247.2	247.2	247.1	247.1	247.0	246.9	246.9	246.9	246.9
								246.8	246.8	246.8	246.8	246.8						
0.25	15.25	142.2	0.099	4.508	0	38	38	145.3	144.9	144.5	144.2	144.1	143.9	143.9	143.7	143.6	143.5	143.3
								143.3	143.3	143.1	143.0	143.0	142.9	142.9	142.8	142.8	142.7	142.7
								142.7	142.6	142.5	142.5	142.5	142.4	142.3	142.3	142.2	142.2	142.2
								142.2	142.1	142.1	142.1	142.0						
0.25	15.50	116.4	0.095	4.967	0	18	18	117.2	117.0	117.0	116.9	116.8	116.7	116.7	116.6	116.5	116.5	116.4
								116.5	116.4	116.4	116.4	116.3	116.3	116.3				
0.25	15.75	103.4	0.099	5.198	0	16	16	103.8	103.7	103.7	103.7	103.6	103.6	103.5	103.5	103.4	103.4	103.4

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)										
								103.4	103.3	103.3	103.3	103.3						
0.25	16.00	94.8	0.088	5.352	0	11	11	94.9	94.9	94.9	94.8	94.8	94.8	94.7	94.7	94.7	94.7	94.7
0.25	16.25	88.3	0.063	5.468	0	11	11	88.4	88.4	88.4	88.3	88.3	88.3	88.3	88.3	88.3	88.2	88.2
0.25	16.50	83.0	0.074	5.562	0	11	11	83.1	83.1	83.0	83.0	83.0	83.0	83.0	82.9	82.9	82.9	82.9
0.25	16.75	78.5	0.067	5.642	0	11	11	78.6	78.5	78.5	78.5	78.5	78.5	78.4	78.4	78.4	78.4	78.4
0.25	17.00	74.7	0.053	5.710	0	11	11	74.7	74.7	74.7	74.7	74.7	74.6	74.6	74.6	74.6	74.6	74.6
0.25	17.25	71.3	0.052	5.771	0	11	11	71.3	71.3	71.3	71.3	71.3	71.3	71.2	71.2	71.2	71.2	71.2
0.25	17.50	68.2	0.048	5.825	0	11	11	68.3	68.3	68.3	68.2	68.2	68.2	68.2	68.2	68.2	68.2	68.2
0.25	17.75	65.5	0.053	5.874	0	11	11	65.5	65.5	65.5	65.5	65.5	65.4	65.4	65.4	65.4	65.4	65.4
0.25	18.00	62.9	0.048	5.920	0	11	11	63.0	63.0	63.0	62.9	62.9	62.9	62.9	62.9	62.9	62.9	62.9
0.25	18.25	60.6	0.000	5.960	0	11	11	60.6	60.6	60.6	60.6	60.6	60.6	60.6	60.6	60.6	60.6	60.6
0.25	18.50	58.4	0.048	5.999	0	11	11	58.5	58.5	58.5	58.4	58.4	58.4	58.4	58.4	58.4	58.4	58.4
0.25	18.75	56.4	0.032	6.035	0	11	11	56.4	56.4	56.5	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4
0.25	19.00	54.6	0.048	6.068	0	11	11	54.6	54.6	54.6	54.6	54.5	54.6	54.6	54.5	54.6	54.5	54.6
0.25	19.25	52.9	0.053	6.098	0	11	11	52.8	52.9	52.9	52.9	52.8	52.9	52.9	52.8	52.8	52.8	52.8
0.25	19.50	51.2	0.000	6.127	0	11	11	51.2	51.2	51.2	51.2	51.2	51.2	51.2	51.2	51.2	51.2	51.2
0.25	19.75	49.7	0.000	6.154	0	11	11	49.7	49.7	49.7	49.7	49.7	49.7	49.7	49.7	49.7	49.7	49.7
0.25	20.00	48.3	0.000	6.179	0	11	11	48.3	48.3	48.3	48.3	48.3	48.3	48.3	48.3	48.3	48.3	48.3
0.25	20.25	47.0	0.048	6.204	0	11	11	47.0	47.0	47.0	46.9	47.0	47.0	46.9	47.0	47.0	46.9	46.9
0.25	20.50	45.7	0.000	6.226	0	11	11	45.7	45.7	45.7	45.7	45.7	45.7	45.7	45.7	45.7	45.7	45.7
0.25	20.75	44.4	0.048	6.248	0	11	11	44.4	44.5	44.4	44.4	44.4	44.5	44.4	44.4	44.5	44.4	44.4

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	21.00	43.2	0.053	6.270	0	11	11	43.3	43.2	43.3	43.3	43.3	43.3	43.2	43.2	43.2	43.2	43.2
0.25	21.25	42.1	0.048	6.291	0	11	11	42.0	42.1	42.1	42.1	42.1	42.1	42.1	42.0	42.0	42.1	42.1
0.25	21.50	40.9	0.000	6.311	0	11	11	40.9	40.9	40.9	40.9	40.9	40.9	40.9	40.9	40.9	40.9	40.9
0.25	21.75	39.9	0.048	6.331	0	11	11	39.9	39.9	39.9	39.9	39.8	39.9	39.8	39.9	39.9	39.8	39.9
0.25	22.00	38.8	0.000	6.350	0	11	11	38.8	38.8	38.8	38.8	38.8	38.8	38.8	38.8	38.8	38.8	38.8
0.25	22.25	37.7	0.000	6.369	0	11	11	37.7	37.7	37.7	37.7	37.7	37.7	37.7	37.7	37.7	37.7	37.7
0.25	22.50	36.7	0.000	6.387	0	11	11	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7
0.25	22.75	35.7	0.000	6.405	0	11	11	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7
0.25	23.00	34.7	0.000	6.423	0	11	11	34.7	34.7	34.7	34.7	34.7	34.7	34.7	34.7	34.7	34.7	34.7
0.25	23.25	33.7	0.032	6.441	0	11	11	33.6	33.7	33.7	33.7	33.7	33.7	33.7	33.7	33.7	33.7	33.7
0.25	23.50	32.7	0.000	6.459	0	11	11	32.7	32.7	32.7	32.7	32.7	32.7	32.7	32.7	32.7	32.7	32.7
0.25	23.75	31.7	0.052	6.475	0	11	11	31.7	31.8	31.8	31.8	31.7	31.7	31.8	31.7	31.7	31.7	31.7
0.25	24.00	30.8	0.000	6.492	0	11	11	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8
0.25	24.25	29.9	0.000	6.508	0	11	11	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9
0.25	24.50	29.1	0.000	6.523	0	11	11	29.1	29.1	29.1	29.1	29.1	29.1	29.1	29.1	29.1	29.1	29.1
0.25	24.75	28.2	0.000	6.539	0	11	11	28.2	28.2	28.2	28.2	28.2	28.2	28.2	28.2	28.2	28.2	28.2
0.25	25.00	27.3	0.000	6.554	0	11	11	27.3	27.3	27.3	27.3	27.3	27.3	27.3	27.3	27.3	27.3	27.3
0.25	25.25	26.5	0.000	6.570	0	11	11	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5
0.25	25.50	25.6	0.000	6.585	0	11	11	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6
0.25	25.75	24.8	0.052	6.601	0	11	11	24.7	24.8	24.8	24.7	24.7	24.8	24.8	24.8	24.8	24.7	24.8
0.25	26.00	23.9	0.000	6.616	0	11	11	23.9	23.9	23.9	23.9	23.9	23.9	23.9	23.9	23.9	23.9	23.9

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	26.25	23.0	0.042	6.631	0	11	11	23.0	23.0	23.0	23.0	23.0	23.1	23.0	23.1	23.0	23.0	23.0
0.25	26.50	22.2	0.032	6.646	0	11	11	22.1	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2	22.2
0.25	26.75	21.4	0.000	6.660	0	11	11	21.4	21.4	21.4	21.4	21.4	21.4	21.4	21.4	21.4	21.4	21.4
0.25	27.00	20.6	0.000	6.674	0	11	11	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6
0.25	27.25	19.8	0.000	6.688	0	11	11	19.8	19.8	19.8	19.8	19.8	19.8	19.8	19.8	19.8	19.8	19.8
0.25	27.50	19.0	0.042	6.702	0	11	11	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.1	19.1	19.1
0.25	27.75	18.2	0.032	6.717	0	11	11	18.2	18.2	18.2	18.2	18.2	18.3	18.2	18.2	18.2	18.2	18.2
0.25	28.00	17.4	0.000	6.732	0	11	11	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4
0.25	28.25	16.6	0.032	6.746	0	11	11	16.5	16.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6
0.25	28.50	15.7	0.000	6.762	0	11	11	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7
0.25	28.75	14.9	0.000	6.777	0	11	11	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9
0.25	29.00	14.0	0.000	6.793	0	11	11	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
0.25	29.25	13.1	0.000	6.808	0	11	11	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1
0.25	29.50	12.2	0.000	6.825	0	11	11	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2
0.25	29.75	11.3	0.000	6.841	0	11	11	11.3	11.3	11.3	11.3	11.3	11.3	11.3	11.3	11.3	11.3	11.3
0.25	30.00	10.4	0.048	6.857	0	11	11	10.3	10.3	10.4	10.3	10.4	10.4	10.4	10.4	10.4	10.4	10.4
0.25	30.25	9.5	0.032	6.873	0	11	11	9.4	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5
0.25	30.50	8.6	0.000	6.889	0	11	11	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6
0.25	30.75	7.7	0.052	6.906	0	11	11	7.6	7.6	7.6	7.6	7.7	7.7	7.7	7.7	7.7	7.7	7.7
0.25	31.00	6.8	0.069	6.921	0	10	10	6.7	6.7	6.8	6.7	6.8	6.8	6.8	6.8	6.8	6.8	
0.25	31.25	5.9	0.063	6.935	0	11	11	5.8	5.9	5.9	5.9	5.9	5.9	5.9	6.0	6.0	6.0	6.0

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	31.50	5.1	0.042	6.950	0	11	11	5.0	5.0	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.2
0.25	31.75	4.3	0.048	6.965	0	11	11	4.2	4.2	4.2	4.3	4.3	4.3	4.3	4.3	4.3	4.3
0.25	32.00	3.4	0.042	6.981	0	11	11	3.3	3.3	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
0.25	32.25	2.5	0.070	6.998	0	11	11	2.3	2.4	2.4	2.5	2.5	2.5	2.5	2.5	2.5	2.5
0.25	32.50	1.4	0.070	7.015	0	11	11	1.3	1.4	1.4	1.5	1.4	1.4	1.5	1.5	1.5	1.5
0.25	32.75	0.4	0.079	7.034	0	11	11	0.3	0.3	0.4	0.4	0.4	0.5	0.4	0.5	0.5	0.5
0.25	33.00	-0.7	0.074	7.053	0	11	11	-0.8	-0.8	-0.7	-0.7	-0.7	-0.7	-0.7	-0.6	-0.6	-0.6
0.25	33.25	-1.8	0.079	7.073	0	11	11	-1.9	-1.9	-1.8	-1.8	-1.8	-1.8	-1.7	-1.7	-1.7	-1.7
0.25	33.50	-3.0	0.099	7.094	0	11	11	-3.2	-3.1	-3.1	-3.0	-3.0	-3.0	-2.9	-3.0	-2.9	-2.9
0.25	33.75	-4.2	0.084	7.116	0	11	11	-4.4	-4.3	-4.3	-4.3	-4.2	-4.2	-4.2	-4.2	-4.2	-4.1	-4.2
0.25	34.00	-5.5	0.099	7.139	0	13	13	-5.8	-5.7	-5.7	-5.6	-5.6	-5.5	-5.5	-5.5	-5.5	-5.4	-5.4
								-5.4	-5.4									
0.25	34.25	-7.0	0.079	7.164	0	11	11	-7.1	-7.1	-7.0	-7.0	-7.0	-7.0	-6.9	-6.9	-6.9	-6.9	-6.9
0.25	34.50	-8.4	0.095	7.191	0	13	13	-8.7	-8.7	-8.6	-8.5	-8.5	-8.5	-8.4	-8.4	-8.4	-8.4	-8.3
								-8.3	-8.3									
0.25	34.75	-10.0	0.099	7.218	0	13	13	-10.4	-10.3	-10.2	-10.1	-10.1	-10.0	-10.0	-10.0	-10.0	-9.9	-9.9
								-9.9	-9.9									
0.25	35.00	-11.7	0.084	7.248	0	14	14	-12.1	-12.0	-11.9	-11.8	-11.8	-11.7	-11.7	-11.6	-11.6	-11.6	-11.6
								-11.6	-11.6	-11.6								
0.25	35.25	-13.5	0.092	7.281	0	14	14	-13.9	-13.8	-13.8	-13.7	-13.6	-13.6	-13.5	-13.5	-13.5	-13.5	-13.5
								-13.4	-13.4	-13.4								

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	35.50	-15.5	0.099	7.318	0	18	18	-16.1	-16.0	-15.9	-15.9	-15.8	-15.8	-15.7	-15.7	-15.6	-15.6	-15.5
								-15.5	-15.5	-15.5	-15.4	-15.4	-15.4	-15.4				
0.25	35.75	-17.8	0.099	7.358	0	17	17	-18.4	-18.4	-18.3	-18.2	-18.1	-18.0	-18.0	-17.9	-17.9	-17.8	-17.8
								-17.8	-17.8	-17.7	-17.7	-17.7	-17.6					
0.25	36.00	-20.4	0.097	7.403	0	18	18	-21.0	-20.9	-20.9	-20.8	-20.7	-20.7	-20.6	-20.5	-20.5	-20.4	-20.4
								-20.3	-20.3	-20.3	-20.3	-20.3	-20.2	-20.2				
0.25	36.25	-23.3	0.088	7.455	0	20	20	-24.2	-24.1	-24.0	-23.9	-23.8	-23.7	-23.6	-23.6	-23.5	-23.4	-23.4
								-23.4	-23.3	-23.3	-23.3	-23.2	-23.2	-23.2	-23.2	-23.2		
0.25	36.50	-26.7	0.088	7.516	0	25	25	-27.9	-27.8	-27.7	-27.6	-27.5	-27.4	-27.3	-27.3	-27.2	-27.1	-27.0
								-27.0	-26.9	-26.9	-26.8	-26.8	-26.8	-26.7	-26.7	-26.7	-26.6	-26.6
								-26.6	-26.6	-26.6								
0.25	36.75	-30.9	0.097	7.592	0	27	27	-32.6	-32.4	-32.3	-32.2	-32.1	-31.9	-31.8	-31.7	-31.6	-31.5	-31.5
								-31.4	-31.3	-31.3	-31.2	-31.2	-31.1	-31.1	-31.0	-31.0	-30.9	-30.9
								-30.9	-30.9	-30.9	-30.8	-30.8						
0.25	37.00	-36.7	0.097	7.693	0	31	31	-38.7	-38.5	-38.4	-38.3	-38.1	-38.0	-37.9	-37.8	-37.7	-37.6	-37.5
								-37.4	-37.3	-37.2	-37.1	-37.1	-37.0	-37.0	-36.9	-36.9	-36.8	-36.8
								-36.7	-36.7	-36.7	-36.6	-36.6	-36.6	-36.6	-36.5	-36.5		
0.25	37.25	-45.0	0.084	7.843	0	41	41	-48.0	-47.9	-47.8	-47.5	-47.4	-47.2	-47.1	-46.8	-46.7	-46.5	-46.4
								-46.4	-46.3	-46.1	-46.0	-45.9	-45.8	-45.7	-45.7	-45.6	-45.5	-45.4
								-45.4	-45.4	-45.3	-45.3	-45.2	-45.2	-45.2	-45.1	-45.1	-45.0	-45.0
								-44.9	-44.9	-44.9	-44.9	-44.9	-44.9	-44.8				

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	37.50	-61.3	0.097	8.132	0	48	48	-64.7	-64.5	-64.3	-64.0	-63.9	-63.7	-63.5	-63.3	-63.2	-63.0	-63.0
								-62.8	-62.6	-62.5	-62.5	-62.3	-62.2	-62.1	-62.0	-62.0	-61.9	-61.9
								-61.8	-61.7	-61.7	-61.6	-61.5	-61.5	-61.5	-61.4	-61.4	-61.3	-61.3
								-61.3	-61.2	-61.2	-61.2	-61.2	-61.1	-61.1				
0.25	37.75	-129.6	0.084	9.354	0	19	19	-131.5	-131.0	-130.7	-130.6	-130.3	-130.0	-129.9	-129.9	-129.8	-129.7	-129.6
								-129.6	-129.7	-129.7	-129.6	-129.6	-129.6	-129.5	-129.4			
0.25	38.00	-229.2	0.097	11.153	0	44	44	-226.1	-226.2	-226.5	-226.6	-227.0	-227.0	-227.2	-227.4	-227.5	-227.5	-227.7
								-227.8	-227.9	-228.0	-228.1	-228.1	-228.1	-228.2	-228.3	-228.4	-228.4	-228.5
								-228.5	-228.6	-228.7	-228.8	-228.8	-228.9	-228.9	-229.0	-229.0	-229.1	-229.1
								-229.2	-229.2	-229.2	-229.2	-229.2	-229.3	-229.3				
0.25	38.25	-256.3	0.097	11.636	0	29	29	-255.3	-255.4	-255.4	-255.4	-255.5	-255.6	-255.7	-255.7	-255.8	-255.8	-255.9
								-255.9	-255.9	-256.0	-256.0	-256.1	-256.1	-256.2	-256.2	-256.2	-256.3	-256.3
								-256.4	-256.3	-256.4	-256.4	-256.5	-256.4	-256.5				
0.25	38.50	-269.4	0.099	11.868	0	15	15	-268.9	-269.0	-269.0	-269.2	-269.2	-269.3	-269.3	-269.4	-269.4	-269.4	-269.4
								-269.5	-269.5	-269.5	-269.5							
0.25	38.75	-278.1	0.099	12.022	0	16	16	-277.5	-277.6	-277.7	-277.8	-277.9	-277.9	-278.0	-278.0	-278.1	-278.1	-278.1
								-278.1	-278.2	-278.2	-278.2	-278.2						
0.25	39.00	-284.7	0.097	12.140	0	13	13	-284.3	-284.4	-284.5	-284.5	-284.6	-284.7	-284.7	-284.7	-284.7	-284.7	-284.8
								-284.7	-284.8									
0.25	39.25	-289.8	0.084	12.232	0	12	12	-289.6	-289.7	-289.7	-289.8	-289.8	-289.9	-289.9	-289.9	-289.9	-289.9	-289.9
								-289.9										

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
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	-297.9	-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	-301.2	-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.

Table E1. Learning set of data loaded in the neural networks of the initial experimental design

	Input titration data																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	ml of NaOH solution added																			
	0.000	0.250	0.500	0.750	1.000	1.250	1.500	1.750	2.000	2.250	2.500	2.750	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750
Sample #	Change in pH (normalised pH values)																			
1	0.000	0.003	0.009	0.015	0.021	0.026	0.030	0.034	0.038	0.043	0.047	0.052	0.057	0.063	0.071	0.078	0.087	0.094	0.104	0.113
2	0.000	0.005	0.010	0.016	0.023	0.027	0.030	0.032	0.033	0.035	0.038	0.041	0.046	0.052	0.058	0.064	0.073	0.080	0.089	0.098
3	0.000	0.006	0.014	0.021	0.028	0.037	0.045	0.054	0.063	0.072	0.081	0.090	0.100	0.110	0.119	0.129	0.138	0.148	0.159	0.168
4	0.000	0.000	0.002	0.005	0.010	0.017	0.024	0.033	0.043	0.053	0.063	0.073	0.080	0.087	0.094	0.102	0.109	0.118	0.128	0.141
5	0.000	0.000	0.004	0.009	0.013	0.019	0.025	0.033	0.040	0.049	0.059	0.070	0.081	0.094	0.107	0.120	0.134	0.147	0.161	0.175
6	0.000	0.005	0.011	0.018	0.026	0.034	0.042	0.050	0.058	0.068	0.076	0.086	0.095	0.106	0.116	0.127	0.138	0.149	0.160	0.172
7	0.000	0.007	0.014	0.021	0.029	0.036	0.044	0.052	0.060	0.069	0.077	0.086	0.095	0.104	0.115	0.125	0.135	0.146	0.157	0.168
8	0.000	0.005	0.010	0.016	0.024	0.031	0.039	0.047	0.056	0.065	0.075	0.085	0.095	0.106	0.117	0.128	0.140	0.152	0.164	0.177
9	0.000	0.004	0.009	0.016	0.024	0.033	0.042	0.052	0.062	0.072	0.083	0.095	0.107	0.119	0.132	0.145	0.157	0.171	0.186	0.202
10	0.000	0.006	0.015	0.026	0.037	0.048	0.060	0.073	0.086	0.098	0.111	0.123	0.133	0.141	0.148	0.157	0.165	0.176	0.187	0.200
11	0.000	0.006	0.012	0.019	0.028	0.036	0.043	0.052	0.060	0.067	0.075	0.084	0.092	0.101	0.112	0.121	0.132	0.143	0.154	0.166
12	0.000	0.003	0.003	0.004	0.012	0.017	0.022	0.027	0.029	0.032	0.037	0.042	0.043	0.049	0.055	0.061	0.069	0.076	0.085	0.094
13	0.000	0.002	0.006	0.007	0.009	0.011	0.012	0.018	0.024	0.030	0.036	0.043	0.051	0.059	0.067	0.076	0.087	0.098	0.110	0.121
14	0.000	0.010	0.022	0.032	0.042	0.046	0.046	0.049	0.053	0.059	0.067	0.076	0.087	0.098	0.110	0.122	0.135	0.148	0.163	0.177
15	0.000	0.004	0.011	0.020	0.030	0.040	0.052	0.063	0.075	0.088	0.102	0.114	0.128	0.143	0.158	0.175	0.190	0.207	0.225	0.244
16	0.000	0.003	0.008	0.015	0.022	0.030	0.039	0.048	0.057	0.067	0.077	0.087	0.097	0.108	0.119	0.131	0.143	0.156	0.169	0.182
17	0.000	0.003	0.009	0.016	0.024	0.033	0.044	0.055	0.066	0.077	0.088	0.099	0.110	0.121	0.133	0.146	0.159	0.172	0.185	0.201
18	0.000	-0.001	0.004	0.010	0.018	0.027	0.036	0.047	0.058	0.069	0.081	0.093	0.105	0.119	0.132	0.146	0.161	0.176	0.191	0.207
19	0.000	0.000	-0.001	0.000	0.001	0.004	0.008	0.013	0.019	0.026	0.034	0.042	0.052	0.063	0.074	0.084	0.096	0.110	0.123	0.137
20	0.000	0.003	0.007	0.008	0.015	0.021	0.029	0.037	0.042	0.046	0.055	0.056	0.062	0.067	0.073	0.078	0.090	0.104	0.119	0.136
21	0.000	0.006	0.013	0.021	0.030	0.041	0.052	0.064	0.076	0.090	0.104	0.119	0.133	0.147	0.161	0.174	0.187	0.199	0.210	0.219
22	0.000	0.005	0.011	0.019	0.027	0.036	0.046	0.056	0.067	0.078	0.089	0.101	0.113	0.123	0.132	0.143	0.152	0.163	0.172	0.181
23	0.000	0.003	0.009	0.017	0.025	0.035	0.045	0.056	0.067	0.079	0.091	0.103	0.116	0.129	0.143	0.158	0.173	0.188	0.205	0.222
24	0.000	0.007	0.015	0.025	0.036	0.048	0.060	0.073	0.086	0.099	0.113	0.127	0.142	0.158	0.174	0.191	0.208	0.226	0.245	0.265
25	0.000	0.006	0.015	0.025	0.035	0.048	0.061	0.075	0.089	0.104	0.120	0.136	0.154	0.171	0.190	0.209	0.230	0.251	0.274	0.297

APPENDIX E

	Input titration data																			
	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
	ml of NaOH solution added																			
	5.000	5.250	5.500	5.750	6.000	6.250	6.500	6.750	7.000	7.250	7.500	7.750	8.000	8.250	8.500	8.750	9.000	9.250	9.500	9.750
Sample #	Change in pH (normalised pH values)																			
1	0.123	0.133	0.144	0.153	0.165	0.176	0.187	0.200	0.212	0.224	0.238	0.252	0.266	0.280	0.296	0.312	0.328	0.345	0.364	0.383
2	0.108	0.118	0.129	0.139	0.150	0.162	0.175	0.187	0.200	0.213	0.228	0.242	0.257	0.272	0.289	0.306	0.325	0.344	0.363	0.383
3	0.179	0.190	0.201	0.212	0.225	0.238	0.250	0.264	0.277	0.293	0.308	0.324	0.341	0.359	0.377	0.397	0.417	0.440	0.463	0.488
4	0.151	0.163	0.176	0.192	0.209	0.225	0.243	0.262	0.280	0.299	0.319	0.339	0.359	0.382	0.405	0.429	0.455	0.483	0.513	0.546
5	0.189	0.205	0.223	0.242	0.263	0.285	0.308	0.331	0.354	0.379	0.404	0.430	0.456	0.485	0.516	0.549	0.585	0.626	0.670	0.720
6	0.184	0.196	0.208	0.222	0.235	0.249	0.263	0.277	0.292	0.308	0.324	0.341	0.358	0.377	0.395	0.415	0.436	0.458	0.481	0.504
7	0.179	0.191	0.203	0.216	0.228	0.241	0.254	0.269	0.283	0.297	0.312	0.329	0.345	0.362	0.381	0.400	0.419	0.441	0.463	0.487
8	0.190	0.204	0.217	0.232	0.247	0.263	0.279	0.296	0.313	0.332	0.351	0.371	0.391	0.412	0.434	0.457	0.482	0.507	0.536	0.565
9	0.218	0.235	0.252	0.269	0.287	0.304	0.320	0.338	0.357	0.375	0.395	0.418	0.441	0.466	0.493	0.522	0.553	0.586	0.623	0.663
10	0.213	0.227	0.243	0.260	0.278	0.297	0.318	0.339	0.362	0.388	0.415	0.443	0.475	0.509	0.547	0.587	0.633	0.685	0.746	0.815
11	0.178	0.190	0.203	0.216	0.230	0.244	0.259	0.274	0.289	0.306	0.323	0.340	0.359	0.378	0.399	0.420	0.443	0.467	0.493	0.519
12	0.103	0.114	0.125	0.136	0.149	0.163	0.175	0.190	0.205	0.222	0.238	0.255	0.274	0.294	0.315	0.338	0.361	0.387	0.414	0.442
13	0.134	0.148	0.162	0.176	0.191	0.206	0.223	0.240	0.258	0.277	0.296	0.317	0.339	0.363	0.388	0.415	0.444	0.475	0.508	0.544
14	0.192	0.208	0.223	0.241	0.259	0.277	0.297	0.317	0.338	0.361	0.385	0.410	0.437	0.467	0.499	0.534	0.572	0.614	0.661	0.713
15	0.263	0.283	0.304	0.326	0.349	0.374	0.400	0.428	0.457	0.488	0.522	0.559	0.598	0.644	0.694	0.749	0.814	0.889	0.980	1.094
16	0.196	0.210	0.224	0.239	0.255	0.271	0.288	0.305	0.323	0.342	0.361	0.382	0.404	0.426	0.451	0.476	0.503	0.532	0.563	0.595
17	0.217	0.235	0.253	0.270	0.287	0.304	0.321	0.339	0.357	0.377	0.397	0.419	0.441	0.464	0.490	0.517	0.547	0.578	0.613	0.651
18	0.224	0.240	0.258	0.276	0.296	0.315	0.337	0.358	0.380	0.404	0.429	0.456	0.484	0.515	0.548	0.583	0.621	0.663	0.709	0.759
19	0.151	0.167	0.182	0.200	0.218	0.237	0.257	0.279	0.302	0.327	0.353	0.382	0.413	0.447	0.485	0.527	0.573	0.626	0.688	0.761
20	0.152	0.171	0.191	0.212	0.235	0.260	0.286	0.314	0.344	0.378	0.415	0.456	0.502	0.554	0.616	0.688	0.776	0.890	1.047	1.307
21	0.226	0.233	0.238	0.240	0.244	0.250	0.259	0.270	0.283	0.299	0.316	0.335	0.356	0.378	0.403	0.428	0.457	0.488	0.522	0.558
22	0.191	0.200	0.210	0.219	0.229	0.238	0.248	0.260	0.274	0.289	0.304	0.321	0.339	0.358	0.378	0.402	0.430	0.463	0.501	0.543
23	0.239	0.257	0.275	0.295	0.316	0.338	0.360	0.384	0.409	0.436	0.465	0.495	0.528	0.564	0.603	0.646	0.693	0.746	0.806	0.876
24	0.285	0.306	0.328	0.352	0.376	0.402	0.430	0.459	0.490	0.523	0.559	0.598	0.641	0.689	0.743	0.803	0.873	0.956	1.059	1.190
25	0.322	0.347	0.374	0.403	0.435	0.467	0.503	0.541	0.583	0.629	0.680	0.738	0.804	0.883	0.979	1.100	1.267	1.542	2.422	4.093

APPENDIX E

	Input titration data																			
	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
	ml of NaOH solution added																			
	10.000	10.250	10.500	10.750	11.000	11.250	11.500	11.750	12.000	12.250	12.500	12.750	13.000	13.250	13.500	13.750	14.000	14.250	14.500	14.750
Sample #	Change in pH (normalised pH values)																			
1	0.403	0.423	0.445	0.468	0.493	0.519	0.547	0.576	0.609	0.645	0.683	0.727	0.775	0.831	0.894	0.971	1.065	1.186	1.357	1.653
2	0.405	0.429	0.453	0.480	0.508	0.538	0.570	0.606	0.644	0.688	0.737	0.793	0.859	0.936	1.032	1.158	1.340	1.661	3.224	4.101
3	0.514	0.543	0.573	0.607	0.643	0.683	0.727	0.776	0.833	0.899	0.978	1.076	1.209	1.402	1.766	3.488	4.218	4.489	4.660	4.785
4	0.580	0.619	0.661	0.709	0.763	0.825	0.898	0.987	1.101	1.260	1.514	2.228	3.966	4.343	4.549	4.692	4.802	4.890	4.964	5.027
5	0.779	0.846	0.927	1.028	1.162	1.358	1.742	3.502	4.185	4.454	4.622	4.747	4.848	4.930	4.999	5.060	5.114	5.162	5.206	5.246
6	0.530	0.557	0.585	0.615	0.647	0.682	0.719	0.759	0.804	0.854	0.910	0.974	1.051	1.143	1.259	1.418	1.671	2.290	4.074	4.485
7	0.513	0.540	0.569	0.600	0.634	0.672	0.713	0.760	0.811	0.872	0.943	1.030	1.142	1.293	1.532	2.119	3.949	4.371	4.592	4.743
8	0.598	0.633	0.672	0.715	0.762	0.815	0.876	0.947	1.035	1.144	1.291	1.520	2.073	3.939	4.393	4.622	4.775	4.890	4.981	5.058
9	0.708	0.758	0.815	0.881	0.960	1.057	1.182	1.361	1.683	3.253	4.186	4.486	4.673	4.805	4.909	4.994	5.067	5.130	5.185	5.235
10	0.900	1.006	1.148	1.360	1.797	3.703	4.232	4.480	4.646	4.769	4.866	4.948	5.019	5.079	5.134	5.183	5.227	5.268	5.305	5.340
11	0.548	0.578	0.610	0.645	0.683	0.724	0.770	0.822	0.881	0.949	1.030	1.128	1.256	1.436	1.750	3.182	4.270	4.573	4.756	4.888
12	0.473	0.506	0.544	0.584	0.629	0.681	0.739	0.808	0.890	0.994	1.131	1.335	1.752	3.639	4.226	4.484	4.652	4.776	4.875	4.958
13	0.584	0.629	0.679	0.736	0.803	0.882	0.980	1.106	1.291	1.619	3.250	4.158	4.456	4.637	4.769	4.871	4.955	5.026	5.088	5.142
14	0.774	0.845	0.931	1.037	1.181	1.397	1.853	3.756	4.295	4.542	4.704	4.825	4.923	5.003	5.071	5.132	5.186	5.233	5.278	5.317
15	1.249	1.490	2.070	3.920	4.340	4.553	4.697	4.806	4.894	4.969	5.032	5.088	5.139	5.184	5.226	5.264	5.300	5.333	5.364	5.394
16	0.631	0.670	0.711	0.757	0.810	0.867	0.934	1.012	1.108	1.231	1.401	1.689	2.715	4.192	4.523	4.713	4.846	4.949	5.032	5.103
17	0.692	0.739	0.791	0.851	0.920	1.002	1.104	1.238	1.440	1.832	3.685	4.313	4.577	4.746	4.871	4.972	5.055	5.126	5.188	5.243
18	0.817	0.882	0.959	1.051	1.167	1.324	1.570	2.166	4.029	4.435	4.646	4.792	4.903	4.992	5.066	5.130	5.187	5.237	5.283	5.325
19	0.851	0.967	1.128	1.398	2.325	3.930	4.272	4.465	4.605	4.712	4.798	4.871	4.936	4.991	5.042	5.087	5.129	5.167	5.202	5.236
20	2.077	3.844	4.212	4.414	4.556	4.666	4.755	4.829	4.894	4.951	5.002	5.048	5.090	5.130	5.166	5.200	5.232	5.262	5.291	5.318
21	0.600	0.646	0.699	0.759	0.830	0.916	1.024	1.172	1.407	2.004	3.888	4.316	4.539	4.690	4.806	4.899	4.977	5.045	5.103	5.156
22	0.594	0.653	0.722	0.808	0.918	1.070	1.309	1.925	3.805	4.219	4.436	4.588	4.704	4.798	4.877	4.945	5.005	5.057	5.105	5.149
23	0.959	1.061	1.192	1.380	1.728	3.435	4.237	4.513	4.687	4.812	4.909	4.990	5.059	5.119	5.173	5.221	5.264	5.304	5.341	5.376
24	1.381	1.722	3.425	4.257	4.540	4.713	4.836	4.933	5.015	5.084	5.143	5.196	5.245	5.289	5.329	5.367	5.402	5.435	5.465	5.494
25	4.441	4.637	4.773	4.877	4.962	5.033	5.095	5.149	5.199	5.244	5.285	5.323	5.359	5.392	5.424	5.453	5.482	5.509	5.534	5.559

APPENDIX E

Input titration data

	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
	ml of NaOH solution added																			
	15.000	15.250	15.500	15.750	16.000	16.250	16.500	16.750	17.000	17.250	17.500	17.750	18.000	18.250	18.500	18.750	19.000	19.250	19.500	19.750
Sample #	Change in pH (normalised pH values)																			
1	2.947	4.091	4.404	4.592	4.725	4.826	4.909	4.980	5.041	5.095	5.144	5.188	5.229	5.266	5.302	5.335	5.365	5.394	5.422	5.448
2	4.388	4.566	4.693	4.794	4.875	4.944	5.004	5.058	5.106	5.149	5.189	5.226	5.261	5.294	5.325	5.354	5.382	5.407	5.432	5.456
3	4.883	4.963	5.030	5.091	5.143	5.190	5.233	5.273	5.309	5.343	5.376	5.406	5.434	5.461	5.488	5.512	5.536	5.557	5.578	5.599
4	5.083	5.133	5.178	5.219	5.257	5.291	5.324	5.355	5.384	5.411	5.437	5.462	5.486	5.508	5.530	5.551	5.572	5.591	5.610	5.628
5	5.283	5.317	5.349	5.379	5.408	5.434	5.460	5.485	5.507	5.530	5.552	5.572	5.592	5.611	5.630	5.648	5.666	5.682	5.699	5.716
6	4.697	4.840	4.949	5.037	5.110	5.173	5.228	5.277	5.322	5.363	5.401	5.437	5.470	5.501	5.530	5.559	5.585	5.610	5.634	5.658
7	4.859	4.951	5.028	5.094	5.153	5.204	5.250	5.292	5.331	5.367	5.401	5.432	5.462	5.491	5.519	5.544	5.569	5.593	5.616	5.638
8	5.124	5.181	5.232	5.278	5.320	5.358	5.394	5.428	5.458	5.488	5.516	5.542	5.567	5.591	5.614	5.636	5.658	5.678	5.699	5.718
9	5.280	5.321	5.359	5.394	5.427	5.457	5.487	5.514	5.541	5.565	5.590	5.614	5.635	5.657	5.679	5.699	5.719	5.738	5.757	5.776
10	5.373	5.404	5.433	5.460	5.487	5.512	5.536	5.558	5.580	5.601	5.622	5.642	5.662	5.681	5.700	5.718	5.736	5.753	5.770	5.786
11	4.990	5.073	5.143	5.204	5.259	5.306	5.350	5.390	5.427	5.462	5.495	5.525	5.555	5.582	5.609	5.634	5.658	5.681	5.703	5.724
12	5.029	5.089	5.143	5.192	5.237	5.276	5.314	5.349	5.382	5.412	5.441	5.469	5.496	5.521	5.546	5.569	5.591	5.614	5.635	5.655
13	5.192	5.236	5.277	5.315	5.350	5.382	5.413	5.442	5.471	5.497	5.521	5.546	5.569	5.591	5.612	5.633	5.653	5.672	5.691	5.709
14	5.355	5.390	5.422	5.453	5.481	5.508	5.533	5.557	5.580	5.603	5.624	5.645	5.666	5.685	5.706	5.724	5.743	5.761	5.779	5.796
15	5.422	5.447	5.473	5.497	5.520	5.541	5.563	5.584	5.604	5.623	5.642	5.660	5.679	5.696	5.715	5.731	5.748	5.764	5.781	5.797
16	5.165	5.219	5.267	5.311	5.351	5.388	5.422	5.455	5.485	5.514	5.542	5.568	5.593	5.617	5.641	5.664	5.685	5.707	5.727	5.747
17	5.293	5.338	5.378	5.417	5.452	5.485	5.516	5.545	5.572	5.599	5.625	5.649	5.673	5.696	5.718	5.740	5.760	5.780	5.800	5.819
18	5.363	5.398	5.432	5.463	5.493	5.520	5.547	5.572	5.597	5.620	5.643	5.664	5.686	5.706	5.727	5.747	5.766	5.784	5.803	5.821
19	5.268	5.296	5.325	5.351	5.377	5.401	5.424	5.446	5.466	5.487	5.506	5.526	5.544	5.562	5.580	5.599	5.616	5.633	5.650	5.667
20	5.343	5.368	5.392	5.415	5.437	5.459	5.479	5.500	5.519	5.537	5.555	5.573	5.590	5.607	5.624	5.640	5.656	5.673	5.689	5.705
21	5.203	5.246	5.286	5.323	5.357	5.389	5.419	5.448	5.475	5.502	5.527	5.552	5.575	5.599	5.621	5.643	5.663	5.683	5.702	5.721
22	5.189	5.225	5.260	5.293	5.323	5.352	5.379	5.405	5.431	5.454	5.478	5.501	5.524	5.545	5.567	5.587	5.607	5.626	5.645	5.663
23	5.408	5.439	5.467	5.495	5.521	5.545	5.569	5.592	5.615	5.636	5.657	5.678	5.698	5.717	5.737	5.756	5.774	5.792	5.810	5.828
24	5.522	5.548	5.574	5.598	5.622	5.644	5.665	5.687	5.707	5.727	5.747	5.766	5.785	5.803	5.822	5.840	5.858	5.875	5.893	5.910
25	5.583	5.606	5.628	5.650	5.671	5.691	5.710	5.729	5.748	5.767	5.785	5.803	5.821	5.839	5.856	5.874	5.891	5.908	5.925	5.942

APPENDIX E

	Input titration data																			
	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
	ml of NaOH solution added																			
	20.000	20.250	20.500	20.750	21.000	21.250	21.500	21.750	22.000	22.250	22.500	22.750	23.000	23.250	23.500	23.750	24.000	24.250	24.500	24.750
Sample #	Change in pH (normalised pH values)																			
1	5.472	5.496	5.518	5.539	5.560	5.579	5.599	5.617	5.635	5.653	5.670	5.687	5.703	5.719	5.736	5.751	5.766	5.782	5.797	5.811
2	5.479	5.500	5.522	5.542	5.561	5.580	5.598	5.616	5.633	5.650	5.666	5.682	5.697	5.713	5.728	5.743	5.758	5.773	5.787	5.801
3	5.618	5.638	5.657	5.675	5.692	5.709	5.726	5.743	5.758	5.775	5.790	5.806	5.821	5.836	5.851	5.865	5.880	5.894	5.908	5.923
4	5.646	5.664	5.681	5.698	5.713	5.730	5.745	5.760	5.776	5.791	5.806	5.820	5.835	5.849	5.863	5.878	5.892	5.906	5.920	5.934
5	5.732	5.748	5.763	5.778	5.793	5.808	5.823	5.838	5.852	5.866	5.881	5.894	5.908	5.923	5.936	5.950	5.964	5.978	5.991	6.005
6	5.680	5.701	5.722	5.742	5.761	5.780	5.798	5.816	5.833	5.850	5.867	5.883	5.899	5.916	5.931	5.947	5.962	5.978	5.992	6.007
7	5.658	5.679	5.699	5.718	5.736	5.753	5.770	5.787	5.803	5.819	5.836	5.851	5.866	5.882	5.898	5.912	5.927	5.942	5.957	5.971
8	5.738	5.756	5.774	5.791	5.809	5.825	5.842	5.858	5.874	5.890	5.905	5.920	5.936	5.950	5.966	5.980	5.995	6.010	6.025	6.039
9	5.793	5.810	5.827	5.843	5.860	5.875	5.890	5.905	5.920	5.934	5.949	5.963	5.978	5.992	6.007	6.022	6.036	6.050	6.064	6.079
10	5.802	5.817	5.832	5.846	5.861	5.876	5.891	5.905	5.920	5.934	5.948	5.963	5.977	5.992	6.007	6.021	6.035	6.050	6.064	6.080
11	5.745	5.765	5.784	5.803	5.820	5.838	5.855	5.872	5.889	5.905	5.921	5.937	5.953	5.969	5.985	6.000	6.015	6.030	6.044	6.060
12	5.675	5.693	5.712	5.730	5.748	5.765	5.782	5.798	5.814	5.829	5.845	5.861	5.876	5.891	5.907	5.922	5.938	5.953	5.968	5.983
13	5.727	5.744	5.762	5.779	5.796	5.812	5.828	5.844	5.859	5.875	5.891	5.906	5.922	5.937	5.953	5.968	5.983	5.999	6.014	6.029
14	5.813	5.830	5.847	5.863	5.879	5.895	5.911	5.927	5.941	5.957	5.973	5.988	6.004	6.019	6.034	6.050	6.066	6.081	6.097	6.112
15	5.813	5.828	5.844	5.859	5.874	5.889	5.904	5.919	5.934	5.949	5.964	5.979	5.994	6.009	6.024	6.040	6.055	6.072	6.087	6.104
16	5.766	5.785	5.804	5.822	5.839	5.857	5.874	5.891	5.907	5.924	5.940	5.956	5.972	5.989	6.005	6.021	6.037	6.053	6.069	6.084
17	5.838	5.855	5.874	5.891	5.907	5.924	5.941	5.957	5.973	5.989	6.005	6.021	6.037	6.053	6.069	6.084	6.101	6.117	6.133	6.149
18	5.838	5.856	5.873	5.890	5.906	5.922	5.939	5.954	5.971	5.987	6.003	6.018	6.034	6.051	6.067	6.083	6.100	6.116	6.132	6.149
19	5.683	5.699	5.716	5.732	5.747	5.763	5.779	5.794	5.810	5.825	5.841	5.857	5.873	5.889	5.905	5.921	5.938	5.955	5.972	5.989
20	5.721	5.737	5.753	5.768	5.783	5.799	5.815	5.831	5.846	5.862	5.878	5.894	5.911	5.928	5.945	5.962	5.980	5.998	6.017	6.035
21	5.739	5.756	5.774	5.791	5.808	5.825	5.842	5.858	5.875	5.892	5.908	5.925	5.942	5.959	5.976	5.993	6.010	6.027	6.045	6.063
22	5.680	5.698	5.714	5.731	5.748	5.764	5.781	5.797	5.813	5.830	5.847	5.863	5.880	5.897	5.914	5.932	5.949	5.967	5.985	6.004
23	5.845	5.862	5.879	5.896	5.913	5.929	5.946	5.962	5.979	5.996	6.012	6.029	6.046	6.064	6.082	6.099	6.117	6.136	6.155	6.174
24	5.927	5.944	5.961	5.978	5.995	6.012	6.028	6.045	6.062	6.079	6.097	6.114	6.132	6.151	6.169	6.188	6.208	6.228	6.248	6.270
25	5.959	5.976	5.993	6.010	6.027	6.044	6.061	6.078	6.096	6.114	6.133	6.151	6.171	6.191	6.211	6.232	6.255	6.277	6.301	6.327

APPENDIX E

	Input titration data																			
	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
	ml of NaOH solution added																			
	25.000	25.250	25.500	25.750	26.000	26.250	26.500	26.750	27.000	27.250	27.500	27.750	28.000	28.250	28.500	28.750	29.000	29.250	29.500	29.750
Sample #	Change in pH (normalised pH values)																			
1	5.826	5.840	5.855	5.869	5.882	5.896	5.910	5.924	5.937	5.951	5.964	5.978	5.992	6.006	6.020	6.034	6.048	6.062	6.077	6.091
2	5.815	5.829	5.843	5.857	5.870	5.883	5.897	5.910	5.923	5.937	5.951	5.964	5.978	5.992	6.005	6.019	6.033	6.047	6.062	6.076
3	5.937	5.951	5.964	5.977	5.992	6.005	6.019	6.032	6.046	6.059	6.074	6.087	6.102	6.115	6.130	6.145	6.159	6.175	6.190	6.205
4	5.948	5.961	5.975	5.988	6.002	6.016	6.030	6.043	6.057	6.071	6.086	6.100	6.115	6.129	6.144	6.159	6.175	6.190	6.207	6.223
5	6.019	6.032	6.047	6.061	6.074	6.089	6.103	6.116	6.132	6.146	6.161	6.176	6.192	6.207	6.224	6.241	6.258	6.276	6.294	6.313
6	6.022	6.037	6.051	6.066	6.080	6.095	6.109	6.123	6.137	6.151	6.166	6.180	6.195	6.210	6.225	6.241	6.256	6.272	6.288	6.304
7	5.986	6.000	6.014	6.028	6.043	6.057	6.071	6.085	6.100	6.114	6.129	6.144	6.159	6.174	6.189	6.205	6.221	6.237	6.253	6.271
8	6.054	6.068	6.082	6.096	6.111	6.126	6.140	6.154	6.169	6.184	6.199	6.214	6.231	6.246	6.263	6.279	6.296	6.313	6.331	6.350
9	6.093	6.108	6.122	6.137	6.151	6.166	6.181	6.196	6.212	6.227	6.243	6.260	6.277	6.294	6.311	6.329	6.348	6.367	6.388	6.405
10	6.094	6.109	6.125	6.140	6.155	6.171	6.187	6.203	6.219	6.236	6.254	6.272	6.291	6.311	6.331	6.353	6.375	6.398	6.423	6.450
11	6.075	6.089	6.104	6.119	6.134	6.149	6.164	6.179	6.194	6.209	6.225	6.241	6.258	6.274	6.291	6.307	6.322	6.337	6.354	6.373
12	5.998	6.013	6.029	6.044	6.059	6.074	6.090	6.106	6.121	6.138	6.154	6.171	6.189	6.206	6.225	6.243	6.263	6.283	6.304	6.326
13	6.045	6.060	6.076	6.092	6.107	6.123	6.140	6.155	6.172	6.189	6.207	6.225	6.244	6.264	6.283	6.304	6.326	6.349	6.372	6.397
14	6.129	6.145	6.161	6.177	6.195	6.212	6.228	6.245	6.265	6.284	6.303	6.322	6.344	6.365	6.388	6.413	6.438	6.466	6.495	6.527
15	6.120	6.136	6.154	6.173	6.190	6.208	6.226	6.246	6.267	6.287	6.310	6.334	6.359	6.386	6.415	6.447	6.482	6.520	6.564	6.615
16	6.099	6.115	6.131	6.147	6.164	6.180	6.198	6.214	6.232	6.250	6.269	6.289	6.309	6.329	6.351	6.374	6.398	6.423	6.449	6.478
17	6.166	6.183	6.199	6.215	6.233	6.251	6.269	6.287	6.306	6.325	6.345	6.366	6.390	6.413	6.438	6.464	6.492	6.523	6.556	6.592
18	6.167	6.184	6.201	6.219	6.237	6.256	6.275	6.294	6.314	6.336	6.358	6.381	6.406	6.432	6.460	6.491	6.523	6.559	6.600	6.646
19	6.007	6.025	6.043	6.062	6.082	6.102	6.123	6.145	6.167	6.192	6.217	6.245	6.276	6.308	6.344	6.385	6.430	6.484	6.549	6.633
20	6.055	6.076	6.097	6.119	6.142	6.167	6.192	6.219	6.249	6.281	6.317	6.356	6.403	6.455	6.520	6.603	6.717	6.903	7.385	9.701
21	6.081	6.100	6.118	6.137	6.157	6.177	6.198	6.221	6.242	6.266	6.291	6.317	6.346	6.377	6.410	6.448	6.489	6.536	6.591	6.658
22	6.022	6.042	6.062	6.082	6.102	6.124	6.147	6.170	6.195	6.221	6.250	6.280	6.314	6.350	6.391	6.439	6.494	6.560	6.646	6.766
23	6.194	6.215	6.236	6.258	6.281	6.305	6.330	6.357	6.386	6.417	6.451	6.488	6.531	6.581	6.639	6.713	6.809	6.948	7.214	8.526
24	6.292	6.316	6.340	6.365	6.393	6.422	6.453	6.487	6.525	6.568	6.617	6.675	6.748	6.842	6.982	7.248	8.585	10.358	10.741	10.940
25	6.354	6.383	6.413	6.447	6.484	6.525	6.572	6.626	6.695	6.779	6.900	7.104	7.755	10.085	10.626	10.859	11.004	11.109	11.191	11.259

APPENDIX E

	Input titration data																			
	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140
	ml of NaOH solution added																			
	30.000	30.250	30.500	30.750	31.000	31.250	31.500	31.750	32.000	32.250	32.500	32.750	33.000	33.250	33.500	33.750	34.000	34.250	34.500	34.750
Sample #	Change in pH (normalised pH values)																			
1	6.106	6.120	6.135	6.150	6.165	6.181	6.197	6.213	6.231	6.247	6.265	6.283	6.302	6.323	6.344	6.366	6.389	6.414	6.441	6.469
2	6.090	6.105	6.120	6.136	6.151	6.167	6.184	6.199	6.217	6.235	6.254	6.273	6.293	6.315	6.337	6.361	6.386	6.413	6.443	6.475
3	6.221	6.237	6.253	6.270	6.287	6.304	6.322	6.341	6.360	6.380	6.402	6.425	6.449	6.475	6.504	6.534	6.567	6.604	6.646	6.694
4	6.241	6.258	6.275	6.294	6.314	6.333	6.354	6.376	6.400	6.424	6.451	6.479	6.511	6.545	6.583	6.627	6.678	6.738	6.815	6.917
5	6.334	6.353	6.375	6.398	6.421	6.447	6.473	6.503	6.535	6.571	6.612	6.658	6.711	6.777	6.862	6.982	7.177	7.727	10.028	10.613
6	6.321	6.338	6.354	6.372	6.392	6.410	6.430	6.450	6.471	6.494	6.518	6.544	6.572	6.602	6.635	6.671	6.711	6.757	6.812	6.878
7	6.288	6.306	6.324	6.343	6.362	6.382	6.403	6.425	6.449	6.473	6.500	6.529	6.561	6.595	6.634	6.678	6.728	6.789	6.865	6.965
8	6.369	6.388	6.409	6.430	6.452	6.476	6.500	6.526	6.555	6.586	6.621	6.659	6.702	6.752	6.813	6.888	6.988	7.136	7.432	9.059
9	6.432	6.455	6.479	6.504	6.532	6.561	6.594	6.630	6.670	6.716	6.770	6.836	6.920	7.038	7.239	7.804	10.099	10.684	10.927	11.076
10	6.478	6.509	6.543	6.580	6.622	6.670	6.727	6.797	6.888	7.019	7.258	8.230	10.272	10.698	10.912	11.047	11.146	11.225	11.289	11.344
11	6.394	6.415	6.437	6.460	6.484	6.510	6.538	6.569	6.601	6.637	6.679	6.726	6.780	6.848	6.936	7.059	7.263	7.872	10.171	10.734
12	6.348	6.373	6.397	6.425	6.454	6.484	6.519	6.557	6.599	6.648	6.708	6.781	6.876	7.016	7.286	8.582	10.353	10.734	10.934	11.065
13	6.424	6.453	6.483	6.517	6.554	6.595	6.643	6.700	6.768	6.856	6.983	7.199	7.907	10.156	10.673	10.899	11.042	11.145	11.226	11.292
14	6.563	6.601	6.645	6.695	6.755	6.828	6.927	7.071	7.348	8.724	10.419	10.781	10.973	11.101	11.197	11.273	11.336	11.388	11.435	11.474
15	6.677	6.752	6.855	7.014	7.339	9.133	10.422	10.751	10.930	11.056	11.153	11.231	11.295	11.350	11.400	11.443	11.482	11.517	11.548	11.578
16	6.509	6.542	6.579	6.621	6.667	6.723	6.789	6.876	6.997	7.201	7.857	10.129	10.695	10.933	11.084	11.193	11.278	11.348	11.408	11.459
17	6.633	6.679	6.733	6.798	6.880	6.991	7.171	7.601	9.473	10.521	10.826	10.996	11.112	11.200	11.271	11.329	11.377	11.420	11.458	11.490
18	6.699	6.763	6.845	6.957	7.135	7.548	9.711	10.576	10.855	11.019	11.137	11.228	11.301	11.363	11.416	11.463	11.505	11.542	11.576	11.607
19	6.749	6.938	7.446	9.702	10.396	10.649	10.806	10.918	11.003	11.073	11.130	11.179	11.222	11.260	11.295	11.325	11.353	11.378	11.402	11.424
20	10.385	10.633	10.786	10.896	10.979	11.046	11.103	11.151	11.194	11.230	11.264	11.295	11.321	11.347	11.370	11.391	11.411	11.429	11.447	11.462
21	6.744	6.863	7.061	7.630	9.923	10.524	10.767	10.917	11.024	11.105	11.174	11.230	11.277	11.319	11.356	11.389	11.418	11.445	11.469	11.492
22	6.968	7.543	9.841	10.435	10.674	10.820	10.925	11.007	11.072	11.127	11.175	11.216	11.253	11.285	11.315	11.341	11.365	11.387	11.408	11.427
23	10.319	10.704	10.904	11.038	11.138	11.216	11.282	11.338	11.387	11.430	11.470	11.505	11.537	11.566	11.594	11.619	11.642	11.664	11.685	11.704
24	11.072	11.168	11.246	11.311	11.366	11.414	11.456	11.495	11.529	11.560	11.589	11.616	11.640	11.663	11.685	11.705	11.724	11.742	11.759	11.775
25	11.317	11.367	11.411	11.450	11.484	11.516	11.545	11.571	11.596	11.619	11.640	11.660	11.679	11.697	11.714	11.730	11.745	11.760	11.773	11.786

APPENDIX E

	Input titration data																					Output	
	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161		
	ml of NaOH solution added																						
	35.000	35.250	35.500	35.750	36.000	36.250	36.500	36.750	37.000	37.250	37.500	37.750	38.000	38.250	38.500	38.750	39.000	39.250	39.500	39.750	40.000		
Sample #	Change in pH (normalised pH values)																					Total Cr(VI) (g/L)	Cr(VI) from CrO_3
1	6.500	6.536	6.574	6.617	6.666	6.727	6.802	6.901	7.053	7.357	9.017	10.310	10.641	10.824	10.948	11.040	11.116	11.178	11.230	11.276	11.317	572.000	387.484
2	6.510	6.550	6.595	6.648	6.711	6.792	6.904	7.080	7.510	9.641	10.403	10.664	10.824	10.938	11.025	11.095	11.154	11.205	11.249	11.288	11.323	572.000	371.298
3	6.750	6.821	6.912	7.041	7.273	8.156	10.246	10.692	10.909	11.051	11.154	11.235	11.302	11.360	11.409	11.451	11.490	11.524	11.554	11.582	11.608	572.000	352.000
4	7.072	7.395	9.207	10.434	10.752	10.931	11.053	11.146	11.220	11.283	11.336	11.382	11.423	11.460	11.493	11.523	11.550	11.576	11.598	11.619	11.638	572.000	328.596
5	10.851	11.000	11.108	11.191	11.258	11.316	11.365	11.408	11.446	11.480	11.512	11.540	11.566	11.590	11.612	11.632	11.650	11.667	11.683	11.698	11.711	572.000	299.619
6	6.963	7.082	7.279	7.796	9.716	10.580	10.862	11.027	11.143	11.233	11.306	11.367	11.420	11.467	11.508	11.544	11.577	11.607	11.635	11.660	11.684	546.000	369.871
7	7.117	7.428	9.072	10.479	10.813	11.000	11.125	11.219	11.294	11.358	11.412	11.458	11.499	11.536	11.569	11.599	11.626	11.651	11.674	11.695	11.715	546.000	354.421
8	10.496	10.835	11.022	11.147	11.240	11.316	11.378	11.431	11.477	11.517	11.554	11.586	11.616	11.644	11.669	11.692	11.714	11.734	11.752	11.769	11.785	546.000	336.000
9	11.184	11.268	11.336	11.392	11.441	11.483	11.521	11.554	11.585	11.614	11.640	11.663	11.685	11.706	11.724	11.742	11.758	11.773	11.787	11.799	11.812	546.000	313.660
10	11.391	11.432	11.469	11.501	11.530	11.557	11.581	11.604	11.625	11.645	11.663	11.680	11.696	11.711	11.726	11.739	11.751	11.763	11.773	11.783	11.793	546.000	286.000
11	10.974	11.125	11.233	11.317	11.384	11.440	11.490	11.532	11.570	11.604	11.636	11.664	11.689	11.713	11.735	11.754	11.773	11.790	11.807	11.822	11.838	520.000	352.258
12	11.162	11.239	11.303	11.356	11.402	11.442	11.479	11.511	11.540	11.568	11.593	11.615	11.636	11.656	11.674	11.690	11.707	11.722	11.736	11.749	11.762	520.000	337.544
13	11.348	11.396	11.438	11.475	11.507	11.537	11.565	11.589	11.612	11.633	11.653	11.671	11.689	11.704	11.720	11.734	11.747	11.760	11.773	11.785	11.797	520.000	320.000
14	11.510	11.542	11.571	11.597	11.620	11.642	11.662	11.680	11.697	11.714	11.729	11.744	11.758	11.772	11.785	11.798	11.811	11.824	11.836	11.848	11.860	520.000	298.723
15	11.605	11.630	11.654	11.675	11.696	11.715	11.733	11.751	11.767	11.782	11.797	11.811	11.825	11.839	11.851	11.863	11.875	11.885	11.896	11.907	11.917	520.000	272.381
16	11.505	11.546	11.582	11.615	11.645	11.673	11.698	11.723	11.745	11.766	11.786	11.805	11.822	11.839	11.856	11.871	11.885	11.899	11.913	11.925	11.938	494.000	334.645
17	11.519	11.545	11.569	11.591	11.610	11.629	11.646	11.662	11.676	11.690	11.703	11.715	11.727	11.737	11.747	11.757	11.766	11.774	11.782	11.790	11.796	494.000	320.667
18	11.635	11.661	11.685	11.708	11.728	11.748	11.767	11.784	11.800	11.816	11.832	11.845	11.859	11.872	11.885	11.897	11.909	11.920	11.931	11.940	11.950	494.000	304.000
19	11.443	11.461	11.477	11.492	11.505	11.516	11.527	11.537	11.546	11.554	11.563	11.570	11.579	11.587	11.595	11.603	11.610	11.619	11.626	11.635	11.642	494.000	283.787
20	11.478	11.492	11.504	11.515	11.526	11.535	11.543	11.551	11.559	11.566	11.573	11.579	11.586	11.591	11.597	11.603	11.610	11.616	11.623	11.629	11.635	494.000	258.762
21	11.512	11.532	11.550	11.566	11.581	11.595	11.608	11.619	11.630	11.640	11.648	11.656	11.664	11.671	11.678	11.684	11.690	11.696	11.703	11.709	11.715	468.000	317.032
22	11.445	11.461	11.476	11.490	11.503	11.515	11.526	11.535	11.544	11.552	11.559	11.565	11.571	11.577	11.582	11.588	11.594	11.600	11.606	11.612	11.618	468.000	303.789
23	11.722	11.739	11.755	11.770	11.785	11.799	11.812	11.824	11.836	11.848	11.859	11.870	11.880	11.890	11.900	11.909	11.918	11.927	11.936	11.944	11.951	468.000	288.000
24	11.790	11.804	11.818	11.831	11.844	11.856	11.867	11.878	11.888	11.898	11.908	11.917	11.927	11.935	11.944	11.952	11.960	11.968	11.975	11.983	11.990	468.000	268.851
25	11.799	11.810	11.822	11.833	11.843	11.853	11.863	11.872	11.881	11.889	11.898	11.906	11.914	11.921	11.929	11.936	11.943	11.949	11.956	11.962	11.968	468.000	245.143

APPENDIX E

Table E2. Training set of data loaded in the neural networks of the initial experimental design

	Input titration data																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	ml of NaOH solution added																			
	0.000	0.250	0.500	0.750	1.000	1.250	1.500	1.750	2.000	2.250	2.500	2.750	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750
Sample#	Change in pH (normalised pH values)																			
1	0.000	0.007	0.016	0.026	0.036	0.046	0.057	0.067	0.077	0.087	0.097	0.107	0.118	0.129	0.139	0.151	0.163	0.175	0.187	0.199
2	0.000	0.005	0.012	0.020	0.029	0.037	0.046	0.055	0.064	0.073	0.083	0.093	0.103	0.114	0.125	0.135	0.148	0.159	0.171	0.183
3	0.000	0.007	0.015	0.024	0.033	0.042	0.051	0.061	0.071	0.082	0.092	0.103	0.115	0.126	0.138	0.150	0.162	0.175	0.189	0.203
4	0.000	0.004	0.012	0.020	0.029	0.039	0.049	0.059	0.070	0.081	0.092	0.103	0.115	0.127	0.139	0.152	0.166	0.179	0.193	0.208
5	0.000	-0.002	0.000	0.004	0.010	0.016	0.025	0.032	0.041	0.050	0.059	0.068	0.078	0.088	0.099	0.110	0.122	0.133	0.145	0.157
6	0.000	0.005	0.012	0.019	0.026	0.035	0.044	0.054	0.064	0.074	0.085	0.095	0.106	0.117	0.128	0.140	0.153	0.165	0.178	0.191
7	0.000	0.004	0.011	0.018	0.026	0.035	0.044	0.053	0.062	0.072	0.083	0.094	0.104	0.116	0.127	0.138	0.150	0.161	0.173	0.185
8	0.000	0.007	0.017	0.027	0.038	0.048	0.059	0.071	0.082	0.094	0.106	0.119	0.131	0.145	0.159	0.173	0.188	0.203	0.219	0.235
9	0.000	0.004	0.011	0.018	0.026	0.034	0.043	0.052	0.062	0.072	0.083	0.094	0.104	0.115	0.127	0.139	0.151	0.164	0.177	0.190
10	0.000	0.003	0.008	0.015	0.023	0.032	0.043	0.054	0.067	0.079	0.092	0.104	0.116	0.127	0.139	0.149	0.160	0.171	0.183	0.195
11	0.000	0.007	0.014	0.021	0.027	0.034	0.042	0.050	0.058	0.067	0.077	0.086	0.096	0.107	0.119	0.130	0.142	0.156	0.169	0.182
12	0.000	0.010	0.021	0.032	0.044	0.057	0.069	0.082	0.095	0.108	0.121	0.135	0.149	0.163	0.179	0.196	0.213	0.231	0.250	0.269
13	0.000	0.013	0.027	0.041	0.055	0.067	0.080	0.092	0.104	0.116	0.128	0.140	0.152	0.165	0.177	0.189	0.202	0.215	0.229	0.243
14	0.000	0.008	0.017	0.027	0.037	0.048	0.059	0.070	0.082	0.094	0.106	0.118	0.131	0.145	0.158	0.172	0.187	0.203	0.218	0.234
15	0.000	0.009	0.020	0.031	0.043	0.054	0.067	0.079	0.092	0.105	0.118	0.132	0.146	0.161	0.177	0.193	0.209	0.226	0.244	0.262
16	0.000	0.011	0.023	0.036	0.049	0.062	0.075	0.090	0.104	0.118	0.134	0.150	0.166	0.182	0.199	0.217	0.236	0.256	0.277	0.297

	Input titration data																			
	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
	ml of NaOH solution added																			
	5.000	5.250	5.500	5.750	6.000	6.250	6.500	6.750	7.000	7.250	7.500	7.750	8.000	8.250	8.500	8.750	9.000	9.250	9.500	9.750
Sample#	Change in pH (normalised pH values)																			
1	0.211	0.223	0.236	0.250	0.264	0.280	0.297	0.314	0.331	0.349	0.366	0.384	0.402	0.420	0.438	0.458	0.478	0.500	0.523	0.547
2	0.196	0.209	0.223	0.237	0.251	0.266	0.282	0.297	0.313	0.330	0.348	0.366	0.386	0.406	0.428	0.450	0.473	0.498	0.524	0.551
3	0.217	0.231	0.246	0.262	0.278	0.295	0.312	0.330	0.349	0.368	0.389	0.410	0.433	0.456	0.481	0.508	0.536	0.566	0.598	0.632
4	0.223	0.238	0.254	0.272	0.290	0.308	0.327	0.348	0.369	0.391	0.415	0.440	0.466	0.495	0.527	0.561	0.599	0.639	0.682	0.728
5	0.169	0.182	0.195	0.209	0.223	0.238	0.253	0.268	0.284	0.300	0.318	0.336	0.355	0.375	0.395	0.417	0.440	0.464	0.490	0.516
6	0.204	0.219	0.233	0.248	0.263	0.279	0.296	0.313	0.331	0.350	0.369	0.389	0.410	0.433	0.457	0.481	0.508	0.536	0.567	0.598
7	0.198	0.212	0.226	0.241	0.257	0.273	0.289	0.307	0.326	0.345	0.365	0.387	0.409	0.434	0.460	0.488	0.518	0.550	0.585	0.623
8	0.252	0.269	0.287	0.306	0.326	0.347	0.369	0.391	0.416	0.441	0.468	0.497	0.528	0.562	0.599	0.638	0.682	0.730	0.785	0.847
9	0.203	0.217	0.231	0.246	0.261	0.277	0.294	0.310	0.328	0.347	0.366	0.387	0.408	0.431	0.455	0.480	0.506	0.534	0.565	0.596
10	0.207	0.220	0.232	0.246	0.261	0.277	0.294	0.313	0.334	0.356	0.380	0.405	0.432	0.460	0.489	0.521	0.554	0.590	0.628	0.670
11	0.197	0.212	0.227	0.244	0.261	0.279	0.298	0.318	0.338	0.360	0.383	0.407	0.434	0.462	0.493	0.526	0.562	0.601	0.646	0.695
12	0.289	0.310	0.332	0.354	0.378	0.403	0.429	0.456	0.485	0.516	0.549	0.584	0.623	0.665	0.712	0.763	0.821	0.888	0.966	1.059
13	0.257	0.271	0.286	0.302	0.318	0.334	0.351	0.369	0.388	0.407	0.428	0.449	0.472	0.496	0.522	0.550	0.579	0.611	0.645	0.683
14	0.250	0.267	0.285	0.304	0.323	0.343	0.364	0.386	0.409	0.433	0.458	0.485	0.514	0.544	0.578	0.613	0.651	0.694	0.740	0.791
15	0.280	0.300	0.320	0.341	0.363	0.385	0.410	0.435	0.462	0.490	0.521	0.553	0.588	0.627	0.669	0.714	0.765	0.822	0.888	0.963
16	0.319	0.342	0.365	0.389	0.415	0.443	0.473	0.504	0.538	0.574	0.613	0.655	0.702	0.754	0.814	0.882	0.963	1.062	1.188	1.360

APPENDIX E

Input titration data

	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
	ml of NaOH solution added																			
	10.000	10.250	10.500	10.750	11.000	11.250	11.500	11.750	12.000	12.250	12.500	12.750	13.000	13.250	13.500	13.750	14.000	14.250	14.500	14.750
Sample#	Change in pH (normalised pH values)																			
1	0.573	0.599	0.627	0.657	0.688	0.721	0.756	0.795	0.837	0.885	0.938	0.999	1.072	1.160	1.271	1.423	1.661	2.218	4.046	4.498
2	0.581	0.612	0.645	0.681	0.720	0.763	0.810	0.861	0.921	0.990	1.070	1.169	1.298	1.479	1.787	3.100	4.257	4.562	4.747	4.879
3	0.669	0.709	0.754	0.802	0.856	0.918	0.989	1.072	1.177	1.314	1.509	1.869	3.604	4.330	4.602	4.771	4.895	4.992	5.072	5.141
4	0.781	0.841	0.910	0.991	1.093	1.225	1.415	1.755	3.446	4.249	4.532	4.709	4.837	4.937	5.019	5.089	5.150	5.204	5.251	5.295
5	0.545	0.576	0.609	0.644	0.682	0.724	0.769	0.820	0.878	0.945	1.023	1.119	1.244	1.418	1.709	2.864	4.165	4.481	4.669	4.802
6	0.633	0.670	0.711	0.756	0.805	0.860	0.924	0.996	1.086	1.197	1.345	1.572	2.075	3.935	4.397	4.624	4.776	4.888	4.979	5.055
7	0.666	0.714	0.768	0.830	0.904	0.993	1.104	1.255	1.493	2.084	3.922	4.346	4.569	4.720	4.836	4.929	5.007	5.073	5.133	5.185
8	0.919	1.006	1.114	1.257	1.473	1.927	3.794	4.318	4.563	4.723	4.841	4.935	5.014	5.081	5.139	5.191	5.238	5.280	5.319	5.355
9	0.631	0.669	0.710	0.755	0.805	0.861	0.925	1.000	1.091	1.206	1.360	1.600	2.176	4.036	4.450	4.666	4.813	4.923	5.012	5.086
10	0.715	0.765	0.820	0.883	0.956	1.041	1.146	1.283	1.484	1.861	3.663	4.347	4.616	4.786	4.909	5.007	5.087	5.155	5.214	5.268
11	0.752	0.819	0.897	0.994	1.123	1.306	1.635	3.267	4.181	4.470	4.652	4.783	4.886	4.971	5.043	5.106	5.161	5.211	5.255	5.297
12	1.179	1.341	1.596	2.255	4.094	4.474	4.685	4.828	4.938	5.027	5.102	5.166	5.223	5.275	5.321	5.363	5.402	5.438	5.472	5.504
13	0.725	0.772	0.825	0.885	0.956	1.042	1.150	1.294	1.522	2.047	3.964	4.434	4.669	4.825	4.942	5.036	5.116	5.183	5.241	5.295
14	0.850	0.916	0.994	1.088	1.207	1.369	1.627	2.314	4.119	4.501	4.705	4.847	4.957	5.045	5.120	5.183	5.240	5.290	5.336	5.378
15	1.054	1.169	1.322	1.553	2.086	4.001	4.449	4.672	4.825	4.939	5.030	5.106	5.173	5.231	5.283	5.329	5.372	5.412	5.448	5.482
16	1.654	2.759	4.203	4.531	4.723	4.856	4.958	5.043	5.114	5.177	5.231	5.281	5.327	5.368	5.407	5.443	5.477	5.508	5.538	5.566

Input titration data

	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
	ml of NaOH solution added																			
	15.000	15.250	15.500	15.750	16.000	16.250	16.500	16.750	17.000	17.250	17.500	17.750	18.000	18.250	18.500	18.750	19.000	19.250	19.500	19.750
Sample#	Change in pH (normalised pH values)																			
1	4.726	4.877	4.992	5.086	5.164	5.230	5.288	5.340	5.387	5.430	5.469	5.506	5.540	5.572	5.603	5.632	5.659	5.685	5.709	5.733
2	4.980	5.063	5.133	5.194	5.248	5.296	5.339	5.380	5.417	5.451	5.484	5.514	5.543	5.571	5.597	5.622	5.646	5.669	5.691	5.713
3	5.201	5.253	5.300	5.343	5.383	5.419	5.453	5.485	5.515	5.543	5.570	5.596	5.621	5.644	5.668	5.690	5.711	5.731	5.752	5.771
4	5.335	5.371	5.405	5.437	5.467	5.495	5.522	5.548	5.572	5.596	5.618	5.641	5.662	5.682	5.703	5.722	5.741	5.759	5.777	5.795
5	4.904	4.986	5.056	5.118	5.171	5.219	5.262	5.302	5.339	5.374	5.406	5.436	5.465	5.492	5.519	5.544	5.568	5.591	5.613	5.634
6	5.119	5.175	5.226	5.272	5.313	5.351	5.387	5.420	5.451	5.480	5.508	5.535	5.560	5.584	5.608	5.631	5.653	5.673	5.694	5.714
7	5.233	5.276	5.316	5.353	5.387	5.419	5.449	5.478	5.505	5.531	5.557	5.581	5.604	5.626	5.648	5.670	5.691	5.711	5.732	5.751
8	5.388	5.420	5.449	5.477	5.503	5.528	5.552	5.575	5.597	5.618	5.639	5.660	5.679	5.698	5.717	5.736	5.754	5.771	5.788	5.805
9	5.150	5.206	5.256	5.302	5.344	5.381	5.416	5.450	5.481	5.510	5.538	5.565	5.590	5.615	5.639	5.661	5.683	5.704	5.725	5.745
10	5.316	5.359	5.399	5.436	5.470	5.502	5.532	5.560	5.587	5.613	5.637	5.661	5.683	5.704	5.726	5.746	5.765	5.784	5.803	5.821
11	5.336	5.370	5.404	5.434	5.464	5.491	5.517	5.543	5.568	5.591	5.614	5.635	5.657	5.677	5.698	5.718	5.736	5.754	5.773	5.790
12	5.535	5.563	5.590	5.616	5.640	5.664	5.687	5.709	5.730	5.751	5.772	5.791	5.811	5.829	5.848	5.867	5.884	5.902	5.920	5.937
13	5.343	5.386	5.425	5.462	5.496	5.527	5.557	5.585	5.612	5.637	5.662	5.686	5.709	5.731	5.753	5.774	5.795	5.814	5.834	5.853
14	5.417	5.452	5.485	5.517	5.547	5.575	5.601	5.627	5.651	5.675	5.698	5.720	5.742	5.763	5.783	5.804	5.823	5.842	5.860	5.879
15	5.515	5.545	5.574	5.601	5.627	5.652	5.676	5.699	5.721	5.743	5.764	5.784	5.804	5.824	5.844	5.863	5.881	5.899	5.917	5.935
16	5.593	5.619	5.643	5.668	5.690	5.712	5.734	5.754	5.775	5.794	5.814	5.833	5.852	5.870	5.888	5.906	5.923	5.940	5.958	5.975

APPENDIX E

	Input titration data																		
	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
	ml of NaOH solution added																			
	20.000	20.250	20.500	20.750	21.000	21.250	21.500	21.750	22.000	22.250	22.500	22.750	23.000	23.250	23.500	23.750	24.000	24.250	24.500	24.750
Sample#	Change in pH (normalised pH values)																			
1	5.755	5.777	5.798	5.818	5.837	5.856	5.874	5.891	5.908	5.926	5.942	5.958	5.975	5.991	6.007	6.022	6.037	6.052	6.067	6.082
2	5.733	5.753	5.773	5.791	5.810	5.827	5.844	5.861	5.878	5.894	5.910	5.926	5.942	5.958	5.973	5.988	6.003	6.018	6.033	6.047
3	5.790	5.808	5.826	5.843	5.860	5.876	5.893	5.909	5.924	5.940	5.955	5.971	5.986	6.001	6.016	6.030	6.044	6.059	6.074	6.088
4	5.812	5.829	5.845	5.862	5.877	5.893	5.908	5.923	5.938	5.953	5.968	5.983	5.997	6.012	6.026	6.041	6.055	6.070	6.084	6.098
5	5.654	5.674	5.694	5.713	5.731	5.749	5.766	5.783	5.800	5.816	5.832	5.848	5.864	5.880	5.896	5.911	5.927	5.941	5.957	5.971
6	5.733	5.752	5.770	5.788	5.805	5.822	5.839	5.855	5.871	5.887	5.903	5.918	5.934	5.949	5.965	5.980	5.995	6.010	6.025	6.039
7	5.769	5.787	5.804	5.821	5.837	5.853	5.869	5.884	5.899	5.915	5.930	5.945	5.960	5.975	5.990	6.005	6.019	6.034	6.048	6.061
8	5.821	5.837	5.854	5.869	5.885	5.900	5.915	5.930	5.945	5.960	5.975	5.989	6.004	6.019	6.034	6.048	6.064	6.078	6.093	6.108
9	5.765	5.783	5.802	5.819	5.837	5.855	5.871	5.888	5.905	5.921	5.937	5.953	5.969	5.985	6.001	6.016	6.032	6.048	6.063	6.079
10	5.838	5.855	5.872	5.888	5.904	5.920	5.936	5.952	5.967	5.982	5.998	6.013	6.029	6.044	6.060	6.075	6.091	6.106	6.122	6.138
11	5.808	5.825	5.842	5.858	5.875	5.891	5.907	5.922	5.938	5.954	5.970	5.985	6.001	6.017	6.033	6.048	6.064	6.080	6.097	6.113
12	5.953	5.970	5.987	6.003	6.018	6.035	6.050	6.066	6.081	6.096	6.111	6.127	6.142	6.156	6.172	6.187	6.202	6.217	6.233	6.249
13	5.871	5.890	5.908	5.925	5.942	5.959	5.976	5.993	6.010	6.026	6.043	6.059	6.075	6.092	6.109	6.126	6.142	6.159	6.176	6.194
14	5.897	5.915	5.932	5.950	5.967	5.983	6.000	6.016	6.033	6.049	6.066	6.082	6.100	6.117	6.134	6.150	6.167	6.185	6.202	6.220
15	5.952	5.970	5.987	6.004	6.020	6.037	6.053	6.070	6.086	6.103	6.120	6.136	6.153	6.171	6.188	6.205	6.223	6.241	6.260	6.279
16	5.992	6.009	6.026	6.043	6.059	6.076	6.092	6.109	6.125	6.142	6.159	6.176	6.194	6.212	6.230	6.249	6.268	6.287	6.307	6.328

	Input titration data																			
	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
	ml of NaOH solution added																			
	25.000	25.250	25.500	25.750	26.000	26.250	26.500	26.750	27.000	27.250	27.500	27.750	28.000	28.250	28.500	28.750	29.000	29.250	29.500	29.750
Sample#	Change in pH (normalised pH values)																			
1	6.097	6.112	6.127	6.140	6.154	6.168	6.182	6.196	6.210	6.224	6.238	6.252	6.266	6.281	6.296	6.310	6.325	6.340	6.356	6.371
2	6.062	6.076	6.090	6.105	6.118	6.133	6.147	6.160	6.175	6.189	6.203	6.218	6.233	6.248	6.263	6.278	6.294	6.309	6.325	6.342
3	6.102	6.117	6.131	6.145	6.159	6.173	6.188	6.202	6.216	6.231	6.246	6.261	6.276	6.292	6.308	6.324	6.340	6.357	6.374	6.392
4	6.113	6.127	6.142	6.156	6.171	6.185	6.200	6.215	6.230	6.246	6.261	6.277	6.294	6.310	6.328	6.345	6.362	6.380	6.399	6.418
5	5.986	6.001	6.016	6.030	6.045	6.060	6.074	6.090	6.104	6.119	6.135	6.150	6.166	6.182	6.198	6.215	6.232	6.249	6.266	6.284
6	6.055	6.070	6.085	6.100	6.115	6.130	6.145	6.160	6.176	6.192	6.208	6.224	6.240	6.258	6.275	6.293	6.311	6.330	6.349	6.369
7	6.075	6.087	6.101	6.114	6.128	6.143	6.157	6.173	6.189	6.205	6.221	6.239	6.257	6.275	6.294	6.313	6.335	6.354	6.375	6.399
8	6.124	6.139	6.155	6.170	6.186	6.203	6.220	6.236	6.253	6.271	6.290	6.309	6.329	6.349	6.371	6.394	6.418	6.443	6.471	6.500
9	6.095	6.110	6.126	6.142	6.158	6.174	6.190	6.206	6.223	6.241	6.258	6.276	6.295	6.314	6.334	6.355	6.376	6.398	6.421	6.446
10	6.154	6.170	6.186	6.202	6.218	6.235	6.252	6.270	6.287	6.306	6.324	6.344	6.365	6.385	6.407	6.430	6.455	6.481	6.508	6.538
11	6.130	6.146	6.164	6.181	6.198	6.216	6.235	6.253	6.273	6.293	6.313	6.336	6.359	6.383	6.409	6.436	6.466	6.498	6.533	6.572
12	6.266	6.282	6.300	6.317	6.336	6.355	6.376	6.396	6.418	6.441	6.466	6.492	6.520	6.550	6.583	6.621	6.662	6.709	6.764	6.831
13	6.211	6.229	6.247	6.265	6.284	6.303	6.322	6.342	6.363	6.384	6.407	6.431	6.457	6.483	6.513	6.544	6.579	6.616	6.658	6.707
14	6.238	6.257	6.275	6.295	6.315	6.335	6.356	6.377	6.400	6.424	6.449	6.477	6.506	6.537	6.571	6.609	6.651	6.700	6.757	6.828
15	6.299	6.318	6.338	6.360	6.381	6.404	6.427	6.452	6.479	6.508	6.538	6.572	6.609	6.650	6.697	6.751	6.818	6.902	7.020	7.214
16	6.350	6.372	6.395	6.419	6.444	6.471	6.500	6.531	6.565	6.603	6.645	6.693	6.751	6.822	6.914	7.047	7.280	8.075	10.000	10.636

APPENDIX E

	Input titration data																			
	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140
	ml of NaOH solution added																			
	30.000	30.250	30.500	30.750	31.000	31.250	31.500	31.750	32.000	32.250	32.500	32.750	33.000	33.250	33.500	33.750	34.000	34.250	34.500	34.750
Sample#	Change in pH (normalised pH values)																			
1	6.387	6.403	6.420	6.436	6.454	6.471	6.490	6.509	6.528	6.548	6.570	6.592	6.616	6.642	6.670	6.700	6.732	6.768	6.808	6.854
2	6.359	6.376	6.393	6.411	6.430	6.449	6.468	6.489	6.511	6.534	6.558	6.585	6.612	6.643	6.676	6.713	6.754	6.802	6.857	6.925
3	6.410	6.429	6.448	6.469	6.490	6.511	6.535	6.559	6.585	6.613	6.644	6.678	6.715	6.757	6.806	6.864	6.935	7.026	7.160	7.394
4	6.438	6.458	6.480	6.504	6.530	6.558	6.588	6.622	6.659	6.701	6.750	6.808	6.878	6.970	7.105	7.341	8.142	10.050	10.663	10.908
5	6.304	6.322	6.343	6.364	6.385	6.408	6.432	6.458	6.485	6.515	6.548	6.585	6.625	6.672	6.728	6.795	6.881	7.001	7.201	7.747
6	6.390	6.412	6.434	6.459	6.484	6.511	6.540	6.572	6.606	6.645	6.690	6.741	6.804	6.882	6.991	7.157	7.517	9.023	10.341	10.706
7	6.423	6.449	6.477	6.507	6.539	6.574	6.613	6.658	6.710	6.774	6.855	6.965	7.137	7.526	9.200	10.363	10.699	10.882	11.008	11.100
8	6.532	6.566	6.605	6.649	6.700	6.760	6.835	6.935	7.086	7.382	8.694	10.219	10.635	10.841	10.978	11.077	11.154	11.217	11.272	11.318
9	6.473	6.501	6.530	6.563	6.599	6.639	6.685	6.738	6.802	6.882	6.996	7.174	7.591	9.254	10.449	10.789	10.976	11.104	11.202	11.280
10	6.571	6.606	6.646	6.691	6.744	6.805	6.884	6.990	7.153	7.505	9.114	10.440	10.791	10.976	11.101	11.192	11.264	11.324	11.374	11.417
11	6.615	6.665	6.725	6.799	6.896	7.036	7.297	8.293	10.069	10.596	10.832	10.977	11.082	11.164	11.231	11.287	11.335	11.377	11.414	11.447
12	6.918	7.036	7.232	7.757	9.634	10.531	10.827	10.997	11.112	11.201	11.273	11.333	11.383	11.427	11.466	11.501	11.532	11.561	11.587	11.611
13	6.765	6.834	6.925	7.054	7.278	8.011	10.019	10.653	10.897	11.046	11.153	11.235	11.301	11.356	11.404	11.444	11.479	11.511	11.539	11.564
14	6.919	7.048	7.272	8.003	9.919	10.611	10.875	11.036	11.149	11.238	11.311	11.373	11.426	11.471	11.513	11.550	11.583	11.614	11.641	11.667
15	7.729	9.577	10.540	10.843	11.016	11.135	11.228	11.302	11.365	11.418	11.465	11.507	11.544	11.578	11.609	11.638	11.663	11.687	11.709	11.729
16	10.888	11.040	11.151	11.237	11.307	11.366	11.416	11.461	11.501	11.536	11.569	11.599	11.626	11.650	11.674	11.696	11.716	11.735	11.753	11.769

	Input titration data																				Output	
	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	
	ml of NaOH solution added																					Total Cr(VI) (g/L) Cr(VI) from CrO3
	35.000	35.250	35.500	35.750	36.000	36.250	36.500	36.750	37.000	37.250	37.500	37.750	38.000	38.250	38.500	38.750	39.000	39.250	39.500	39.750	40.000	
Sample#	Change in pH (normalised pH values)																					
1	6.908	6.974	7.058	7.173	7.358	7.817	9.557	10.593	10.903	11.078	11.195	11.284	11.355	11.414	11.464	11.506	11.544	11.577	11.607	11.633	11.658	559.000 371.101
2	7.013	7.137	7.346	7.926	9.764	10.624	10.914	11.085	11.208	11.303	11.380	11.444	11.500	11.549	11.593	11.632	11.667	11.699	11.729	11.756	11.782	559.000 353.862
3	8.192	10.068	10.702	10.954	11.111	11.225	11.315	11.387	11.449	11.503	11.551	11.593	11.631	11.666	11.698	11.727	11.754	11.779	11.802	11.824	11.844	559.000 333.141
4	11.061	11.172	11.257	11.325	11.384	11.434	11.477	11.515	11.548	11.579	11.606	11.631	11.654	11.678	11.700	11.721	11.741	11.760	11.778	11.795	11.811	559.000 307.764
5	9.555	10.455	10.750	10.921	11.041	11.133	11.208	11.271	11.325	11.373	11.416	11.454	11.489	11.520	11.550	11.577	11.602	11.626	11.647	11.667	11.687	533.000 353.840
6	10.899	11.028	11.124	11.197	11.259	11.312	11.357	11.397	11.433	11.464	11.493	11.518	11.543	11.564	11.585	11.603	11.621	11.638	11.653	11.668	11.682	533.000 337.404
7	11.175	11.237	11.289	11.335	11.374	11.409	11.441	11.469	11.495	11.519	11.541	11.562	11.581	11.599	11.615	11.631	11.646	11.659	11.673	11.685	11.697	533.000 317.646
8	11.359	11.394	11.427	11.455	11.481	11.505	11.527	11.547	11.566	11.584	11.600	11.616	11.630	11.644	11.657	11.669	11.681	11.692	11.702	11.712	11.722	533.000 293.449
9	11.345	11.400	11.449	11.492	11.530	11.565	11.596	11.625	11.652	11.677	11.700	11.722	11.743	11.763	11.781	11.798	11.814	11.829	11.844	11.858	11.872	507.000 336.580
10	11.455	11.489	11.519	11.545	11.569	11.591	11.611	11.628	11.644	11.659	11.674	11.687	11.700	11.712	11.724	11.735	11.746	11.757	11.767	11.778	11.789	507.000 320.945
11	11.477	11.504	11.529	11.551	11.573	11.592	11.611	11.628	11.645	11.661	11.677	11.692	11.707	11.721	11.735	11.748	11.761	11.774	11.787	11.799	11.811	507.000 302.152
12	11.633	11.654	11.672	11.689	11.706	11.722	11.739	11.754	11.769	11.784	11.798	11.811	11.823	11.836	11.847	11.858	11.869	11.879	11.888	11.897	11.907	507.000 279.135
13	11.586	11.606	11.625	11.642	11.659	11.674	11.688	11.703	11.716	11.729	11.742	11.755	11.767	11.778	11.790	11.800	11.811	11.821	11.830	11.840	11.848	481.000 319.319
14	11.691	11.713	11.734	11.753	11.771	11.788	11.804	11.819	11.833	11.848	11.861	11.874	11.886	11.898	11.909	11.919	11.930	11.940	11.949	11.958	11.967	481.000 304.486
15	11.749	11.768	11.785	11.800	11.815	11.830	11.844	11.857	11.869	11.881	11.892	11.903	11.913	11.924	11.934	11.943	11.952	11.960	11.968	11.976	11.985	481.000 286.657
16	11.785	11.799	11.813	11.826	11.839	11.851	11.862	11.873	11.883	11.893	11.903	11.913	11.923	11.932	11.940	11.948	11.957	11.965	11.972	11.979	11.986	481.000 264.820

Table E3. Test set of data loaded in the neural networks of the initial experimental design

	Input titration data																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	mL of NaOH solution added																			
	0.000	0.250	0.500	0.750	1.000	1.250	1.500	1.750	2.000	2.250	2.500	2.750	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750
Sample#	Change in pH (normalised pH values)																			
1	0.000	0.006	0.012	0.020	0.027	0.036	0.044	0.053	0.062	0.071	0.080	0.089	0.100	0.110	0.120	0.131	0.142	0.153	0.165	0.177
2	0.000	0.002	0.006	0.011	0.018	0.025	0.034	0.042	0.052	0.061	0.071	0.083	0.095	0.107	0.119	0.132	0.144	0.156	0.169	0.183
3	0.000	0.004	0.011	0.019	0.028	0.038	0.048	0.059	0.070	0.081	0.093	0.105	0.117	0.129	0.142	0.156	0.169	0.183	0.198	0.213
4	0.000	0.004	0.009	0.017	0.024	0.032	0.041	0.050	0.059	0.069	0.079	0.089	0.100	0.110	0.121	0.132	0.143	0.155	0.167	0.179
5	0.000	0.006	0.014	0.022	0.030	0.038	0.047	0.055	0.065	0.074	0.083	0.093	0.102	0.113	0.123	0.134	0.145	0.156	0.168	0.180
6	0.000	0.003	0.010	0.017	0.026	0.034	0.044	0.054	0.064	0.074	0.085	0.095	0.106	0.119	0.130	0.143	0.156	0.169	0.183	0.197
7	0.000	-0.001	0.002	0.007	0.012	0.019	0.027	0.036	0.045	0.056	0.067	0.079	0.092	0.105	0.119	0.133	0.149	0.165	0.181	0.197
8	0.000	0.007	0.013	0.020	0.026	0.032	0.040	0.047	0.055	0.062	0.071	0.080	0.088	0.097	0.107	0.116	0.127	0.137	0.148	0.159
9	0.000	0.009	0.017	0.027	0.035	0.044	0.054	0.063	0.073	0.083	0.094	0.104	0.116	0.128	0.139	0.152	0.164	0.178	0.190	0.204
10	0.000	0.014	0.025	0.036	0.046	0.058	0.079	0.087	0.094	0.103	0.113	0.124	0.135	0.146	0.158	0.171	0.184	0.197	0.211	0.225
11	0.000	0.009	0.020	0.028	0.038	0.048	0.058	0.068	0.078	0.089	0.100	0.111	0.122	0.134	0.146	0.158	0.171	0.184	0.198	0.212
12	0.000	0.010	0.020	0.030	0.042	0.052	0.063	0.073	0.085	0.096	0.107	0.119	0.131	0.144	0.157	0.170	0.183	0.197	0.211	0.225
13	0.000	0.008	0.016	0.026	0.035	0.045	0.056	0.065	0.076	0.087	0.098	0.109	0.121	0.133	0.146	0.159	0.171	0.186	0.199	0.215
14	0.000	0.008	0.019	0.029	0.040	0.053	0.065	0.077	0.089	0.102	0.115	0.129	0.143	0.157	0.172	0.187	0.203	0.220	0.237	0.254
15	0.000	0.009	0.020	0.030	0.041	0.052	0.063	0.074	0.086	0.097	0.109	0.121	0.134	0.146	0.160	0.173	0.187	0.200	0.215	0.230
16	0.000	-0.006	0.003	0.006	0.009	0.011	0.015	0.020	0.025	0.031	0.037	0.044	0.052	0.060	0.069	0.078	0.088	0.099	0.110	0.122
17	0.000	0.008	0.017	0.027	0.037	0.047	0.056	0.066	0.077	0.086	0.096	0.106	0.117	0.128	0.139	0.151	0.164	0.177	0.191	0.205
18	0.000	0.005	0.015	0.027	0.040	0.053	0.065	0.078	0.092	0.107	0.123	0.138	0.153	0.169	0.183	0.198	0.212	0.227	0.243	0.258
19	0.000	0.006	0.017	0.031	0.048	0.067	0.086	0.105	0.122	0.138	0.153	0.168	0.182	0.197	0.211	0.225	0.240	0.254	0.269	0.284
20	0.000	0.006	0.014	0.022	0.032	0.041	0.051	0.063	0.073	0.084	0.097	0.108	0.121	0.134	0.149	0.163	0.178	0.194	0.211	0.228
21	0.000	0.006	0.010	0.015	0.019	0.023	0.027	0.031	0.036	0.040	0.045	0.051	0.058	0.065	0.074	0.084	0.094	0.106	0.119	0.132
22	0.000	0.007	0.016	0.025	0.034	0.045	0.054	0.064	0.074	0.086	0.097	0.108	0.119	0.132	0.145	0.157	0.171	0.184	0.199	0.213
23	0.000	0.005	0.012	0.020	0.029	0.038	0.049	0.060	0.071	0.083	0.095	0.107	0.119	0.131	0.143	0.154	0.166	0.177	0.190	0.202
24	0.000	0.007	0.017	0.029	0.041	0.054	0.067	0.080	0.094	0.108	0.122	0.137	0.152	0.167	0.183	0.200	0.217	0.235	0.253	0.271

APPENDIX E

	Input titration data																			
	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
	mL of NaOH solution added																			
	5.000	5.250	5.500	5.750	6.000	6.250	6.500	6.750	7.000	7.250	7.500	7.750	8.000	8.250	8.500	8.750	9.000	9.250	9.500	9.750
Sample#	Change in pH (normalised pH values)																			
1	0.189	0.202	0.215	0.228	0.242	0.256	0.271	0.286	0.301	0.317	0.334	0.352	0.370	0.389	0.409	0.430	0.452	0.475	0.499	0.525
2	0.197	0.210	0.225	0.240	0.255	0.271	0.287	0.304	0.322	0.340	0.359	0.379	0.400	0.422	0.445	0.469	0.494	0.522	0.550	0.580
3	0.228	0.243	0.260	0.277	0.295	0.313	0.332	0.351	0.371	0.393	0.415	0.439	0.464	0.491	0.519	0.548	0.580	0.615	0.652	0.692
4	0.191	0.204	0.217	0.231	0.245	0.259	0.273	0.288	0.304	0.320	0.337	0.355	0.373	0.392	0.412	0.433	0.455	0.478	0.502	0.527
5	0.193	0.205	0.219	0.234	0.250	0.268	0.286	0.304	0.324	0.345	0.366	0.386	0.407	0.429	0.451	0.474	0.498	0.523	0.549	0.576
6	0.211	0.226	0.242	0.258	0.275	0.292	0.310	0.329	0.348	0.369	0.390	0.412	0.436	0.461	0.487	0.516	0.546	0.578	0.613	0.651
7	0.213	0.229	0.245	0.263	0.282	0.302	0.323	0.344	0.367	0.391	0.417	0.444	0.473	0.504	0.537	0.572	0.611	0.653	0.700	0.753
8	0.171	0.183	0.195	0.207	0.220	0.234	0.248	0.263	0.278	0.294	0.310	0.328	0.347	0.366	0.387	0.408	0.432	0.456	0.483	0.510
9	0.219	0.234	0.248	0.264	0.282	0.299	0.316	0.334	0.352	0.372	0.392	0.414	0.437	0.461	0.487	0.514	0.543	0.574	0.608	0.643
10	0.240	0.255	0.270	0.287	0.305	0.322	0.341	0.360	0.380	0.402	0.425	0.448	0.474	0.502	0.531	0.563	0.598	0.636	0.678	0.724
11	0.225	0.240	0.254	0.270	0.286	0.301	0.319	0.335	0.353	0.372	0.391	0.411	0.431	0.454	0.477	0.502	0.527	0.554	0.583	0.613
12	0.240	0.255	0.271	0.287	0.305	0.322	0.340	0.359	0.378	0.399	0.420	0.442	0.465	0.490	0.516	0.544	0.573	0.605	0.638	0.675
13	0.231	0.244	0.261	0.278	0.296	0.314	0.334	0.354	0.376	0.398	0.421	0.446	0.472	0.500	0.531	0.562	0.598	0.636	0.678	0.723
14	0.272	0.292	0.311	0.331	0.354	0.376	0.400	0.425	0.451	0.479	0.509	0.542	0.576	0.614	0.656	0.700	0.751	0.807	0.873	0.948
15	0.245	0.260	0.276	0.293	0.311	0.328	0.347	0.365	0.385	0.406	0.427	0.450	0.473	0.498	0.525	0.553	0.583	0.614	0.648	0.684
16	0.134	0.147	0.160	0.174	0.189	0.205	0.221	0.238	0.256	0.275	0.296	0.319	0.343	0.369	0.396	0.426	0.458	0.493	0.530	0.572
17	0.221	0.237	0.253	0.272	0.291	0.311	0.332	0.354	0.377	0.401	0.428	0.455	0.485	0.518	0.553	0.592	0.634	0.683	0.737	0.800
18	0.272	0.288	0.303	0.318	0.334	0.351	0.367	0.385	0.403	0.422	0.441	0.462	0.483	0.506	0.530	0.555	0.582	0.611	0.643	0.676
19	0.299	0.315	0.331	0.348	0.365	0.383	0.401	0.420	0.440	0.461	0.483	0.506	0.530	0.557	0.585	0.614	0.647	0.682	0.720	0.762
20	0.245	0.262	0.281	0.300	0.320	0.342	0.363	0.387	0.411	0.436	0.463	0.490	0.520	0.552	0.586	0.623	0.663	0.709	0.759	0.816
21	0.147	0.163	0.179	0.197	0.217	0.238	0.260	0.284	0.310	0.338	0.369	0.403	0.440	0.482	0.530	0.583	0.646	0.721	0.813	0.930
22	0.228	0.244	0.260	0.277	0.294	0.313	0.332	0.352	0.373	0.394	0.418	0.442	0.468	0.496	0.526	0.557	0.592	0.629	0.669	0.714
23	0.215	0.229	0.243	0.258	0.274	0.291	0.309	0.328	0.348	0.370	0.393	0.418	0.445	0.475	0.507	0.542	0.581	0.624	0.672	0.728
24	0.291	0.310	0.331	0.353	0.377	0.401	0.427	0.454	0.484	0.515	0.549	0.585	0.625	0.669	0.717	0.771	0.832	0.903	0.987	1.090

APPENDIX E

	Input titration data																			
	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
	mL of NaOH solution added																			
	10.000	10.250	10.500	10.750	11.000	11.250	11.500	11.750	12.000	12.250	12.500	12.750	13.000	13.250	13.500	13.750	14.000	14.250	14.500	14.750
Sample#	Change in pH (normalised pH values)																			
1	0.552	0.580	0.610	0.644	0.678	0.716	0.757	0.802	0.853	0.910	0.975	1.052	1.146	1.265	1.429	1.692	2.408	4.121	4.500	4.708
2	0.614	0.649	0.687	0.728	0.774	0.824	0.880	0.944	1.020	1.111	1.224	1.379	1.622	2.198	4.023	4.450	4.668	4.813	4.924	5.015
3	0.736	0.785	0.840	0.901	0.972	1.057	1.159	1.293	1.489	1.843	3.495	4.298	4.580	4.754	4.878	4.976	5.057	5.125	5.184	5.238
4	0.554	0.582	0.612	0.644	0.678	0.715	0.754	0.797	0.846	0.901	0.964	1.038	1.131	1.249	1.412	1.682	2.483	4.144	4.510	4.717
5	0.606	0.638	0.672	0.709	0.750	0.795	0.845	0.903	0.971	1.053	1.154	1.289	1.492	1.888	3.708	4.341	4.606	4.772	4.894	4.992
6	0.691	0.737	0.787	0.842	0.906	0.980	1.068	1.178	1.326	1.550	2.015	3.892	4.415	4.654	4.812	4.930	5.024	5.102	5.167	5.226
7	0.814	0.885	0.970	1.074	1.215	1.423	1.832	3.670	4.288	4.548	4.716	4.841	4.941	5.024	5.093	5.155	5.208	5.256	5.300	5.341
8	0.541	0.574	0.610	0.649	0.692	0.740	0.794	0.855	0.926	1.012	1.117	1.256	1.464	1.862	3.696	4.359	4.630	4.800	4.926	5.028
9	0.682	0.725	0.773	0.824	0.884	0.952	1.032	1.129	1.256	1.435	1.738	2.926	4.207	4.520	4.705	4.836	4.938	5.020	5.089	5.150
10	0.777	0.838	0.909	0.994	1.100	1.243	1.458	1.900	3.785	4.301	4.539	4.696	4.814	4.908	4.985	5.051	5.109	5.160	5.206	5.249
11	0.646	0.680	0.718	0.759	0.803	0.853	0.907	0.970	1.042	1.129	1.237	1.380	1.596	2.030	3.887	4.439	4.685	4.843	4.959	5.053
12	0.714	0.756	0.804	0.856	0.915	0.982	1.062	1.157	1.281	1.452	1.732	2.637	4.219	4.561	4.756	4.892	4.997	5.081	5.152	5.215
13	0.775	0.833	0.900	0.978	1.072	1.192	1.357	1.622	2.410	4.097	4.453	4.657	4.798	4.905	4.992	5.065	5.128	5.183	5.232	5.277
14	1.039	1.155	1.309	1.545	2.083	3.969	4.405	4.629	4.780	4.893	4.982	5.057	5.123	5.181	5.232	5.279	5.321	5.360	5.396	5.429
15	0.724	0.767	0.815	0.868	0.927	0.996	1.075	1.172	1.298	1.474	1.764	2.787	4.261	4.589	4.779	4.914	5.018	5.101	5.172	5.234
16	0.618	0.672	0.732	0.803	0.889	0.999	1.148	1.380	1.948	3.816	4.249	4.473	4.628	4.746	4.840	4.919	4.988	5.047	5.100	5.148
17	0.875	0.967	1.084	1.246	1.512	2.344	4.027	4.387	4.594	4.738	4.847	4.937	5.013	5.079	5.136	5.188	5.235	5.277	5.316	5.352
18	0.713	0.754	0.798	0.848	0.906	0.972	1.049	1.145	1.272	1.453	1.771	3.322	4.316	4.613	4.794	4.924	5.025	5.108	5.179	5.240
19	0.809	0.862	0.923	0.993	1.079	1.186	1.329	1.546	2.023	3.936	4.437	4.675	4.834	4.952	5.045	5.124	5.191	5.249	5.301	5.347
20	0.884	0.965	1.065	1.197	1.391	1.752	3.540	4.258	4.533	4.709	4.835	4.934	5.018	5.088	5.150	5.204	5.253	5.297	5.337	5.375
21	1.097	1.374	2.346	3.942	4.290	4.491	4.631	4.741	4.831	4.907	4.974	5.032	5.086	5.133	5.178	5.218	5.256	5.291	5.323	5.354
22	0.763	0.819	0.883	0.956	1.044	1.155	1.301	1.521	1.989	3.910	4.395	4.629	4.786	4.901	4.992	5.070	5.136	5.193	5.244	5.290
23	0.793	0.872	0.968	1.093	1.274	1.595	3.177	4.149	4.453	4.637	4.771	4.876	4.963	5.037	5.102	5.159	5.210	5.256	5.298	5.337
24	1.226	1.423	1.795	3.610	4.313	4.581	4.749	4.872	4.969	5.050	5.118	5.178	5.232	5.281	5.325	5.366	5.403	5.437	5.469	5.500

APPENDIX E

	Input titration data																			
	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
	mL of NaOH solution added																			
	15.000	15.250	15.500	15.750	16.000	16.250	16.500	16.750	17.000	17.250	17.500	17.750	18.000	18.250	18.500	18.750	19.000	19.250	19.500	19.750
Sample#	Change in pH (normalised pH values)																			
1	4.849	4.955	5.041	5.114	5.176	5.231	5.280	5.325	5.365	5.403	5.438	5.471	5.502	5.531	5.559	5.587	5.611	5.635	5.658	5.681
2	5.090	5.154	5.211	5.261	5.306	5.347	5.384	5.420	5.452	5.483	5.512	5.541	5.567	5.593	5.617	5.641	5.663	5.684	5.705	5.725
3	5.286	5.329	5.368	5.405	5.439	5.470	5.500	5.528	5.555	5.581	5.606	5.629	5.652	5.674	5.696	5.717	5.736	5.756	5.774	5.793
4	4.861	4.971	5.061	5.137	5.202	5.259	5.310	5.357	5.399	5.438	5.475	5.510	5.542	5.572	5.602	5.629	5.655	5.680	5.704	5.727
5	5.073	5.141	5.199	5.253	5.300	5.342	5.381	5.417	5.451	5.482	5.513	5.541	5.567	5.593	5.618	5.641	5.663	5.685	5.706	5.727
6	5.278	5.324	5.367	5.405	5.441	5.474	5.505	5.533	5.560	5.586	5.610	5.633	5.655	5.676	5.697	5.717	5.737	5.756	5.774	5.792
7	5.378	5.412	5.444	5.474	5.503	5.529	5.554	5.579	5.602	5.624	5.646	5.667	5.687	5.707	5.727	5.746	5.765	5.782	5.800	5.817
8	5.112	5.184	5.245	5.301	5.350	5.395	5.436	5.474	5.510	5.542	5.574	5.604	5.632	5.659	5.685	5.709	5.733	5.755	5.778	5.799
9	5.204	5.252	5.296	5.336	5.373	5.407	5.439	5.468	5.497	5.524	5.550	5.575	5.599	5.622	5.644	5.666	5.686	5.706	5.725	5.745
10	5.288	5.324	5.357	5.389	5.418	5.446	5.472	5.497	5.522	5.545	5.567	5.589	5.610	5.631	5.651	5.670	5.689	5.707	5.725	5.743
11	5.131	5.197	5.254	5.306	5.353	5.395	5.433	5.469	5.503	5.535	5.565	5.594	5.620	5.646	5.671	5.696	5.718	5.741	5.763	5.783
12	5.270	5.319	5.363	5.404	5.442	5.476	5.509	5.540	5.569	5.596	5.623	5.648	5.672	5.696	5.719	5.741	5.762	5.782	5.802	5.822
13	5.319	5.356	5.390	5.423	5.454	5.482	5.510	5.535	5.560	5.583	5.606	5.629	5.650	5.671	5.691	5.712	5.730	5.748	5.767	5.785
14	5.461	5.491	5.519	5.546	5.571	5.595	5.619	5.641	5.662	5.683	5.704	5.724	5.743	5.762	5.781	5.799	5.816	5.834	5.850	5.867
15	5.289	5.337	5.382	5.422	5.460	5.494	5.527	5.557	5.587	5.614	5.640	5.666	5.690	5.714	5.737	5.759	5.780	5.800	5.820	5.840
16	5.193	5.238	5.282	5.319	5.351	5.380	5.406	5.433	5.458	5.482	5.506	5.529	5.551	5.572	5.594	5.614	5.634	5.653	5.672	5.690
17	5.386	5.417	5.447	5.474	5.501	5.526	5.550	5.573	5.595	5.617	5.638	5.658	5.678	5.697	5.716	5.735	5.752	5.770	5.788	5.805
18	5.295	5.344	5.388	5.429	5.466	5.501	5.533	5.563	5.592	5.619	5.645	5.670	5.694	5.717	5.740	5.762	5.782	5.802	5.823	5.842
19	5.390	5.428	5.464	5.498	5.530	5.559	5.587	5.613	5.639	5.663	5.687	5.710	5.732	5.753	5.774	5.795	5.814	5.834	5.852	5.871
20	5.411	5.443	5.474	5.502	5.529	5.555	5.580	5.603	5.626	5.648	5.668	5.690	5.709	5.729	5.748	5.767	5.785	5.803	5.821	5.838
21	5.384	5.411	5.438	5.463	5.487	5.511	5.533	5.555	5.575	5.596	5.616	5.636	5.655	5.674	5.693	5.710	5.728	5.746	5.763	5.781
22	5.333	5.372	5.407	5.441	5.472	5.502	5.530	5.557	5.582	5.607	5.631	5.654	5.676	5.697	5.719	5.739	5.758	5.778	5.797	5.815
23	5.373	5.407	5.439	5.468	5.497	5.524	5.549	5.575	5.598	5.621	5.643	5.665	5.686	5.707	5.727	5.747	5.765	5.784	5.802	5.820
24	5.529	5.557	5.583	5.608	5.633	5.655	5.678	5.699	5.720	5.741	5.761	5.781	5.800	5.819	5.838	5.856	5.874	5.891	5.909	5.926

APPENDIX E

	Input titration data																			
	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
	mL of NaOH solution added																			
	20.000	20.250	20.500	20.750	21.000	21.250	21.500	21.750	22.000	22.250	22.500	22.750	23.000	23.250	23.500	23.750	24.000	24.250	24.500	24.750
Sample#	Change in pH (normalised pH values)																			
1	5.702	5.723	5.743	5.763	5.781	5.799	5.817	5.834	5.851	5.868	5.884	5.900	5.916	5.932	5.948	5.963	5.978	5.993	6.008	6.022
2	5.745	5.763	5.782	5.799	5.817	5.834	5.850	5.866	5.882	5.898	5.913	5.928	5.943	5.959	5.973	5.988	6.003	6.018	6.032	6.046
3	5.810	5.828	5.845	5.861	5.877	5.893	5.909	5.924	5.939	5.955	5.970	5.984	5.999	6.014	6.028	6.043	6.057	6.071	6.086	6.100
4	5.748	5.769	5.789	5.808	5.827	5.845	5.862	5.879	5.896	5.912	5.928	5.944	5.960	5.975	5.991	6.006	6.021	6.036	6.050	6.065
5	5.746	5.765	5.784	5.802	5.820	5.837	5.854	5.869	5.886	5.902	5.918	5.934	5.949	5.965	5.980	5.996	6.010	6.025	6.040	6.054
6	5.810	5.828	5.844	5.860	5.877	5.893	5.909	5.924	5.939	5.955	5.970	5.985	6.000	6.015	6.030	6.044	6.059	6.075	6.088	6.103
7	5.834	5.851	5.867	5.883	5.898	5.914	5.929	5.944	5.959	5.974	5.989	6.004	6.018	6.033	6.048	6.063	6.078	6.099	6.116	6.134
8	5.819	5.839	5.859	5.877	5.895	5.913	5.931	5.947	5.964	5.981	5.997	6.013	6.029	6.045	6.062	6.077	6.093	6.108	6.123	6.138
9	5.763	5.781	5.798	5.816	5.833	5.849	5.865	5.881	5.897	5.912	5.928	5.943	5.958	5.973	5.988	6.004	6.019	6.034	6.048	6.063
10	5.760	5.777	5.794	5.810	5.826	5.842	5.857	5.872	5.887	5.902	5.917	5.933	5.948	5.962	5.977	5.992	6.008	6.023	6.038	6.052
11	5.803	5.824	5.842	5.861	5.878	5.896	5.913	5.930	5.947	5.963	5.980	5.997	6.012	6.028	6.044	6.060	6.075	6.091	6.107	6.122
12	5.840	5.859	5.877	5.895	5.911	5.929	5.944	5.961	5.977	5.994	6.009	6.025	6.041	6.057	6.072	6.088	6.103	6.119	6.134	6.149
13	5.802	5.819	5.836	5.852	5.868	5.884	5.900	5.915	5.930	5.945	5.961	5.976	5.991	6.006	6.021	6.036	6.052	6.067	6.082	6.097
14	5.883	5.899	5.914	5.929	5.943	5.958	5.972	5.987	6.000	6.014	6.028	6.041	6.055	6.069	6.084	6.098	6.113	6.128	6.143	6.158
15	5.859	5.877	5.896	5.913	5.931	5.948	5.964	5.981	5.997	6.013	6.029	6.045	6.061	6.078	6.093	6.109	6.125	6.141	6.156	6.172
16	5.708	5.726	5.744	5.760	5.777	5.794	5.810	5.826	5.842	5.858	5.874	5.889	5.905	5.921	5.937	5.953	5.969	5.985	6.001	6.017
17	5.822	5.838	5.854	5.870	5.886	5.902	5.917	5.933	5.948	5.964	5.980	5.995	6.010	6.026	6.042	6.058	6.074	6.090	6.107	6.123
18	5.861	5.879	5.898	5.915	5.933	5.950	5.966	5.983	6.000	6.016	6.032	6.048	6.065	6.081	6.097	6.113	6.129	6.146	6.162	6.178
19	5.889	5.907	5.925	5.941	5.958	5.975	5.991	6.007	6.023	6.039	6.056	6.072	6.088	6.104	6.120	6.137	6.153	6.169	6.186	6.202
20	5.855	5.872	5.889	5.906	5.922	5.938	5.954	5.969	5.985	6.001	6.017	6.033	6.049	6.065	6.082	6.098	6.115	6.131	6.148	6.165
21	5.797	5.813	5.830	5.846	5.863	5.879	5.895	5.910	5.926	5.943	5.959	5.975	5.992	6.009	6.026	6.043	6.061	6.078	6.096	6.115
22	5.834	5.851	5.869	5.887	5.903	5.920	5.937	5.953	5.970	5.986	6.003	6.019	6.035	6.052	6.068	6.085	6.102	6.119	6.136	6.153
23	5.837	5.855	5.871	5.888	5.905	5.921	5.937	5.953	5.970	5.986	6.002	6.018	6.035	6.052	6.069	6.086	6.103	6.120	6.138	6.156
24	5.943	5.960	5.977	5.994	6.010	6.027	6.043	6.059	6.076	6.092	6.109	6.126	6.143	6.161	6.179	6.196	6.214	6.233	6.251	6.270

APPENDIX E

	Input titration data																			
	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
	mL of NaOH solution added																			
	25.000	25.250	25.500	25.750	26.000	26.250	26.500	26.750	27.000	27.250	27.500	27.750	28.000	28.250	28.500	28.750	29.000	29.250	29.500	29.750
Sample#	Change in pH (normalised pH values)																			
1	6.037	6.051	6.066	6.079	6.094	6.108	6.122	6.136	6.150	6.164	6.179	6.193	6.208	6.222	6.237	6.252	6.268	6.283	6.298	6.315
2	6.061	6.075	6.089	6.103	6.118	6.132	6.146	6.160	6.175	6.189	6.204	6.219	6.234	6.250	6.265	6.281	6.297	6.313	6.330	6.347
3	6.114	6.129	6.143	6.157	6.172	6.186	6.200	6.215	6.229	6.244	6.259	6.275	6.291	6.307	6.324	6.341	6.358	6.376	6.394	6.414
4	6.079	6.094	6.108	6.122	6.136	6.151	6.165	6.186	6.204	6.223	6.241	6.258	6.275	6.291	6.306	6.322	6.338	6.354	6.370	6.387
5	6.069	6.084	6.098	6.113	6.127	6.142	6.156	6.171	6.185	6.200	6.215	6.230	6.246	6.263	6.278	6.295	6.312	6.329	6.347	6.364
6	6.118	6.132	6.147	6.162	6.177	6.191	6.206	6.221	6.236	6.251	6.267	6.283	6.299	6.316	6.333	6.351	6.369	6.388	6.408	6.427
7	6.151	6.167	6.184	6.200	6.216	6.232	6.247	6.263	6.279	6.296	6.313	6.331	6.349	6.368	6.388	6.407	6.427	6.449	6.471	6.495
8	6.154	6.169	6.184	6.199	6.214	6.229	6.245	6.260	6.275	6.291	6.307	6.323	6.340	6.356	6.373	6.391	6.408	6.427	6.445	6.465
9	6.077	6.093	6.107	6.122	6.137	6.153	6.167	6.183	6.198	6.214	6.230	6.247	6.264	6.281	6.299	6.317	6.336	6.356	6.376	6.397
10	6.068	6.083	6.098	6.114	6.130	6.145	6.162	6.178	6.194	6.211	6.229	6.247	6.266	6.285	6.306	6.326	6.348	6.370	6.395	6.421
11	6.138	6.153	6.168	6.183	6.199	6.214	6.229	6.245	6.261	6.277	6.294	6.310	6.328	6.345	6.363	6.382	6.400	6.419	6.441	6.461
12	6.165	6.180	6.196	6.211	6.227	6.243	6.259	6.275	6.292	6.309	6.326	6.343	6.362	6.381	6.400	6.420	6.441	6.462	6.485	6.509
13	6.112	6.128	6.144	6.160	6.175	6.192	6.208	6.225	6.242	6.260	6.277	6.296	6.316	6.336	6.357	6.380	6.402	6.427	6.453	6.481
14	6.173	6.189	6.206	6.222	6.239	6.256	6.274	6.292	6.311	6.330	6.352	6.373	6.396	6.420	6.446	6.474	6.505	6.536	6.571	6.612
15	6.188	6.204	6.220	6.236	6.253	6.269	6.286	6.303	6.320	6.338	6.356	6.375	6.395	6.415	6.436	6.458	6.481	6.505	6.530	6.557
16	6.033	6.050	6.066	6.083	6.100	6.117	6.134	6.152	6.171	6.190	6.210	6.230	6.251	6.274	6.297	6.322	6.349	6.377	6.408	6.442
17	6.140	6.157	6.175	6.192	6.210	6.229	6.248	6.267	6.288	6.308	6.331	6.354	6.379	6.406	6.435	6.466	6.499	6.536	6.578	6.626
18	6.195	6.212	6.228	6.245	6.262	6.279	6.297	6.315	6.333	6.352	6.372	6.392	6.413	6.435	6.459	6.484	6.510	6.537	6.567	6.599
19	6.219	6.236	6.253	6.270	6.289	6.307	6.325	6.344	6.364	6.385	6.407	6.428	6.452	6.477	6.503	6.532	6.562	6.595	6.631	6.672
20	6.183	6.201	6.218	6.237	6.256	6.276	6.296	6.316	6.338	6.361	6.385	6.411	6.438	6.468	6.500	6.535	6.574	6.618	6.670	6.731
21	6.134	6.154	6.174	6.195	6.216	6.240	6.263	6.288	6.315	6.343	6.375	6.409	6.447	6.489	6.538	6.597	6.669	6.761	6.897	7.145
22	6.171	6.189	6.207	6.225	6.244	6.264	6.283	6.304	6.326	6.348	6.372	6.397	6.424	6.452	6.483	6.516	6.554	6.595	6.642	6.698
23	6.175	6.193	6.213	6.232	6.253	6.274	6.296	6.319	6.343	6.369	6.396	6.426	6.458	6.494	6.533	6.578	6.630	6.691	6.769	6.874
24	6.290	6.310	6.331	6.352	6.376	6.399	6.425	6.452	6.482	6.514	6.550	6.590	6.636	6.689	6.753	6.834	6.944	7.115	7.504	9.496

APPENDIX E

	Input titration data																			
	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140
	mL of NaOH solution added																			
	30.000	30.250	30.500	30.750	31.000	31.250	31.500	31.750	32.000	32.250	32.500	32.750	33.000	33.250	33.500	33.750	34.000	34.250	34.500	34.750
Sample#	Change in pH (normalised pH values)																			
1	6.331	6.347	6.364	6.383	6.400	6.418	6.437	6.457	6.477	6.499	6.522	6.547	6.573	6.601	6.632	6.665	6.702	6.744	6.792	6.849
2	6.364	6.382	6.401	6.420	6.439	6.460	6.481	6.504	6.528	6.553	6.581	6.611	6.644	6.681	6.722	6.769	6.825	6.892	6.980	7.102
3	6.434	6.455	6.476	6.499	6.522	6.547	6.574	6.603	6.634	6.669	6.708	6.752	6.803	6.865	6.943	7.047	7.203	7.528	9.339	10.535
4	6.405	6.423	6.441	6.461	6.480	6.500	6.521	6.544	6.567	6.593	6.620	6.649	6.680	6.715	6.754	6.798	6.848	6.909	6.984	7.083
5	6.382	6.402	6.422	6.443	6.464	6.486	6.510	6.535	6.562	6.592	6.623	6.659	6.698	6.742	6.796	6.859	6.938	7.046	7.214	7.583
6	6.448	6.470	6.492	6.516	6.541	6.568	6.597	6.629	6.664	6.702	6.747	6.798	6.860	6.938	7.045	7.208	7.549	9.411	10.576	10.888
7	6.522	6.548	6.578	6.609	6.644	6.682	6.725	6.775	6.834	6.908	7.007	7.153	7.432	8.871	10.472	10.837	11.027	11.156	11.253	11.331
8	6.486	6.506	6.528	6.552	6.575	6.601	6.628	6.657	6.689	6.723	6.763	6.807	6.858	6.919	6.997	7.100	7.253	7.560	9.218	10.585
9	6.420	6.443	6.467	6.494	6.522	6.552	6.585	6.622	6.663	6.710	6.767	6.837	6.927	7.058	7.293	8.202	10.237	10.711	10.936	11.080
10	6.448	6.477	6.509	6.545	6.584	6.628	6.679	6.741	6.818	6.922	7.085	7.436	9.336	10.455	10.764	10.936	11.053	11.143	11.216	11.276
11	6.483	6.506	6.530	6.556	6.583	6.613	6.644	6.680	6.718	6.762	6.814	6.876	6.953	7.058	7.223	7.573	9.441	10.589	10.903	11.079
12	6.534	6.561	6.589	6.620	6.654	6.690	6.732	6.779	6.835	6.903	6.992	7.120	7.339	8.096	10.267	10.759	10.980	11.121	11.224	11.305
13	6.512	6.544	6.581	6.622	6.668	6.722	6.788	6.873	6.989	7.184	7.741	9.953	10.599	10.852	11.006	11.114	11.197	11.265	11.322	11.371
14	6.658	6.710	6.775	6.857	6.968	7.143	7.558	9.643	10.528	10.810	10.974	11.088	11.173	11.242	11.300	11.349	11.392	11.428	11.460	11.490
15	6.586	6.618	6.652	6.690	6.732	6.781	6.839	6.910	7.002	7.136	7.384	8.450	10.359	10.795	11.007	11.142	11.241	11.319	11.384	11.439
16	6.479	6.520	6.567	6.623	6.689	6.766	6.879	7.074	7.624	9.742	10.480	10.741	10.896	11.007	11.093	11.161	11.217	11.266	11.308	11.344
17	6.682	6.751	6.839	6.966	7.179	7.859	10.043	10.591	10.822	10.965	11.069	11.149	11.213	11.267	11.315	11.355	11.390	11.421	11.449	11.474
18	6.635	6.674	6.718	6.769	6.829	6.904	7.005	7.155	7.449	8.960	10.472	10.826	11.010	11.134	11.226	11.298	11.357	11.407	11.451	11.489
19	6.719	6.773	6.838	6.922	7.037	7.220	7.682	9.849	10.617	10.882	11.041	11.150	11.233	11.300	11.357	11.404	11.445	11.481	11.513	11.540
20	6.809	6.911	7.068	7.394	8.986	10.396	10.755	10.945	11.072	11.166	11.242	11.304	11.356	11.402	11.441	11.477	11.508	11.536	11.562	11.585
21	8.196	10.130	10.579	10.791	10.925	11.023	11.101	11.165	11.218	11.265	11.306	11.343	11.375	11.404	11.432	11.457	11.480	11.502	11.522	11.541
22	6.766	6.852	6.973	7.176	7.758	9.897	10.597	10.855	11.010	11.121	11.208	11.278	11.337	11.389	11.434	11.474	11.509	11.541	11.570	11.597
23	7.033	7.362	9.044	10.390	10.725	10.905	11.026	11.117	11.189	11.248	11.299	11.343	11.381	11.415	11.445	11.473	11.497	11.520	11.541	11.560
24	10.525	10.815	10.982	11.096	11.182	11.250	11.308	11.357	11.399	11.436	11.470	11.500	11.527	11.553	11.576	11.598	11.618	11.638	11.657	11.675

APPENDIX E

	Input titration data																					Output	
	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161		
	mL of NaOH solution added																					Total Chromium (g/L)	Chromium from CrO3
	35.000	35.250	35.500	35.750	36.000	36.250	36.500	36.750	37.000	37.250	37.500	37.750	38.000	38.250	38.500	38.750	39.000	39.250	39.500	39.750	40.000		
Sample#	Change in pH (normalised pH values)																						
1	6.918	7.008	7.138	7.360	8.119	10.234	10.733	10.959	11.102	11.209	11.292	11.359	11.417	11.468	11.512	11.551	11.587	11.619	11.648	11.675	11.700	559.000	362.860
2	7.308	7.938	10.154	10.702	10.937	11.084	11.190	11.272	11.339	11.397	11.446	11.489	11.528	11.563	11.594	11.622	11.649	11.673	11.695	11.714	11.733	559.000	344.000
3	10.850	11.026	11.146	11.235	11.307	11.367	11.418	11.462	11.501	11.536	11.568	11.597	11.624	11.649	11.672	11.695	11.716	11.737	11.757	11.776	11.795	559.000	321.128
4	7.231	7.522	9.032	10.514	10.868	11.057	11.183	11.278	11.354	11.419	11.474	11.522	11.565	11.603	11.638	11.670	11.699	11.726	11.750	11.773	11.794	546.000	362.471
5	9.505	10.580	10.889	11.063	11.182	11.272	11.344	11.404	11.455	11.500	11.539	11.574	11.606	11.634	11.660	11.682	11.703	11.722	11.740	11.756	11.770	546.000	345.633
6	11.064	11.184	11.275	11.347	11.406	11.457	11.501	11.540	11.574	11.605	11.633	11.658	11.681	11.702	11.722	11.739	11.756	11.772	11.786	11.800	11.813	546.000	325.394
7	11.395	11.451	11.499	11.541	11.578	11.613	11.643	11.672	11.698	11.723	11.746	11.767	11.787	11.806	11.824	11.841	11.857	11.872	11.887	11.900	11.913	546.000	300.607
8	10.922	11.106	11.230	11.322	11.396	11.457	11.510	11.555	11.597	11.634	11.668	11.698	11.726	11.753	11.777	11.799	11.820	11.840	11.858	11.875	11.892	533.000	345.982
9	11.184	11.267	11.336	11.393	11.443	11.487	11.526	11.561	11.593	11.623	11.651	11.676	11.700	11.723	11.744	11.763	11.781	11.798	11.815	11.831	11.846	533.000	328.000
10	11.328	11.373	11.414	11.450	11.482	11.512	11.539	11.563	11.586	11.608	11.628	11.647	11.665	11.682	11.699	11.714	11.729	11.743	11.757	11.770	11.782	533.000	306.191
11	11.201	11.294	11.368	11.429	11.482	11.529	11.570	11.607	11.640	11.670	11.698	11.723	11.748	11.771	11.791	11.811	11.829	11.847	11.862	11.878	11.893	520.000	345.210
12	11.370	11.427	11.475	11.517	11.554	11.589	11.619	11.647	11.672	11.696	11.718	11.738	11.757	11.775	11.792	11.807	11.822	11.836	11.849	11.862	11.873	520.000	329.174
13	11.414	11.453	11.488	11.519	11.547	11.573	11.597	11.619	11.639	11.659	11.677	11.694	11.710	11.725	11.740	11.754	11.767	11.779	11.790	11.801	11.812	520.000	309.899
14	11.516	11.540	11.562	11.582	11.600	11.618	11.633	11.649	11.662	11.675	11.687	11.698	11.708	11.719	11.729	11.739	11.748	11.758	11.767	11.776	11.784	520.000	286.292
15	11.487	11.529	11.567	11.600	11.630	11.658	11.683	11.707	11.728	11.749	11.768	11.786	11.803	11.819	11.835	11.849	11.862	11.875	11.887	11.899	11.910	507.000	329.105
16	11.378	11.408	11.435	11.461	11.484	11.506	11.527	11.546	11.564	11.581	11.598	11.613	11.629	11.643	11.656	11.669	11.682	11.694	11.706	11.717	11.728	507.000	312.000
17	11.497	11.519	11.539	11.557	11.573	11.589	11.604	11.618	11.632	11.645	11.657	11.668	11.679	11.690	11.700	11.710	11.720	11.729	11.739	11.747	11.756	507.000	291.255
18	11.521	11.551	11.577	11.601	11.622	11.642	11.661	11.678	11.695	11.711	11.727	11.742	11.756	11.770	11.783	11.795	11.808	11.819	11.830	11.841	11.851	494.000	327.950
19	11.566	11.589	11.611	11.631	11.649	11.667	11.684	11.700	11.715	11.730	11.744	11.757	11.769	11.782	11.793	11.804	11.815	11.825	11.834	11.844	11.853	494.000	312.716
20	11.605	11.625	11.642	11.657	11.671	11.684	11.696	11.708	11.719	11.729	11.739	11.749	11.758	11.768	11.777	11.786	11.795	11.803	11.811	11.820	11.828	494.000	294.404
21	11.559	11.576	11.593	11.608	11.623	11.637	11.651	11.664	11.676	11.688	11.700	11.711	11.722	11.733	11.743	11.752	11.762	11.771	11.779	11.787	11.795	494.000	271.978
22	11.622	11.645	11.666	11.686	11.705	11.722	11.738	11.754	11.769	11.783	11.796	11.808	11.821	11.832	11.843	11.854	11.864	11.874	11.883	11.892	11.901	481.000	312.228
23	11.578	11.593	11.608	11.622	11.635	11.647	11.659	11.669	11.679	11.688	11.697	11.706	11.714	11.722	11.730	11.737	11.745	11.752	11.759	11.766	11.773	481.000	296.000
24	11.692	11.708	11.722	11.736	11.749	11.761	11.773	11.784	11.795	11.805	11.815	11.824	11.834	11.842	11.851	11.859	11.867	11.874	11.881	11.888	11.895	481.000	276.319