ON-LINE PROCESS MONITORING

IN ELECTROLYTIC

MANUFACTURING OF CHROMIC ACID

by

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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Chemistry at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

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ABSTRACT

Suitable methods and techniques for the analysis of the chromic acid and sodium dichromate content in concentrated liquors from the electrolytic production of chromic acid were investigated.

Experimental results showed that Artificial Neural Network technology applied to highly diluted hexavalent chromium solutions, which are known to have been prepared from chromic acid and sodium dichromate, do not yield useable results for quantification purposes.

Combining ion selective electrode measurements and ultra-violet – visible spectrophotometric techniques to highly diluted hexavalent chromium solutions, prepared from chromic acid and sodium dichromate, yields errors of about 2.3 % for hexavalent chromium and about 2.8 % for sodium determinations versus a standard titrimetric method.

Tests to prove the suitability of the standard titrimetric acid – base titration technique confirmed an accuracy of 0.6 % for a known chromic acid content and 0.7 % for titrations based on a known sodium dichromate content for liquors highly concentrated in hexavalent chromium.

A simple on-line analytical instrument was developed based on the titrimetric acid – base titration technique. The on-line instrument evidenced average errors of about 1.9 % for the chromic acid content and about 2.6 % for the sodium dichromate content.

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LIST OF SYMBOLS

M	Molar concentration (mol/dm^3)
mM	Millimolar concentration (milli mol/dm^3)
nm	Nanometer
µm	Micrometer
x_i	Input stimulus of a neuron e.g. absorbance value at a specific wavelength
w_i	Synaptic weight allocated to a stimulus received at a neuron
a'	Activation a = $\Sigma\ x_i\ w_i$
o	Output of the neuron
f	The learning process specifies the algorithm used, known as transfer function
E'	The energy of a photon of electromagnetic radiation (J)
h	Planck's constant (6.63 x 10^{-34}J.s)
ν	Frequency of the radiation (s^{-1})
c	The speed of light (3 x 10^8 m.s^{-1})

λ Wavelength (m)

A Absorbance unit (dimensionless unit)

T Transmission (e.g. %)

Po Intensity of light before a beam of radiation has passed through a medium that contains the analyte

P Intensity of light of a beam of radiation after it is passed through a medium that contains the analyte

Ps Intensity of light of stray radiation

a Is a proportionality constant called *absorptivity.* The magnitude and dimensions of a will clearly depend upon the units of b and c in A = $a\ b\ c'$

b Cell length (cm)

c' The *absorptivity* is called *molar absorptivity* and is given the symbol ε

ε *Molar absorptivity* (L $mol^{-1}cm^{-1}$)

π Electron in double or triple bonds. π-electrons are delocalised and require less energy for excitation

t_{2g} In an octahedral environment, a metal ion as two kinds of d orbitals i.e. t_{2g} and e_g. The e_g orbitals are of higher energy than t_{2g}

e_g In an octahedral environment, a metal ion as two kinds of d orbitals i.e. t_{2g} and e_g. The e_g orbitals are of higher energy than t_{2g}

a_i Activity of analyte ion i (mol/dm^3)

γ_i A dimensionless quantity called the activity coefficient

$[i]$ Molar concentration of i (mol/dm^3)

E The potential measured between indicator and reference electrode (V)

$E^{\bullet}$ The sum of the standard potential of the electrode and the junction potential (V)

R Gas constant (8.31441 J.K^{-1}.mol^{-1})

T Absolute temperature (K)

n_i Charge of the analyte ion in the Nernst equation.

F Faraday constant (96 484.56 C.mol^{-1})

z_i Charge of the primary analyte ion (including its sign) in the Nikolsky-Eisenman equation

z_j Charge of the interfering analyte ion (including its sign) in the Nikolsky-Eisenman equation

a_j Activity of analyte ion j – the interfering ion in the Nikolsky-Eisenman equation (mol/dm^3)

K_{ij} Selectivity coefficient in the Nikolsky-Eisenman equation

U Asymmetry potential (mV)

c_x Concentration of species x (e.g. mg/dm^3)

$M_{(x)}$ Molecular mass of species x (g/mol)

F' The determined critical value according to the *F*-test. This test considers the ration of the two sample variances

s_1 The standard deviation of measurement series *1*

t The determined critical value according to the *t*-test. A decision tool measuring the significance of the difference between $\bar{x}_1$ and the population mean

$\bar{x}_1$ The mean of the measurement series *1*

n_1 The degree of freedom for measurement series *1*

G The determined critical value according to Grubbs' test

$\bar{d}$ The mean value, calculated by the difference between paired values, used in a paired t-test

s_d Standard deviation calculated on the difference between paired values, used in a paired t-test

CHAPTER 1

1.1 INTRODUCTION

The aim of this study was to measure the quantities of hexavalent chromium (Cr(VI)) species in concentrated liquours in the electrochemical production process of chromic acid. Knowledge of the general chemistry of chromium is necessary to gain a complete understanding of the above mentioned process.

Chromium occurs naturally and most abundantly as the mineral chromite. This ore, $FeCr_2O_4$, is a spinel and is the only commercial source of chromium. In the production of sodium dichromate, chromite ore is treated with oxygen and molten alkali to convert trivalent chromium (Cr(III)) to hexavalent chromium (Cr(VI)). This is subsequently dissolved in water and precipitated as sodium dichromate.

$$2FeCr_2O_4 + 4Na_2O + 3½O_2 \longrightarrow 4Na_2CrO_4 + Fe_2O_3 \qquad (1.1)$$

Chromium can exist in several oxidation state ranging from 0 to VI. However, only trivalent and hexavalent chromium are stable enough to occur in the environment. The Cr(III) oxidation state is the most stable and substantial energy is required to convert it to a lower or higher energy states.

Cr(III) forms stable salts with all the common anions and is able to complex with most species that are capable of donating an electron pair. Cr(III) complexes with a variety of ligands such as water, ammonia, urea, ethylenediamine and other organic ligands containing oxygen, nitrogen or sulphur donor atoms.

1.2 SPECIATION ANALYSIS

Tandon et al. [1] used published equilibrium constants to calculate the percentage of each Cr(VI) species (CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$ and H_2CrO_4) present in aqueous solution at total Cr(VI) concentrations of 10^{-2} – 10^{-6} M in the

pH range of 1 to 8. Unfortunately, there were errors in this presentation and they were corrected by Shen-Yang et al. [2].

Cr(VI) may be present in aqueous solution as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$), dihydrogen chromate (chromic acid, H_2CrO_4), hydrogen dichromate ($HCr_2O_7^-$), trichromate ($Cr_3O_{10}^{2-}$) and tetrachromate ($Cr_4O_{13}^{2-}$). The last three ions have been detected only in solutions of pH less than zero or at Cr(VI) concentrations greater than 1 M (52 g/dm^3).

Based on spectrophotometrical analysis, Poulopoulou et al. [3] reported that *only CrO_4^{2-} and $Cr_2O_7^{2-}$* were present in the pH range 3 – 11. This was independent of Cr(VI) concentration. It was claimed that *$HCrO_4^-$ did not exist*. Cruywagen et al. [4] by means of a spectrophotometric study of the protonation and dimerisation of CrO_4^{2-} at different concentrations in the pH range 2.5 – 8 at 25°C in 0.1 M NaCl, led to the confirmation that *$HCrO_4^-$* indeed existed.

Marcelo et al. [5] by means of Imbrie Q-mode factor analysis, followed by oblique projection, estimated the composition of the Cr(VI) equilibria from ultraviolet–visable (UV–VIS) spectra. In the pH range from 1 – 12 and concentration ranges of 3.3×10^{-4} and 3.3×10^{-5} M two factors were identified, which were related to the two species, chromate (CrO_4^{2-}) and hydrogen chromate ($HCrO_4^-$). When the analysis was extended to concentrated acid media, another factor appeared which was related to chromic acid (H_2CrO_4).

The dichromate ion is a dimer of $HCrO_4^-$, less a water molecule, which forms when the concentration of chromium exceeds approximately 1 g/dm^3 [6].

The reference work of Cotton et al. [7] supports the presence of chromate, dichromate and hydrogen chromate.

Chromium speciation analysis is shown to predominantly involve two important steps,

- Separation of the species such that they are pre-concentrated (if so required)
- Detection of the species. *Separation techniques* may be directly coupled with the detector or if this is not possible for whatever reason, the sample may be manually transported to the detector.

1.2.1 Separation techniques in speciation analysis

Extraction

Extraction is primarily used to separate analytes from a matrix thus eliminating or reducing interferences from other components. Secondly, it is used to concentrate the analyte up to a detectable concentration level. The process must not only be done in such a way as to prevent loss or contamination but also to prevent changes in the speciation of the metal.

Chen et al. [8] used liquid extraction techniques for the removal of chromium species from an aqueous phase into n-pentanol. The organic phase with extracted chromium complexes was pumped through an optical cell for absorbance measurement at 548 nm. The proposed speciation analysis was sensitive, yet simple, labour-effective, and cost-effective. It has been preliminarily applied for the speciation of Cr(VI) and Cr(III) in spiked river and tap water samples. It can also be used for other automatic liquid-liquid extraction-spectrophotometric determinations.

Lanagan [9] evaluated the solvent extraction behaviour of chromium with Cyanex® 232 (Bis(2,4,4-trimethylpentyl) Phosphinic acid). It was found that the solvent extraction behaviour of Cr(III) and Cr(VI), are distinctly different. For Cr(III), solvent extraction tests showed amongst other things, that it is extracted

in the pH range 4 – 7. Extraction of Cr(VI), on the other hand, occurs at pH less than 2 by solvation of chromic acid.

Ion exchange

Ion exchange methods of separation are not regularly used for separation because they are slow. The preferred method is to couple ion exchange columns to HPLC or ion chromatography systems.

HPLC and Ion Chromatography

High performance liquid chromatography (HPLC) is one of the main separation techniques used. It is a convenient technique and allows for the method to be on-line i.e. a hyphenated technique. In this technique Cr(III) and Cr(VI) are separated on ion exchange columns. Chromatography is generally faster than other separation procedures and allows for the direct determination of the analyte species thus decreasing the risk of contamination by lengthy sample pre-treatment. Anion chromatographic separation of chromium species using Na_2CO_3 as the eluent was proposed by Coetzee et al. [10]. Precolumn derivitisation of Cr(III) with EDTA is needed for optical emission detection following the separation by chromatographic techniques.

1.2.2 Detection techniques

Detection systems may be directly coupled with the separation system or the processed sample may be manually transported to the detector.

Atomic Absorption Spectroscopy (AAS)

A major advantage of AAS is that minimal interferences occur from other elements in the sample as the hollow cathode lamp used is metal specific. AAS has also found wide application due to its simplicity and relatively low cost. Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) offers increased sensitivity and is commonly used. Among its attributes are its versatility in

handling various sample matrices without the need for sample pre-treatment as well as a high power of detection and selectivity. AAS has been employed as a method of detection after separation of chromium species by ion chromatography where the effluent of the column is directly linked to the detector.

Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP–AES)

ICP-AES is a multi-element technique. ICP-AES cannot perform elemental speciation without the prior separation of the species. Coetzee et al. [10] used this detection system for chromium speciation analysis coupled to anionic ion chromatography and cationic ion chromatography.

Inductively Coupled Plasma – Mass Spectroscopy (ICP–MS)

ICP–MS is another multi-element technique, which is rapidly becoming a popular detection technique due to its sensitivity. This technique has the advantage of very low detection limits. It cannot distinguish between species, so prior separation of Cr(III) and Cr(VI) is needed.

Ultraviolet – Visible Spectroscopy

EDTA forms coloured complexes with many cations. In slightly acidic solutions, EDTA forms a violet-coloured complex with Cr(III).

Diphenylcarbazide (DPC) forms an intense red-violet colour on addition to acidic Cr(VI) solutions. de Beer et al. [11] used UV–VIS detection for chromium speciation analysis. The chromophoric species were detected at 545 nm after ion chromatographic separation. Precolumn derivitisation of Cr(III) with EDTA and post column complexation of Cr(VI) with DPC was applied to produce chromophoric species. Vanadium(V) was found to interfere in the analysis of Cr(VI), by also reacting with DPC to produce a similarly coloured complex.

Chromate Conversion Coating (CCC) is a type of conversion coating used to treat aluminum, zinc, cadmium, copper, silver, magnesium and their alloys. The

CCC ingredients include hexavalent chromium. The release of soluble Cr(VI) species by a CCC was monitored quantitatively by UV–VIS spectroscopy [12]. By careful selection of the wavelength (339 nm), the total Cr(VI) concentration could be determined without regard to solution pH or Cr(VI) speciation.

1.3 MEASUREMENT TECHNIQUES AT SPONSORING COMPANY'S PREMISES

The determination and quantification of aqueous forms of Cr(VI) is currently achieved at the sponsoring company's premises using various *laboratory* based measurements. At the time of writing of this dissertation no on-line measurements were available.

Ion chromatography separation techniques coupled with conductivity measurement are available at the company's laboratory. Ion chromatography separation followed by post column derivitisation of Cr(VI) and diphenylcarbazide with spectroscopic UV–VIS detection is also available. Hexavalent chromium is separated as the CrO_4^{2-} anion in an alkaline buffered eluent. Cr(VI) reacts with the colour reagent DPC in the following manner:

$$2CrO_4^{2-} + 3H_4L + 8H^+ \longrightarrow Cr(III)(HL')_2^+ + Cr^{3+} + H_2L + 8H_2O \qquad (1.2)$$

where: H_4L = diphenylcarbazide
H_2L = diphenylcarbazone
$Cr(III)(HL')_2$ = chelated Cr(III) – diphenylcarbazone complex

The reaction is apparently the simultaneous oxidation of diphenylcarbazide to diphenylcarbazone, reduction of Cr(VI) to Cr(III), and the chelation of Cr(III) by diphenylcarbazone.

These two techniques (*i.* ion chromatography with conductivity measurement and *ii.* ion chromatography with post column derivitisation of Cr(VI) with

spectroscopic UV–VIS detection) are suitable for Cr(VI) concentrations in the ranges of approximately 1 to 100 mg/dm^3 (conductivity measurement) and less than 1 mg/dm^3 (UV–VIS detection with post column reaction).

Identification of Cr(VI) species using these types of separation tools i.e. anionic ion chromatography with conductivity measurement or UV–VIS detection, quantify total Cr(VI) and not the composition of the individual contributing species of Cr(VI).

Analysis of Cr(VI) in samples greater than 1 g/dm^3 is achieved by titrimetric technique by redox reaction (according to reaction 1.3) coupled with potentiometric measurement.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+} \qquad (1.3)$$

Identification of Cr(VI) species using redox reactions is not possible because this technique quantifies total Cr(VI) and not the composition of the individual contributing species of Cr(VI).

An acid – base titrimetric technique coupled with automatic pH measurement is also used in the laboratory, according to the following *simplified* equations. This titrimetric technique is used to identify Cr(VI) species.

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O \qquad (1.4)$$

$$2CrO_3 + 2OH^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad (1.5)$$

1.4 CHROMIC ACID PRODUCTION AND THE ELECTROLYSIS CIRCUIT

CrO_3 is a bright orange / purple solid, and is commonly called *chromic acid.* It is usually manufactured by adding concentrated sulphuric acid to a saturated

solution of sodium dichromate. The soluble form of CrO_3 is $CrO_3(H_2O)(aq)$ or more commonly $H_2CrO_4(aq)$.

$$Na_2Cr_2O_7(aq) + H_2SO_4 \longrightarrow 2CrO_3(aq) + Na_2SO_4 + H_2O \qquad (1.6)$$

CrO_3 is toxic and corrosive. The crystal structure consists of chains of fused tetrahedra. CrO_3 dissolves readily in water and is both a very strong acid and an oxidising agent. It is an acidic oxide [13]. CrO_3 is widely used to make chromium plating solutions and finds some application in wood treatment. Chromated Copper Arsenate (CCA) is a wood preservative used for timber treatment. It has been in use since the mid-1930's. It is a mixture of copper, chromium, and arsenic formulated as oxides or salts. It preserves the wood from decay fungi, wood attacking insects, including termites, and marine borers. It also improves the weather-resistance of treated timber and may assist paint adherence in the long term. CCA has achieved excellent results for the preservation of wood such as utility poles, building lumber and wood foundations.
An alternative process in the making of CrO_3 is to use an electrolytic salt splitting cell. Salt splitting is the conversion of a salt (e.g. $Na_2Cr_2O_7$) into an acid (e.g. H_2CrO_4) and an alkali (e.g. NaOH), requiring the input of energy.

Sodium dichromate can be effectively split electrochemically into chromic acid and sodium hydroxide in a two compartment cell illustrated in Figure 1.1. Under the influence of an electric field, sodium ions migrate through the cation exchange membrane into the catholyte compartment where they combine with hydroxide ions formed from the reduction of water at the cathode with consequential hydrogen evolution.

On the other side of the cell, oxygen is evolved at the anode from the electrolysis of water and the released proton reacts with $Cr_2O_7^{2-}$ to form aqueous chromic acid.

The anode is typically manufactured of titanium with a coating that is catalytic for O_2 evolution. Charge transport across the cation exchange membrane is not by sodium ions alone. This gives rise to a significant decrease in current efficiency for the process. The transport of protons occurs more rapidly than sodium in both the aqueous medium and the membrane because it does not migrate as discrete ions but moves through the water structure by a protonation / deprotonation sequence. Fortunately, the formation of H_2CrO_4 reduces the concentration of the free proton.

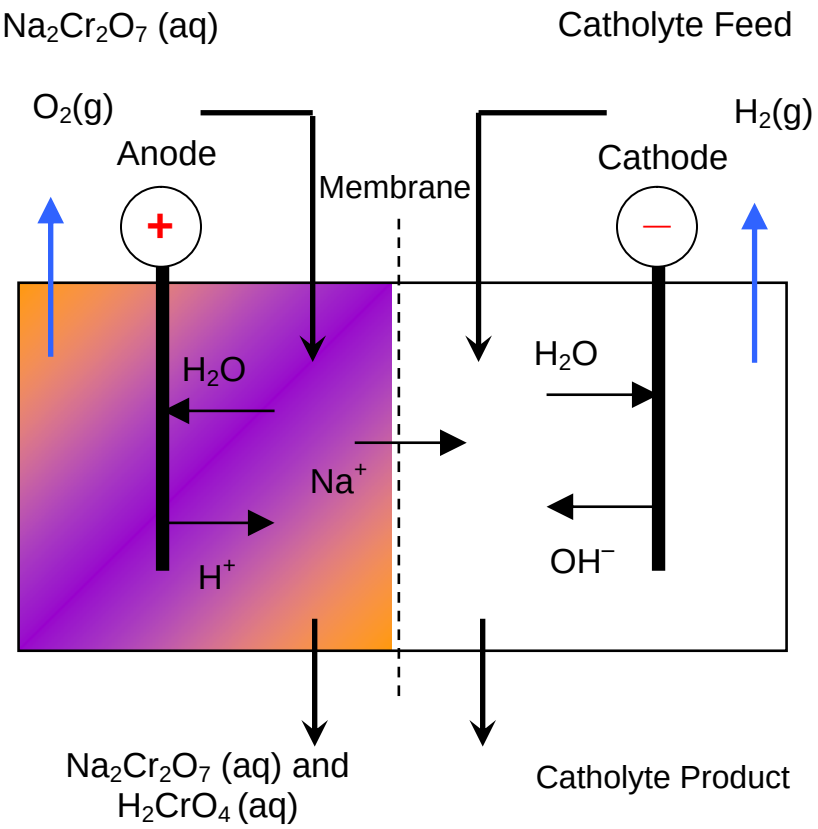

Figure 1.1 Electrolytic production of chromic acid in a two compartment cell, a cation exchange membrane separates the anolyte from the catholyte.

For this electrolytic process route, the anodic cell reactions are as follows:

$$H_2O \longrightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \quad (1.7)$$

$$Cr_2O_7^{2-} + 2H^+ + H_2O \longrightarrow 2H_2CrO_4\,(aq) \quad (1.8)$$

Reaction 1.7, the oxygen evolution reaction (OER), is one of the most important anodic reactions in electrochemical engineering coupled with the cathodic systems occurring in aqueous solutions such as water electrolysis, metal electrowinning, electrosynthesis, etc. The OER generally creates very aggressive corrosion conditions for the electrode material. This is particularly true in acid solutions where these conditions are enhanced. Coated titanium anodes are used in the application for electrolytical chromic acid production. Titanium is used because of its excellent chemical resistance as well as its ability to passivate when subjected to a positive potential. The coating, a precious metal oxide, is an electrocatalyst, used to minimise the overpotential at which oxygen evolves at its surface.

Electrodes used in the production of chromic acid were not designed specifically for the purpose of this electrolytic process. A significant decrease in electrode performance is observed on irregular and largely unpredictable time intervals. There are no obvious links of this lifespan to the technological process or origin of manufacture, etc. The cost of these electrodes and the associated lifespan is a significant contributor to the profitability of the process. In addition, the down-time required for the replacement of electrodes causes unnecessary and unwanted disruptions to the process.

A membrane is used to separate the cathodic and anodic compartments. A membrane is a separator between two fluids of different composition which enforces selectivity in the transport of species between them. With membranes used in electrolysis, the driving force of the transport of species is an electric field leading to the migration of ions through the membrane. In Figure 1.1 above, a

cation permeable membrane selective to sodium ions is in use. Transport within the ion permeable membrane is usually limited to migration (the movement of charged species due to a potential gradient) and secondly and less importantly, by diffusion (the movement of species down a concentration gradient) [14].

The chromic acid content in the production circuit is enriched (or concentrated) as it passes from one stage (comprising several cell compartments) to the next. This is due to two factors. The first is a loss of water. This loss is partly caused by the electrolytical split of the water molecule (into $H_3O^+(aq)$ and $O_2(g)$), and the transport of hydration water surrounding the sodium ions ($Na(H_2O)_x$) as they pass to the cathodic compartment. Secondly, the chromic acid content is enriched as a function of the conversion of sodium dichromate to chromic acid (equation 1.8) as electrolysis proceeds. As a consequence of the enrichment of the chromic acid content, the dichromate content is depleted accordingly.

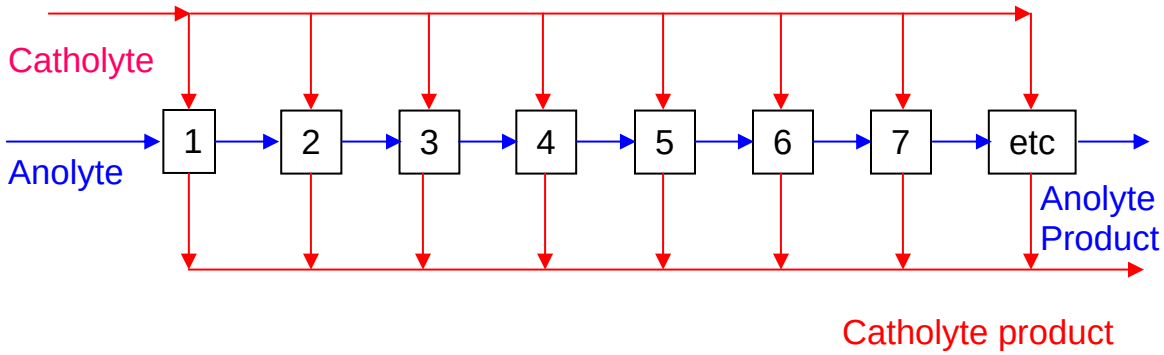

Figure 1.2. Electrolytic production of chromic acid using two compartments cells arranged in series.

The aqueous mixture of chromic acid and sodium dichromate exiting the electrolysis circuit is processed further. Chromic acid, as $CrO_3(s)$, is selectively crystallised (step 1 below) from the aqueous mixture.

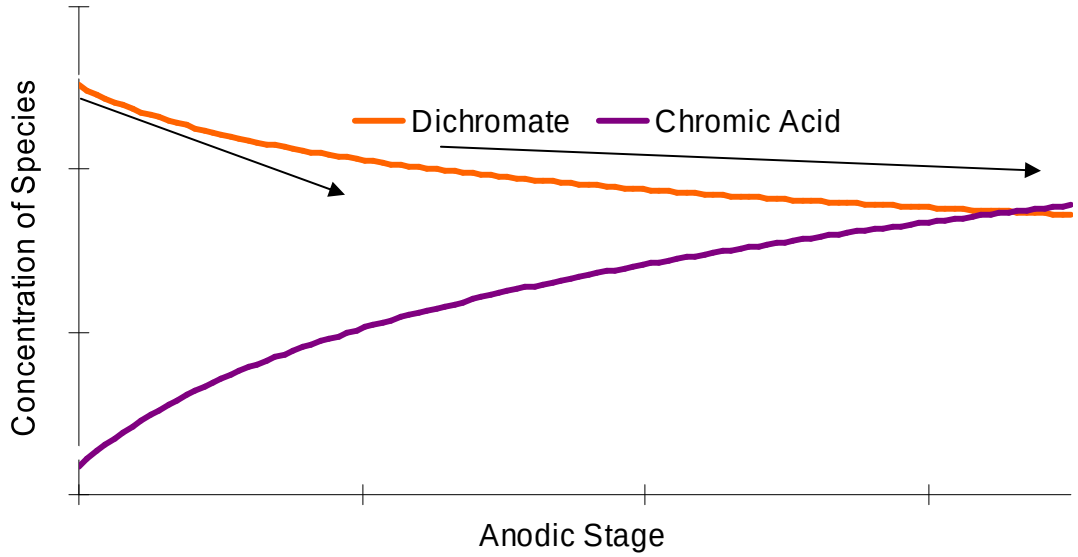

Figure 1.3. Representation of dichromate depletion and chromic acid increase as a function of production stage. The change is rapid initially, as indicated by the steep slope at start of the diagram.

Step 1. Crystallisation: Water is removed by an evaporation process step and crystal formation takes place

Step 2. Solid – liquid separation: the crystallised chromic acid is separated by centrifugation from the non-crystallised portion known as mother liquor; the mother liquor is recycled and / or used for further processing in other plant units

Step 3. Drying of crystals: energy in the form of hot air is applied to dry the supernatant film of liquid remaining around the crystals

Step 4. The hot crystals are cooled in a dehumidified environment

Step 5. The crystals are packaged for distribution and sales

1.5 NEED FOR ALTERNATIVE ANALYTICAL MEASUREMENTS

The chromic acid production plant requires fast and preferably on-line analytical methods which provide real-time data that saves time and money.

The existing practice at the sponsoring company of sample taking and analysis, involves the movement of a sample from the sampling point in the plant to the laboratory in a scheduled fashion. The sample undergoes the necessary analysis and the data is reported to the operating personnel.

This route is time consuming and does not lend itself to effective process control. Ineffective production process control will have its effects seen in erratic production and poor quality of product. These problems necessitated the need for an improved method of analysis and reporting swiftness of the data.

Electrolytic processes are interfacial by nature and involve many physical, chemical and mechanical parameters. Amongst other influences (e.g. temperature), *solution composition* may play a significant role in the overall electrolytic process and associated performance. This can be better evaluated with a relatively rapid on-line measurement.

1.6 PROCESS CONTROL ANALYSIS

The electrochemical manufacture of chromic acid production requires extensive process control. Amongst process control parameters, the chemistry (or product composition) plays an important role. The role of the analytical chemist is to develop methods of analysis that are efficient, cost effective and most importantly accurate and specific. Staying abreast of technological developments in analytical techniques is imperative.

The current methods of analysis which are used at the sponsoring company are all batch mode, point-in-time, laboratory based determinations. Almost exclusively, acid base titrimetric techniques are applied to the samples that are taken in the electrolysis plant. An aliquot of the sample is weighed, diluted and titrated automatically with a strong base. This requires skilled personnel and is subject to errors by human intervention. UV–VIS spectrophotometry coupled with artificial neural network technology will be investigated in this dissertation for on-

line measurements. As an alternative to the above mentioned, ion selective electrode (ISE) measurements coupled with UV–VIS spectrophotometry, and secondly, titrimetry measurements will also be investigated.

1.7 ON-LINE ANALYSIS – ANALYTICAL ASPECTS OF CHEMICAL PROCESS CONTROL

Information generated by process chemistry may be used both to control and optimise the performance of a chemical process in terms of variables such as capacity, quality, cost, consistency and waste reduction [15]. There are two approaches to process control.

The so-called *traditional approach (or off-line)* where samples from the process environment are obtained manually, transported to a centralised analytical laboratory and analysed by technical staff. The staff evaluates the data obtained and report the results to those involved in the operating system. Corrective action is taken if required by adjusting conditions of the operating system accordingly.

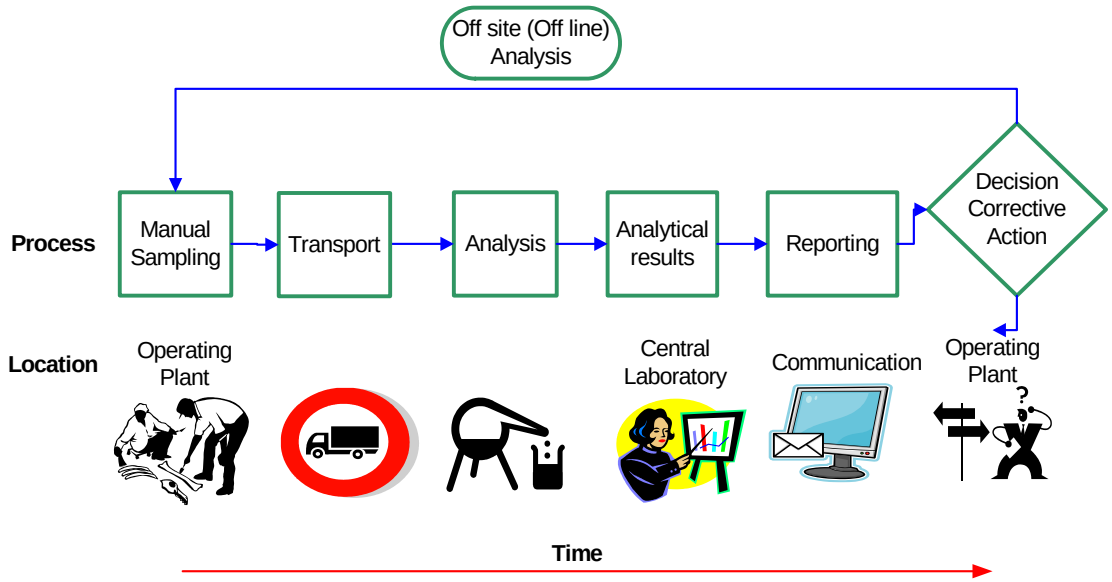

Figure 1.4. Traditional approach to process control showing the time taken for reporting of data – a lengthy approach with human intervention.

In the more modern approach, analysis is performed at or inside an operating system (plant site) with an analytical system (process analytical system or process analyser), where corrective action is immediately taken – sometimes automatically *(known as on-line)*.

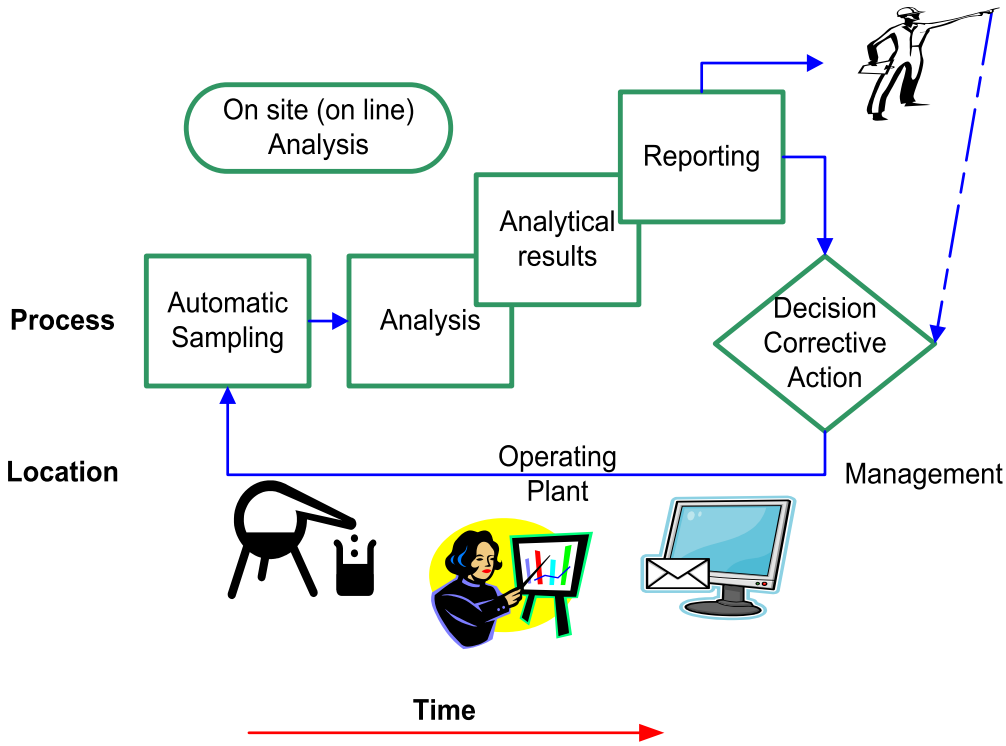

Figure 1.5. Process analytical approach to process control, showing the advantage in timing of reporting data – human intervention less critical.

There is not always direct two-way communication in the traditional approach to process control, and a typical operation from sampling to corrective action may take several hours. This feature is known as *time-delayed* monitoring. Chemical manufacturing plants are usually designed to accommodate this time delay, at a cost of longer cycle times and reduced plant utilisation, when compared to a process using an analytical control approach. Two-way communication is very important in process analytical control where corrective action is immediately implemented once results are computed i.e. results of analysis are evaluated and chemometrics (the application of mathematical or statistical methods to chemical

data) on results applied. This avenue results in real-time (or nearly real-time) operation.

On site (at-site) analysis is divided into three categories. *(i.)* In *at-line* analysis, the sample is still manually sampled, but the measurement is carried out on a dedicated analyser located at the sampling site. Sample preparation is simplified and the measurement technique modified to permit the use of robust reliable instrumentation to cope with the production environment. The term *close-time monitoring* (near real-time monitoring) is used to describe this type of operation. *(ii.)* In *on-line* analysis, the sample is automatically sampled and fed into a dedicated analysing system where analysis is automatically performed with an automatic feedback to the operating system (e.g. process stream for industrial chemical processes) for adjustment and corrective action. (*iii).* In *in-line* analysis, the analysing probe is situated inside the operating system (or process stream). Transduction is performed inside the operating system, with a feedback to the processor outside the operating system, with facilities for automatic adjustment and corrective action.

Real-time monitoring or a good approximation to real time is attained with *on-line* and *in-line* analysis

1.7.1 Planning, design and sample manipulation

In the planning and design of instrumentation the following points should be considered very carefully,

- Selection of the process variable (characterising the quality of the process)
- Quantitative relation between the measured and controllable properties
- Places of sampling (or analysing points)
- Frequency of the measurements and correlation time of the process required
- Time duration of the measurements
- Tolerance limits (upper and lower) of the measured variable
- Selection of sensing or analysing instrument(s)

- Cost and maintenance of instruments
- Calibration frequency of the instruments used
- Total cost of measurements and regulations involved
- Reliability, ease of operation and simplicity

A modern on-line analyzer system normally consists of seven parts:

1. *The sampling point:* The equipment which penetrates the operating system's envelope is called the sampling probe (e.g. a plant's process envelope in industrial chemical processes). The sampling probe must ensure that the sample taken is truly and fully representative of the entire operating system. Once the sample has been extracted from the operating system, it must be transferred to the analyzer
2. *The pre-conditioning system:* A pre-conditioning system, situated close to the sampling point, may be used to treat the sample in such a way as to eliminate problems. For example, solid particles, droplets or condensate (which may lead to blockages or fouling of the transport line) and to regulate the pressure and temperature of the sample provided
3. *The sample – transport line*: This is used to transport the sample from the pre-conditioning system point to the analyzer in an acceptable time and without the composition of the sample being affected appreciably. Speed and representativeness are the key issues
4. *The sample – conditioning system*: It is designed to ensure that the sample is acceptable to the analyzer and that it is still truly representative
5. *The analyzer itself*: Analytical measurement or sensor unit
6. *The analyzer control* unit: This may be used to interface with a control system providing data in an understandable format
7. *The associated output equipment:* An example of this type of equipment may include a PC card or interface junction point

1.7.2 Measurements

Measurements in process analysers are based on physical properties which can be transformed into chemical quantities expressing chemical information. These may be classified as follows.

1. Methods based on measurement of process streams with intensive physical properties (density, light absorption, refraction, etc.).
2. Methods based on the measurement of intensive properties after using chemical reaction(s) for increasing selectivity and sensitivity (spectrophotometry using colour-forming or chromogenic reagents, etc).
3. Measurement of extensive physical properties using chemical reaction(s) (for example gravimetry, titrimetry, coulometry, etc.).
4. Two dimensional analytical methods. One coordinate is related to the *quality* (nature) and the other to the *quantity* of the components (for e.g. polarography, chromatography, spectroscopy, etc.).

The procedures of classification 1 are preferred on the grounds of simplicity in process control, but they are not applicable if high selectivity or sensitivity is required.

1.7.3 Detection systems

The detection system in a process analyser can be a destructive or non-destructive sensor or procedure. In a destructive mode the sample is destroyed, for example in inductively coupled plasma spectroscopy where the sample is eventually fed into plasma. With non-destructive detection, the composition of the original sample is maintained, for example when using a pH probe as detector; although a change at micro level occurs at the electrode surface-solution interface, the bulk of the process stream remains unchanged.

The scope of the process analytical chemistry approach has been broadened with the introduction of a new generation of devices, accompanied by new

terminology, in process analysers. The terms non-invasive and non-intrusive are widely used. With non-invasive techniques, the sensing probe does not physically come into contact with the process stream and all non-invasive measurements rely on the transmission of information through the wall of the vessel. Non-invasive techniques are primarily focused on the measurement of physical parameters. At present, there are a small number of chemical measurements that can be made this way. A transducer, in this context, is a device for converting a chemical or physical parameter into an electrical signal. Non-invasive therefore means that, in all cases the transducer does not come into contact directly with the process medium. A familiar example of this is a thermowell. (Simply a piece of tubing welded into the wall of the vessel and closed at the innermost end). To measure the process temperature, a thermocouple or platinum resistance thermometer is inserted into the tube. To be able to make a representative measurement of the process fluid temperature, this tube needs to extend some distance into the fluid. It is therefore intrusive. An obvious disadvantage of an intrusive technique is that the probe may disturb the process fluid or may be eroded by the passage of entrained abrasive material. A pH probe is an example of an invasive intrusive analyser. For this to function, the pH-sensitive element needs to be in intimate contact with the process fluid, preferably where there is some kind of flow. This suffers the disadvantage of an intrusive monitor.

1.8 POTENTIAL IMPACT ON THE PLANT

On-line measurements are potentially efficient, render quality data, are sometimes more cost effective than traditional approaches, and should provide accurate chemical analysis. In evaluating all of these factors, the evidence is clear that on-line measurements should be more beneficial than a traditional approach to process analysis.

Real-time data (or almost real time data) should be more useful in production control, and this *may* have its consequences seen in the extended life of the anodes used in chromic acid manufacturing.

1.9 SPECIFIC OBJECTIVES OF THE STUDY

This project will address the design and development of an on-line monitoring system, for the liquid product (anolyte) in the production of chromic acid.

The data produced from this on-line instrument *may* be used to determine the historical factors that lead to the reduced performance and lifespan of the anode.

CHAPTER 2

2.1 ARTIFICIAL NEURAL NETWORKS

2.1.1 Introduction

Neural networks are adaptive statistical models based on an analogy with the structure of the brain. They are adaptive because they can learn to estimate the parameters of some population using a small number of examples at a given time. Neural networks are used as statistical models in a variety of fields, including psychology, statistics, engineering and physics.

Neural networks are built from simple units, sometimes called neurons or cells by analogy with the real object in biological terms. These units are linked by a set of weighted connections. Learning is usually accomplished by modification of the connection weights. Each unit codes or corresponds to a feature or a characteristic of a pattern that one wants to analyse, or that one wants to use as a predictor. Networks usually organize their unit into several layers. The first layer is called the *input* layer, the last one the *output* layer. The intermediate layer(s) are called the *hidden layers*.

The information to be analysed is fed to the neurons of the first layer and then propagated to the neurons of the second layer for further processing. The result of this processing is then propagated to the next layer and so on until the last layer. Each unit receives some information from other units and processes this information, which will be converted into the output of the unit. The goal of the network is to learn or to discover some association between input and output patterns. The learning process is achieved through the modification of the connection weights between units. The learning process specifies the algorithm used to estimate the parameters.

2.1.2 The building blocks of neural networks

Neural networks are made of basic units arranged in layers. A unit collects information provided by other units to which it is connected with weighted connections called synapses. These weights, called synaptic weights multiply (i.e. amplify or attenuate) the input information; a positive weight is considered excitatory and a negative weight inhibitory.

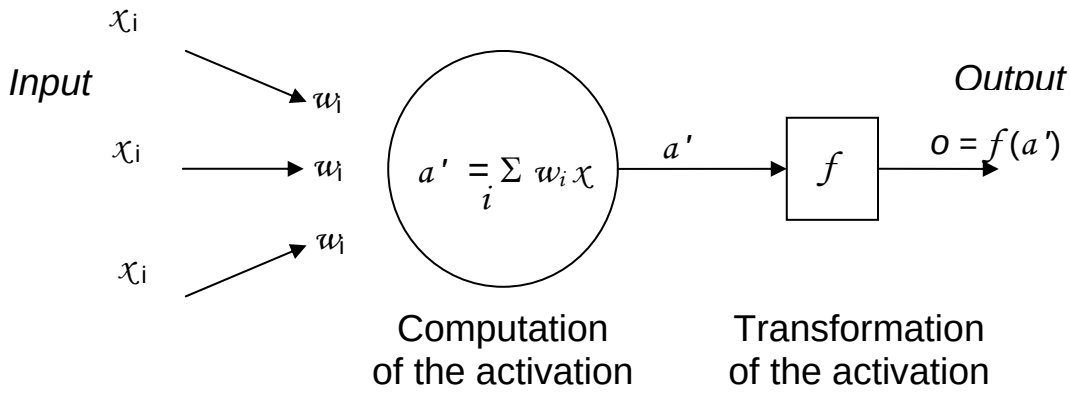

Figure 2.1. Diagrammatic representation of the basic neural unit, showing processing of input information into output information.

Where, x_I = Input e.g. absorbance value at a specific wavelength

w_i = Synaptic weight

a' = Activation

o = Output

f = The learning process specifies the algorithm used, known as transfer function

Each of these units is a simplified model of a neuron and transforms its input information into an output response. This transformation involves two steps. First, the activation of the neuron is computed as the weighted sum of its inputs and second this activation is transformed into a response by using a transfer function.

Formally, if each input is denoted x_i, and each weight w_i, then the activation a' is the $\Sigma\, x_i\, w_i$, and the output denoted o is obtained as $o = f(a')$.

2.1.3 Learning rules

Neural networks are adaptive statistical devices. This means that they can iteratively change the values of their parameters as a function of their performance. These changes are made according to learning rules which can be characterised as supervised (when a desired output is known and used to compute an error signal) or un-supervised. An example of an un-supervised learning rule is the Hebbian rule. In un-supervised learning, the neural networks are not provided with the correct results during training. Un-supervised neural networks usually perform some kind of data compression. An un-supervised method can learn a summary of a probability distribution. That summarised distribution can then be used to make predictions. An example of a supervised learning rule is the Widrow-Hoff rule (also known as the Delta rule). In supervised learning the correct results (desired outputs) are known and are given to the neural networks during training so that the neural networks can adjust their weights to try and match their outputs to the target values. After training, the neural network is tested by giving it only input values, i.e. not target values, and seeing how close they come to outputting the correct target values. The training cycle is then repeated for each input / output pattern pair until the errors becomes acceptable.

Measured variables are presented to the input layer and are processed, by one or more intermediate layers, to produce one or more outputs. For example, in inverse calibration, the inputs could be absorbances at a number of wavelengths, and the output could be the concentration of an analyte. The network is trained by an interactive procedure using a training set. For each member of the training set the neural network predicts the concentration of the analyte. It is important not to over fit the training set: if too high a degree of accuracy is achieved with the training set, the network will perform much less well with the test set. Neural

networks are versatile and flexible tools for modeling complex relationships between variables [16].

2.1.4 Validation

It is important to evaluate the performance of a model. This is done by separating data into two sets, the training set and a testing set. The parameters of the network are computed using the training set. The learning process is then stopped, and the network is evaluated with data from the testing set [17].

2.1.5 Neural networks and their applications in chemistry

Neural networks are studied in analytical chemistry with respect to pattern recognition, modeling and prediction e.g. in multi-component analysis or process control, to classification, clustering or pattern recognition. Thousands of examples are applicable to analytical chemistry. Below, only a few of many are noted.

Examples for applying neural networks in analytical chemistry are known for interpretation of infra-red (IR) spectra. Kazumitsu et al. [18] applied neural networks to the prediction of polyethylene density by near infrared spectroscopy.

Azizul Isha et al. [19] applied neural networks to the simultaneous spectrophotometric determination of Lead(II) and Mercury(II) based on 2-(5-Bromo-2-Piridylazo)-5-Diethylaminophenol. A feed forward neural network using a back-propagation (BP) algorithm was employed in this study. The input layer consisted of 13 neurons, 10 neurons in the hidden layer and 2 output neurons. This was appropriate for the simultaneous determination of Pb(II) and Hg(II).

Yuri Binev et al. [20] applied neural networks for structure-based predictions of 1H nuclear magnetic resonance (NMR) chemical shifts using feed-forward neural networks. Feed-forward neural networks were trained for the general prediction

of 1H NMR chemical shifts of CH*n* protons in organic compounds. The results were significantly better than those obtained with counter propagation neural networks.

Y. Vlasov et al. [21] in a paper entitled “nonspecific sensor arrays (“electronic tongue”) for chemical analysis of liquids” explains the term and use of neural networks, amongst others in their work. The electronic tongue is a multi-sensor system, which consists of a number of low selective sensors and uses advanced mathematical procedures for signal processing based on the pattern recognition (PARC) and / or multivariate analysis (artificial neural networks, principal component analysis (PCA), etc.). Results from the application of the electronic tongue, both for quantitative and qualitative analysis of different mineral water and wine samples were presented and discussed.

Dondeti Satyanarayana et al. [22] used neural networks as a calibration model for the simultaneous spectrophotometric estimation of Atenolol and Losartan Potassium in tablets. The use of a computed calibration spectral data set derived from three spectra of each component has been described. The calibration models were thoroughly evaluated at several concentration levels using spectra obtained for 76 synthetic binary mixtures prepared. Although the components showed significant spectral overlap, the model could accurately estimate the drugs with satisfactory precision and accuracy, in tablet dosage with no interference from other sources as indicated by the recovery study results.

The neural network technique has substantial advantage for spectral discrimination, classification of H-NMR, IR or mass spectra, identification of UV-Spectra, or odours based in a quartz-resonator sensor array, for multi-component analysis in the near infrared range or with ion selective electrodes.

Neural networks cannot do anything that cannot be done using traditional computing techniques, but they can do some things that would otherwise be very

difficult. In particular, they can form a model from their training data. A neural network can adapt to perform many different analog functions such as pattern recognition, image processing, and trend analysis. These tasks are difficult to accomplish with conventional, digital computers. An important function of neural networks is the ability to discover trends in a collection of data. Trend analysis is important in analytical chemistry, chemical engineering, process control, chemical formulation, data mining, and decision support systems.

Neural networks are particularly useful with sensor data, data from a complex chemical, manufacturing, or commercial process and analog problems.

If there is a good algorithm that completely describes a problem then it is best to use this as a solution. However, if no algorithm or other digital solution exists to address a complex problem with many variables, then a neural network that learns from examples may provide an effective handle on the problem.

Some characteristics that make neural networks different from traditional computing are,

(a) Learning by example

(b) Distributed associative memory

(c) Fault tolerance and

(d) Pattern recognition

2.2 ABSORPTIOMETRIC ANALYSIS

Molecular ultraviolet – visible absorption spectroscopy is employed primarily for quantitative analysis and is probably more widely used in chemical and clinical laboratories throughout the world than any other single practice or technique. [23] [24] [25].

2.2.1. Principles of UV–VIS spectroscopy.

Ultraviolet and visible radiation comprises a part (180 to 780 nm) of the electromagnetic spectrum, which includes other forms of radiation known as radio, infrared, cosmic and x-rays as in Figure 2.3 below.

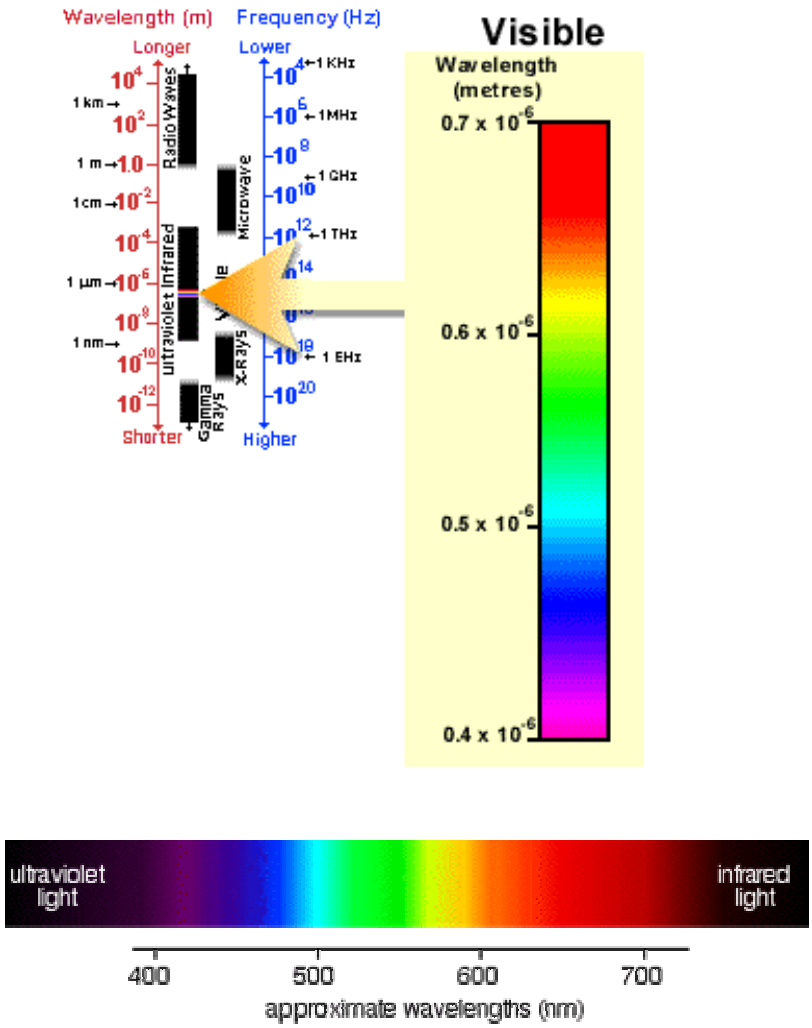

Figure 2.2. The electromagnetic spectrum showing the different forms of radiation including the visible region [26]

The energy of a photon of electromagnetic radiation is defined by

$$E' = h\nu \tag{2.1}$$

where, E' is the energy (J)

h is Planck's constant (6.63 x 10^{-34}J.s)

ν is the frequency of the radiation (s^{-1})

Electromagnetic radiation can be considered as a combination of alternating electric and magnetic fields that travel through space with a wave motion. Because radiation acts as a wave, its properties can be defined either in terms of wavelength or frequency, which is related to the speed of light by the equation,

$$\nu = \frac{c}{\lambda} \qquad (2.2)$$

where, ν is frequency in s^{-1}

c is the speed of light (3 x 10^8 m.s^{-1})

λ is wavelength (m).

In UV–VIS spectroscopy, wavelength is generally expressed in nanometers (nm).

2.2.2 Molecular Absorption

When radiation passes through a layer of solid, liquid or gas, certain frequencies may be selectively removed by absorption. Absorption is a process in which electromagnetic energy is transferred to the atoms, ions or molecules composing the sample. Absorption promotes these particles from their normal room temperature state, or ground state, to one or more higher-energy excited states.

The energy associated with this process is made up of three components namely, electronic, vibrational and rotational energies.

$$E = E_{electronic} + E_{vibrational} + E_{rotational} \qquad (2.3)$$

Figure 2.3 below is a partial energy-level illustration that depicts some of the processes that occur when polyatomic species absorb infrared, visible and ultraviolet radiation. The energies E_1 and E_2, two of the several electronically excited states of a molecule, are shown relative to the energy of its ground state E_0. In addition, the relative energies of a few of many vibrational states associated with each electronic state are indicated by lighter horizontal lines.

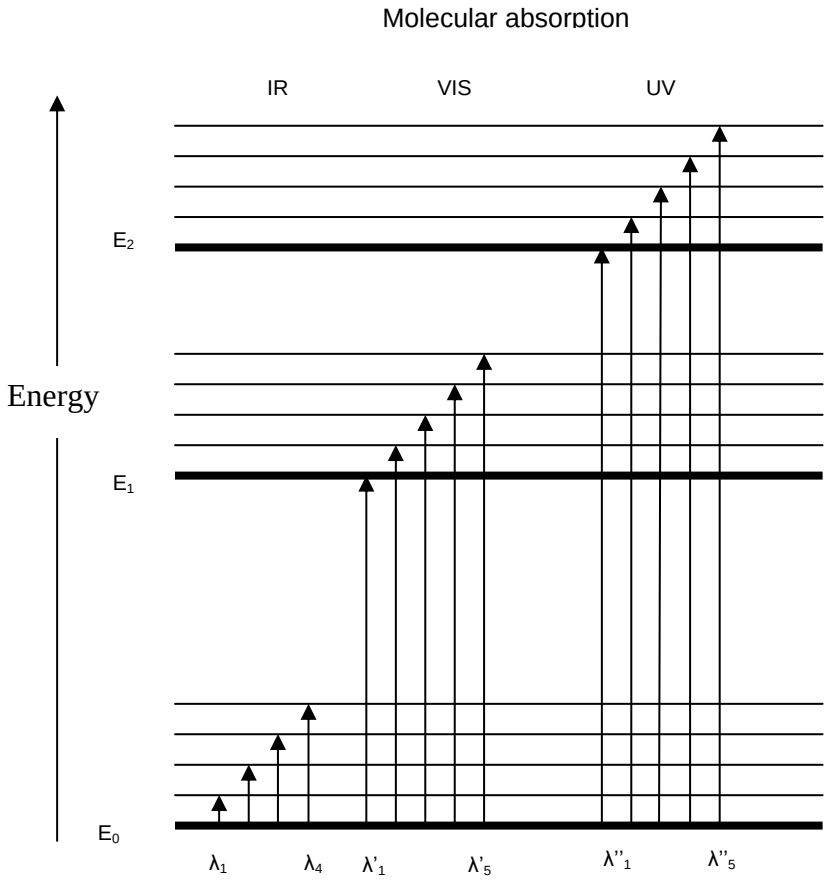

Figure 2.3. Energy level diagram showing some of the energy changes that occur during absorption by a molecular species.

The central arrows of Figure 2.3 above suggests that the molecules under consideration absorb visible radiation of five wavelengths, thereby promoting electrons to four vibrational levels of electronic level E_1. As suggested then, molecular absorption in the ultraviolet and visible regions consists of absorption

bands made up of closely spaced lines. In a solution, the absorbing species are surrounded by solvent, and the band nature of molecular absorption often becomes blurred because collisions tend to spread the energies of the quantum states, thus giving smooth and continuous absorption peaks.

2.2.3 Absorption methods

Absorption methods require two measurements. One before a beam has passed through a medium that contains the analyte (P_0) and the other after (P).

The absorbance A of a medium is defined by

$$A = -\log T = \log \frac{Po}{P} \tag{2.4}$$

where, A = Absorbance unit (dimensionless unit)

T = Transmission (e.g. %)

Po = Intensity before a beam has passed through a medium that contains the analyte

P = Intensity of a beam after it is passed through a medium that contains the analyte

For monochromatic radiation, absorbance is directly proportional to the path length (*b)* through the medium and the concentration *c* of the absorbing species.

This relationship is given by

$$A = abc' \tag{2.5}$$

where, A = Absorbance – a dimensionless value

a = The proportionality constant called *absorptivity.* The magnitude and dimensions of a will clearly depend upon the units of b and c.

b = Cell length is in centimeters,

c' = The *absorptivity* is called *molar absorptivity* and is given the symbol ε, thus

$$A = \varepsilon bc \qquad (2.6)$$

where, ε has the unit L $mol^{-1}cm^{-1}$, and the equation is more commonly known as Beer's law.

This law serves as a basis for quantitative analysis. A high value of ε, means a high probability of absorption of photons of light, and means that the absorbance is high at the wavelength at a given concentration of absorbing molecules.

A brief description of limitations in UV–VIS spectroscopy is given bellow.

Real Limitations

Beer's law is successful in describing the absorption behavior of dilute solutions only and in this sense is a limiting law. At high concentrations (usually greater than 0.01 M), the average distances between particles of the absorbing species are diminished to the point where each particle affects the charge distribution of its neighbours. This interaction can alter their ability to absorb a given wavelength of radiation. Because the extent of interaction depends upon concentration, the occurrence of this phenomenon causes deviations from the linear relationships between absorbance and concentration. A similar effect is sometimes encountered in dilute solutions of absorbers that contain a high concentration of other species, particularly electrolytes. The close proximity of

ions to the absorber alters the molar absorptivity of the latter as a result of electrostatic interactions. The effect is lessened by dilution.

Chemical Deviations

Apparent deviations from Beer's law are frequently encountered as a consequence of association, dissociation, or reaction of the absorbing species with the solvent. These deviations result from shifts in chemical equilibria and not from changes in molar absorptivities.

Instrumental Deviations with Polychromatic Radiation

Beer's law is also a limiting law in the sense that it applies only when absorbance is measured with monochromatic radiation e.g. lasers, which are not practical for routine analytical instrumentation. Instead, a polychromatic source of radiation is employed in conjunction with a grating, or a filter that isolates a more or less symmetric band of wavelengths around a desired one.

Instrumental Deviations in the Presence of Stray Radiation: The radiation employed for absorbance measurements is usually contaminated with small amounts of stray radiation due to instrumental imperfections. Stray radiation is the result of scattering phenomena off the surfaces of prisms, lenses, filters and windows. When measurements are made in the presence of stray radiation, the observed absorbance is given by

$$A = \log \left[\frac{Po/Ps}{P/Ps} \right] \qquad (2.7)$$

where, A = absorbance unit (dimensionless unit)

Po = Intensity before a beam has passed through a medium that contains the analyte

P = Intensity of a beam after it is passed through a medium that contains the analyte

Ps = is the Intensity of stray radiation.

2.2.4 Instrumentation

Instruments for measuring the absorption of ultraviolet, visible and near infrared radiation are made up of the following:

1. Light source
2. Sample container
3. Wavelength selector
4. Radiation transducers, and
5. Signal processors, as per the diagram below.

Figure 2.4. Representation of key components in measuring absorption of ultraviolet, visible and infrared radiation.

1. Light source

For the purposes of molecular absorption measurements, a continuum light source is required whose power does not change sharply over a considerable range of wavelengths. Deuterium lamps are suitable for this. A continuum spectrum in the ultraviolet region is produced by electrical excitation of deuterium at low pressure. Deuterium produces a useful spectrum in the region of 160 – 375 nm. At longer wavelengths, greater than 400 nm, the lamp produces emission lines, which are superimposed on the continuum spectrum. Quartz windows must be employed in deuterium lamps since glass absorbs strongly at wavelengths less than about 350 nm. A tungsten / halogen lamp is useful for the wavelength region between 350 and 2500 nm.

2. Sample holder

A sample holder is required to restrict the volume of sample / solvent to the path of the light source. This may take the form of a cuvette (which must be transparent to the wavelengths under consideration), or a flow-through cell, in which the light travels through the sample / solvent medium only and is captured directly.

3. Wavelength selector

Spectroscopic analysis requires a band of wavelengths which are limited to being narrow and continuous. A narrow band of wavelengths provides for better sensitivity of absorptive measurements, and is also better suited to obtaining linear relationship between absorption and concentration.

Optical filters are means of selecting wavelengths by interference or absorption. Absorption filters are restricted to the visible region of the spectrum and interference filters are useful in the ultraviolet, visible and infrared regions.
Monochromators on the other hand are necessary and sought-after to be able to vary wavelengths of radiation continuously over a considerable range. Monochromators have slits, lenses, mirrors and gratings (prisms) in common. A slit provides a rectangular beam of light, the lens or mirror provides for a parallel beam of radiation and a prism or grating disperses the radiation into its component wavelengths. As mentioned above two types of dispersing options are found in monochromators i.e. reflection gratings or prisms.

4. Detectors

Detection devices have largely been improved by transducers that convert radiant energy into an electrical signal. The ideal transducer should have a high selectivity, a high signal-to-noise ratio and a constant response over a considerable range of wavelengths. In addition, it would exhibit a fast response time and a zero output signal in the absence of illumination. Finally, the electrical signal produced by the transducer would be directly proportional to the radiant

power. Modern multi-channel transducers consist of an array of small photoelectric-sensitive elements arranged either linearly or in a two-dimensional pattern on a single semi-conductor chip.

5. Signal processors

The signal processor is ordinarily an electronic device that amplifies the electrical signal from the transducer. In addition, it may alter the signal from direct current to alternating current, change the phase of the signal, and filter it to remove unwanted components. Furthermore, the signal processor may be called upon to perform such mathematical operations on the signal as differentiation, integration, or conversion to a logarithm.

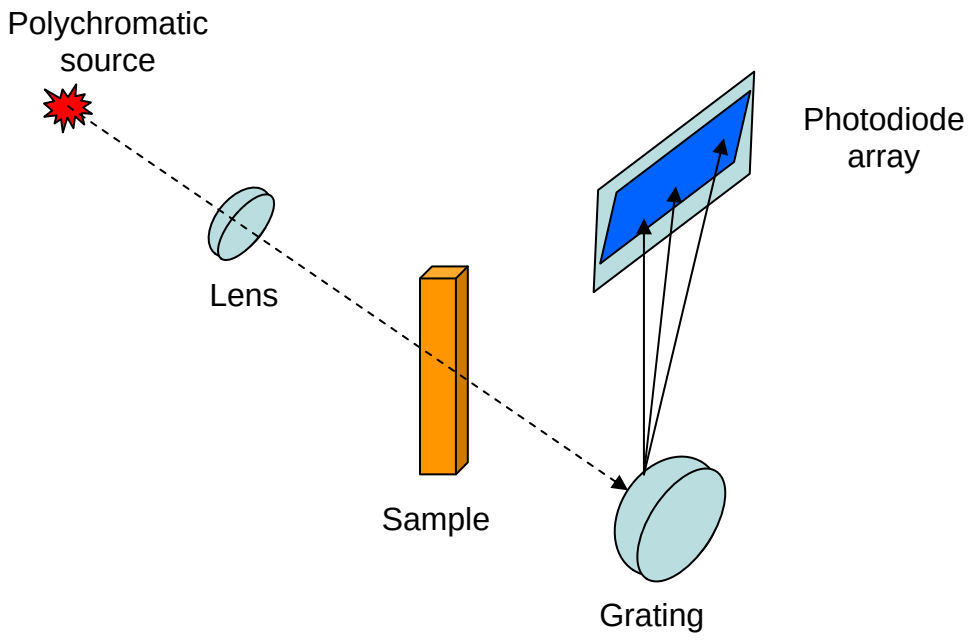

Figure 2.5. Representation of key components of a simple optical instrument.

2.2.5 Fibre optics

Fibre optics [27] are useful in transmitting radiation and images from one component of an instrument to another. Fibre optics are manufactured from fine strands of glass or plastic and are capable of transmitting radiation for distances

of several hundred meters or more. Light transmission in an optical fibre takes place by total internal reflection.

A fibre cable design typically consists of three layers namely, a core, a cladding and a buffer.

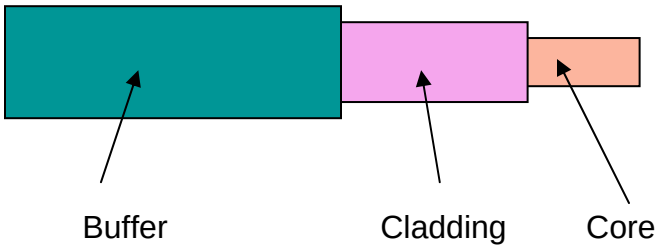

Figure 2.6. Representation of key components of an optical fibre.

Core

Generally multi-mode silica fibres are used. These range in core thickness from 50 µm to 1000 µm. The core is made out of pure silica. A distinction is made between silica with high or low OH content. Silica fibres with high OH (600 – 1000 parts per million) are used in the UV–VIS wavelength range because of the low absorption in this region. The OH content causes strong absorption peaks in the near infrared region. In order to get good fibres for near infrared region, “water” is removed from the silica. This results in low OH content (less than 2 parts per million).

Cladding

In order to get the light guiding effect the core is coated with a lower index of refraction material. For the highest quality fibres with the lowest absorption, this is fluorine-doped silica, the so-called *silica-silica* or *all-silica fibres*.

Buffer

Without further protection fibres would easily be fractured, because of small scratches or other irregularities. The buffer also determines circumstances of use of the fibre. Temperature range, radiation, vacuum, chemical environment and

bending are factors to be considered. Polyamide buffers offer a wide temperature range (–100 to 400°C) and superior solvent resistance. For extreme temperatures (–190 to 750°C) a gold buffer is used. Gold-coated fibres are virtually inert to all environments.

Most spectroscopic applications with fibre optics have been restricted to wavelengths above 230 nm, because standard silica fibres with un-doped cores and fluorine doped cladding are frequently damaged by exposure to deep-UV light (below 230 nm) Recently though, the availability of a modified core (UVM) provides long-term stability transmission for wavelengths below the above-mentioned.

2.2.6 Quantitative applications

The important characteristics of spectrophotometric methods are, 1) *Wide applicability*: Gargantuan numbers of inorganic and organic species absorb ultraviolet or visible radiation and are thus amenable to direct quantitative determination.

Some examples of this *broad* range of applications include:

- Spectrophotometric [28] method for the determination of iodate in table salt using new chromogenic reagents
- A study [29] on the solid phase extraction and spectrophotometric determination of mercury in water and biological samples with 5-(p-aminobenzylidene)-thiorhodanine
- Solid phase [30] extraction and spectrophotometric determination of gold with 5-(2-hydroxy-4-nitrophenylazo)-rhodanine as chromogenic reagent
- A study [31] on the colour reaction of V(V) with 2-(2-quinolylazo)-5-diethylaminophenol and its application
- Spectrophotometric [32] studies of the behavior of multi-dentate ligands with Cu(II) in methanol solution

- Determination [33] of total iron as Fe(II) in multivitamins, haematinics and natural waters using a sequential injection system

The examples mentioned are well suited to typical characteristics of this type of technique, as detailed in points 1 to 4 below.

1) High sensitivity

Typical detection limits for absorption spectrophotometric methods range from 10^{-4} to 10^{-5} M. This range may be extended to 10^{-6} or even 10^{-7} with certain procedural modifications.

2) Moderate to high selectivity

If a wavelength can be found at which the analyte alone absorbs, preliminary separations become unnecessary. If overlap of wavelengths occurs, corrections may be made by measurements at other wavelengths, therefore sometimes eliminating the need for a separation step.

3) Good Accuracy

The relative errors in concentration encountered with typical ultraviolet / visible work lie in the range of 1 to 5 %, and may be further decreased with special precautions.

4 Ease and convenience

Measurements are rapid on modern instruments. Automation is also very often an option.

2.2.7 Transition metal ions in aqueous solution

Transition elements are often defined as those which, *as elements*, have partly filled *d* or *f* shells. The transition elements are all metals that conduct heat and electricity well. They form many *coloured* and paramagnetic compounds because of their partially filled shells [34]. Absorption of radiation involves transitions

between filled and un-filled *d* orbitals, with energies that depend on the ligands bonded to the metal ion.

Crystal Field Theory (is a model that describes the electronic structure of transition metal compounds, all of which can be considered coordination complexes. It successfully accounts for some magnetic properties, colours, hydration enthalpies, and spinel structures of transition metal complexes. It does not attempt to describe bonding but provides a powerful yet simple method of understanding and correlating properties that arise primarily from the presence of partly filled shells. The Crystal Field Theory provides a way of determining, by simple electrostatic considerations, how energies of the metal ion orbitals will be affected by the set of surrounding atoms or ligands.

The focus in this dissertation is on chromium in its hexavalent oxidation state that is *degenerate* in *d* electrons. Cr(VI) leaves no unpaired electrons and therefore rules out ligand field theory (*re-distribution of electrons* among orbitals that are mainly localized on the metal atom) in an approach of describing its colours.

There are also electronic transitions in which an electron moves from an essentially ligand-based orbital to an essentially metal-based orbital or vice versa [35]. When this happens, charge is transferred, and is known as charge-transfer transition (CT). One example is the oxygen-to-chromium charge transfer in the yellow chromate of K_2CrO_4 and the orange dichromate of $(NH_4)_2Cr_2O_7$ [36]. When an electron passes from a ligand-based orbital to a metal-based one, this is known as ligand-to-metal charge transfer (LMCT). In such charge-transfer transitions the electron(s) moves through considerable distance, which means that the transition dipole moment may be large and, because the transitions are not parity-forbidden, the absorptions are correspondingly intense. As an example the permanganate ion, MnO_4^-, is intense in colour [37]. In this case, as in chromate and dichromate spectra, an oxygen lone-pair electron is promoted into a low-lying *e* metal orbital. High metal oxidation states correspond to a low *d*

orbital population (e.g. Cr(VI) is d^0), so the acceptor level is available and low in energy [38]. The colour arises from charge transfer and not *d-d* spectra [39].

Chromate (yellow colour) has two ligand-metal charge transfer bands at wavelengths 258 nm ($O^{2-}(\pi) \rightarrow Cr(3d\ t_{2g})$) and 349 nm ($O^{2-}(\pi) \rightarrow Cr(3d\ e_g)$) [40].

For quantitative purposes, charge-transfer absorption is particularly important because molar absorptivities are unusually large (ε_{max} greater than 10 000), a circumstance that leads to high sensitivity [41].

2.2.8 Chromium(VI) ions in aqueous solution and their spectra

The element chromium has an electronic structure of Cr [Ar] $3d^5\ 4s^1$.

A limited number of Cr(VI) compounds are known. These are very strong oxidising agents and include chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$) and chromium trioxide (CrO_3).

In alkali solutions above pH 6, CrO_3 forms the tetrahedral yellow chromate ion, CrO_4^{2-}. Between pH 2 and 6, $HCrO_4^-$ and the orange-red dichromate, $Cr_2O_7^{2-}$ are in equilibrium. At pH values below 1 the main species is H_2CrO_4. The equilibria are,

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad (2.8)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad (2.9)$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ HCrO_4^- \qquad (2.10)$$

In addition, there are the base-hydrolysis equilibria [42]

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-} \qquad (2.11)$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \qquad (2.12)$$

There appears to be some controversy on the existence of $HCrO_4^-$. It was claimed [3] that $HCrO_4^-$ is spectrophotometrically undetectable and that $Cr_2O_7^{2-}$ is the only species formed upon acidification of CrO_4^{2-}.

This was however cleared up by a spectrophotometric [4] study of the protonation and dimerization of CrO_4^{2-} and led to the evidence that $HCrO_4^-$ existed. The results of the investigation did not corroborate the work in which the non-existence of $HCrO_4^-$ was claimed.

The absorption spectra of Cr(VI) species are dependent on both *concentration* and *pH* [12].

The change in absorption as a function of pH, for two solutions at two Cr(VI) concentrations, differing by a factor of 19, is shown in Figures 2.7 and 2.8.

One can observe the absorbance changes from ca. 0.45 units at point (a) in Figure 2.8 to 0.15 units at point (b), at a *fixed* Cr(VI) concentration of 0.1 mM, simply by varying the pH from 7 (point (a)) to 2.5 (point (b)). This shows that absorption spectra of Cr(VI) species are pH dependent.

In the second example of Figure 2.8, one can observe the absorbance changes from ca. 1.8 units at point (a) to ca. 0.6 units at point (b), at a *fixed* Cr(VI) concentration of 1.92 mM, simply by varying the pH from 8 (point (a)) to 2.1 (point (b)). If one compares this to the similar pH range used in Figure 2.7, it becomes obvious that the change in absorption is now concentration dependent.

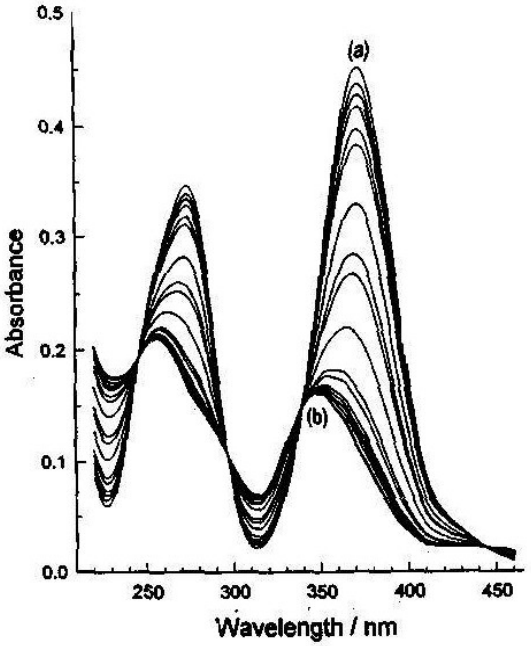

Figure 2.7. Change in absorption spectra with change in pH from 7 (a) to 2.5 (b) of a 0.1 mM Cr(VI) solution measured in a 1 cm cuvette [4].

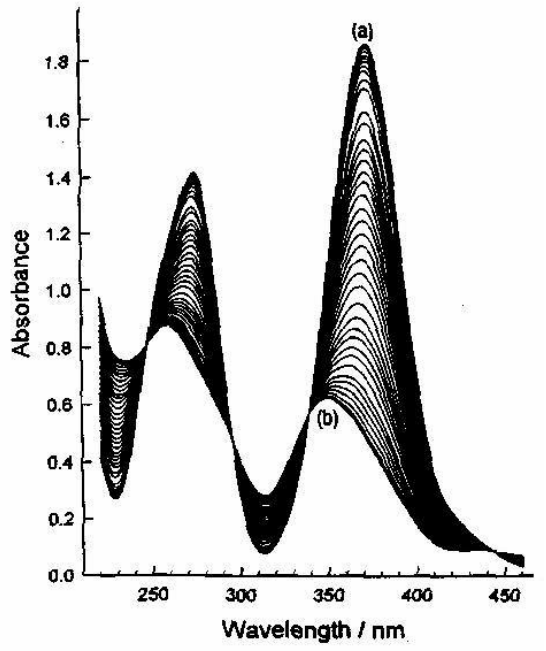

Figure 2.8. Change in absorption spectra with change in pH from 8 (a) to 2.1 (b) of a 1.92 mM Cr(VI) solution measured in a 0.2 cm cuvette. [4].

Literature also describes the dominance and dependence of Cr(VI) species on concentration and pH by means of equilibrium diagrams, as indicated by Figure 2.9.

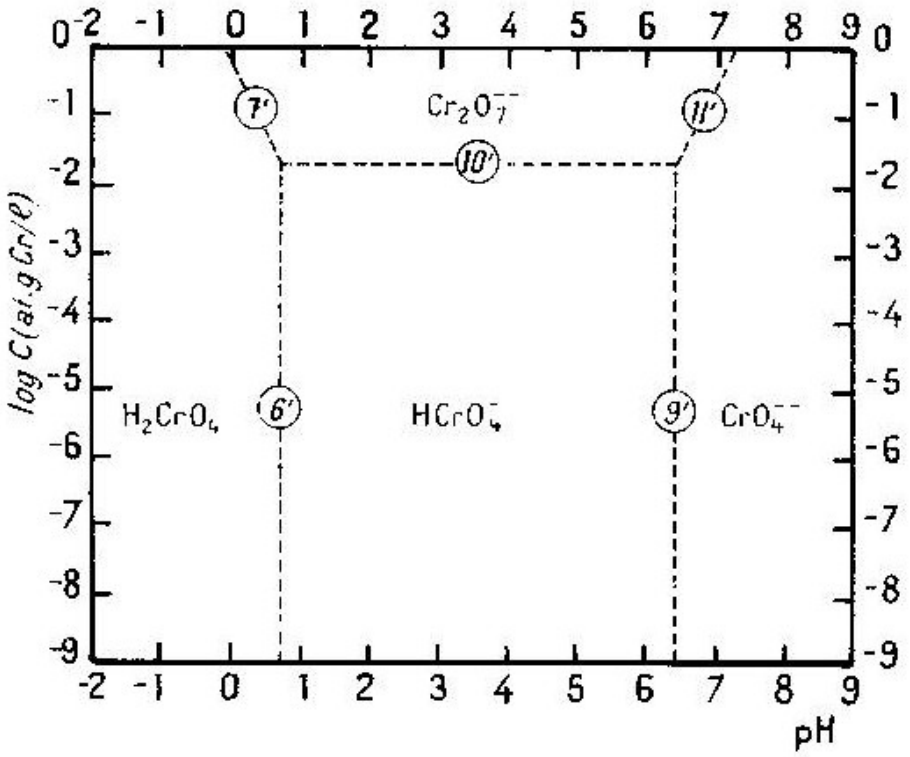

Figure 2.9 Domains of predominance of the ions of hexavalent chromium at 25°C [43].

Where, the dashed lines represent the limits of the domains of relative predominance of the dissolved substances, thus

6′	=	$H_2CrO_4 / HCrO_4^-$	$pH = 0.75$
7′	=	$H_2CrO_4 / Cr_2O_7^{2-}$	$pH = -0.09 - ½ \log C$
9′	=	$HCrO_4^- / CrO_4^{2-}$	$pH = 6.45$
10′	=	$Cr_2O_7^{2-} / HCrO_4^-$	$0 = 1.68 + \log C$
11′	=	$Cr_2O_7^{2-} / CrO_4^{2-}$	$pH = 7.29 + ½ \log C$

The analysis of Cr(VI) by UV–VIS spectroscopy in synthetic and plant streams will be practically investigated.

2.3 ION SELECTIVE ELECTRODE (ISE) AND POTENTIOMETRIC MEASUREMENT

Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells in the absence of appreciable currents. The equipment used in potentiometric methods is simple and inexpensive and includes a *reference electrode*, an *indicator electrode* and a *potential measuring device.*

Measurements include pH and ion quantifications by selective determination.

2.3.1 Cell potential

The electrochemical potential of a cell is related to the activities of the reactants and products of the cell reaction and indirectly to the molar concentrations. The relationship between the *activity* a_i of a chemical species and its molar concentration $[i]$ is given by the expression,

$$a_i = \gamma_i [i] \qquad (2.13)$$

where, a_i = activity of the solution (mol/dm^3)

γ_i = is a dimensionless quantity called the activity coefficient

$[i]$ = molar concentration of i (mol/dm^3)

The activity coefficient and thus the activity of i, varies with the ionic strength of the solution such that the use of a_i instead of $[i]$ in the electrode potential calculation, or equilibrium calculations, renders the numerical value obtained independent of the ionic strength [44].

The potential of all ion selective electrodes is a logarithmic function of the activity of the free ion to which the electrode in question responds. This relationship is given by the well-known *Nernst* equation.

$$E = E^{\bullet} + \frac{RT}{n_i F} \ln\left(a_i\right) \tag{2.14}$$

where, E = The potential measured between indicator and reference electrode

$E^{\bullet}$ = The sum of the standard potential of the electrode and the junction potential

R = Gas constant (8.31441 J.K^{-1}.mol^{-1})

T = Absolute temperature in K (273.15 K + t in °C)

n_i = Charge of the analyte ion (including its sign)

F = Faraday constant (96 484.56 C.mol^{-1})

a_i = Activity of analyte ion i

Selectivity of potentiometric sensors, such as ion selective electrodes is defined by the selectivity coefficient, $K_{i,j}$, for the primary ion, i, against the interfering ion, j, in the Nikolsky-Eisenman equation [21].

$$E = E^{\bullet} + \frac{RT}{z_i F} \ln\left[a_i + \sum_j K_{ij}\left(a_j\right)^{Z_i/Z_j}\right] \tag{2.15}$$

where, Z_i = Charge of the primary analyte ion (including its sign)

Z_j = Charge of the interfering analyte ion (including its sign)

a_i = Activity of analyte ion i – the primary ion

a_j = Activity of analyte ion j – the interfering ion

K_{ij} = The selectivity coefficient

2.3.2 Liquid junction potential and Reference electrode

When two electrolyte solutions of different compositions are brought into contact with one another, a potential develops across the interface. This junction potential arises from the unequal distribution of cations and anions across the boundary due to differences in the rates at which these species diffuse. It has been found experimentally that the magnitude of the junction potential can be greatly reduced by the introduction of a concentrated electrolyte solution between two solutions [45].

In electroanalytical applications, it is advantageous to have a half-cell potential at one of the electrodes that is known and stable, and most importantly insensitive to the composition of the solution under study. The electrode that fits this description best is called the reference electrode. The ideal reference electrode is reversible and obeys the Nernst equation, has a potential that is constant in time, returns to its original potential after being subjected to small currents, and exhibits little hysteresis with temperature cycling [46].

Two types of electrodes are in commercial use; the calomel and silver / silver chloride electrode. A modification of the reference electrode is often used by making use of a double-junction electrode which is filled with a neutral electrolyte (e.g. in the case where potassium ions interfere in the determination of sodium ions). Precautions in the use of reference electrodes include making sure the level of the internal liquid is always above that of the sample solution to prevent contaminations of the electrode solution and plugging of the junction due to reaction of the analyte solution with silver or mercury(I) ions from the internal solution. With the liquid level above the analyte solution, some contamination of the sample is inevitable. If this contamination proves to be detrimental to the analytical result, this may be avoided by the use of a salt bridge, between the

analyte and the reference electrode. Double-junction electrodes described above are useful in this type of application.

2.1.3 Indicator electrodes

An assortment of membrane electrodes is available that allows for the determination of cations and anions by direct potentiometric measurement. Most often these membrane electrodes are termed ion selective electrodes because of their high selectivity.

In membrane electrodes the observed potential is a kind of junction potential that develops across the membrane that separates the analyte solution from the reference solution. Ion selective electrodes share common properties which lead to selectivity and sensitivity; minimal solubility, electrical conductivity and selective reactivity [47].

2.3.3.1 The glass electrode for pH measurements

The indicator electrode consists of a thin, pH-sensitive glass membrane sealed onto one end of a heavy-walled glass or plastic tube. The liquid inside the tube consists of an acid of known concentration, and the construction is completed by a wire (e.g. a silver wire in a solution forms a silver / silver chloride reference electrode) which is connected to the terminals of a potential-measuring device. The reference electrode is connected to the other terminal.

The surface of a glass membrane must be hydrated before it functions as a pH electrode. To serve as an indicator for ions, a glass membrane must conduct electricity. Conduction within the hydrated layer involves the movement of hydrogen ions. Equilibrium conditions are a function of activities between the outside (analyte) and inside (known pH solution) of a glass membrane. In this process a boundary potential is developed and used as the indicating parameter for the potentiometric pH measurement with a membrane electrode.

The condition of the pH electrode assembly is subject to fluctuation in time, and it is necessary to calibrate the assembly periodically.

2.3.3.2 The glass electrode for sodium measurements

The determination of sodium with the ion selective electrode represents a selective, rapid, accurate and favourably priced method. The activity of ions can be determined by means of ion selective electrodes. In very dilute solutions the activity corresponds approximately to the concentrations of the respective ion. Ion selective electrodes that have no cross-sensitivity towards ions that are chemically similar do not exist. Ion selective electrodes cannot therefore be said to be absolutely selective.

The measuring range of the sodium glass electrode is between 1×10^{-5} and 1 mol/dm^3 Na^+ (0.23 mg/dm^3 to 22.99 g/dm^3 Na^+). The glass membrane electrode is primarily used for samples with a difficult matrix. The electrode shaft and the membrane are made of glass. The selectivity for Na^+ ions is determined by the composition of the glass membrane. The glass membrane (composition: Li_2O-Al_2O_3-SiO_2) is immersed in water before use; this generates a gel-like hydrated silicic layer [48].

An Ionic Strength Adjustor (ISA) solution, as the name implies is a solution of high ionic strength. It is used to dilute sample solutions and also to fix the ionic strength of the sample. As a result of a constant ionic strength, the activity coefficient γ_i remains virtually unchanged even when measurements are made in very different sample solutions. Apart from fixing ionic strengths of solutions, ISA solutions can also adjust the pH value at the same time. Such solutions are known as Total Ionic Strength Solutions (TISAB). In sodium determinations using a glass membrane electrode it is necessary to use a TISAB solution that also buffers pH values above 9. The reagent that meets these requirements is tris(hydroxymethyl)-aminomethane.

Selectivity is very important and is high for some types of sensors. In complex solutions (i.e. those containing many ions to which the electrode is responsive), the measured potential may not directly obey the Nernstian equation. Therefore, one further improvement that is made in the determination of sodium is to make use of the standard addition technique. The potential of the electrode system is measured before and after the addition of a small volume (often several additions) of a standard to a known volume of the sample. The assumption is made that this addition does not alter the ionic strength, and thus the activity coefficient, γ_i of the analyte. It is further assumed that the added standard does not significantly alter the junction potential.

In working with and handling a sodium glass membrane electrode, the following needs to be noted:

- The electrode needs to be shaken like a clinical thermometer prior to the first measurement to ensure that the inside of the glass membrane is fully lined with a liquid layer i.e. making sure an air bubble is not locked on the inside of the glass bulb
- The glass membrane electrode should be stored dry if it is out of use for longer periods of time. For short-term storage c_{NaCl} = 0.1 mol/dm^3 is suitable. This solution fully recharges the hydrated sodium layer of the glass bulb
- Before being used for the first time, and after long periods out of use, the glass membrane must be activated / conditioned by overnight immersion in c_{NaCl} = 1 mol/dm^3. This solution, as above, also fully recharges the hydrated sodium layer of the glass bulb
- Care should be taken that the internal parts of the reference electrode are well wetted. Any air bubbles formed when the electrolyte is filled in must be removed
- After each measurement the electrode must be thoroughly rinsed with distilled water and wiped off with a slightly moist tissue
- Potassium interferes if present in 500-fold excess compared to sodium

- Under acidic conditions the electrode responds to H_3O^+ ions like a pH glass electrode, measurements must be carried out under alkaline conditions (pH 8 to 10) [49]. This is achieved by adding tris(hydroxymethyl)-aminomethane to the sample

2.1.4 Instruments for measuring cell potentials

Instruments used for measuring cell potentials need resistance that is large with respect to that of the cell. If not, significant error results as a consequence of the IR drop in the cell.

2.4 TITRIMETRIC ACID / BASE ANALYSIS

The standard solutions employed in neutralisation titrations are strong acids (for example HCl) or strong bases (for example NaOH) because these substances react more completely with an analyte than do their weaker counterparts and thus yield sharper equivalence-points. Completeness of the neutralisation reaction may be indicated visually by making use of a substance that displays colour, dependent on pH of the solution in which it is dissolved. Alternatively, completeness of reaction may be evaluated from plots of pH versus added reagents (known as titration curves), and interpreting the data to yield stoichiometric *equivalence* -points. Sigmoidal [50] (shaped like the letter "S") and linear-segment (relating to a straight line or capable of being represented by a straight line for example in oxidation–reduction titrations) curves are common in analytical chemistry practice. The equivalence point (stoichiometric *equivalence*–point) is characterised by large changes in the relative concentrations of the reagent and analyte.

Whenever a weak acid is titrated with a strong base, a buffer solution consisting of a conjugate acid / base pair is formed. (A buffer is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution). Two examples of this are:

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-} \quad (2.16)$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \quad (2.17)$$

The net reaction of (2.16) and (2.17) is shown as (2.18).

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O \quad (2.18)$$

Equation 2.18 holds true provided that the concentration of chromium exceeds approximately 1 g/dm^3 (19.23 mM). The dichromate ion ($Cr_2O_7^{2-}$) is a dimer of the $HCrO_4^-$, less a water molecule [51].

The ability of a buffer to prevent a significant change in pH is directly related to the total concentration of the buffering species as well as to their concentration ratio. This concept is useful in *dichromate* quantification analysis as in equation 2.18 above.

Similarly then, quantification of *Chromic acid* – CrO_3 (Chromium(VI) Oxide) is possible by titrimetric analysis:

If one dissolves solid chromium trioxide in water, aqueous chromic acid is formed as in Equation 2.19.

$$CrO_3(s) + H_2O \longrightarrow H_2CrO_4(aq) \quad (2.19)$$

Equation 2.19 holds true at certain conditions. Interpretation of Figure 2.9 *suggests* that H_2CrO_4 exists at pH smaller than about 1, or if one dissolves solid chromium trioxide in water and the pH is greater than about 1 then, Equation 2.20 holds true.

$$CrO_3(s) + H_2O \longrightarrow H^+ + HCrO_4^-(aq) \quad (2.20)$$

Between pH 2 and 6, $HCrO_4^-$ and the orange-red dichromate, $Cr_2O_7^{2-}$ are in equilibrium [4].

Mixtures of chromic acid and dichromate are thus also quantifiable by titrimetric acid base analysis.

The analysis of mixtures of chromic acid and dichromate by titrimetric methods in synthetic and plant streams will be practically investigated.

CHAPTER 3

EXPERIMENTAL

In this chapter, the experimental techniques and the experiments performed in order to investigate the possibilities of Cr(VI) measurement and speciation analysis best suited for on-line process development, will be described.

As will be communicated later on in the discussion, this project evolved into three phases.

- A spectrophotometric approach with the aim of speciation prediction and quantification
- A spectrophotometric approach combined with ion selective electrode (ISE) measurements, with the aim of indirect speciation analysis and quantification
- A titrimetric approach with the aim of direct speciation analysis and quantification

3.1 PREPARATION AND STANDARDISATION OF Cr(VI) STOCK SOLUTIONS

Stock solutions of Cr(VI) were prepared from sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$) crystals and chromium(VI) oxide crystals (CrO_3) in water.

These solutions were standardised against Iron(II) Sulphate solutions. See Appendix 1 for the standardisation of the Iron(II) Sulphate titrant.

Hexavalent chromium (the analyte) is reduced to trivalent chromium by ferrous ions (the titrant). The potential of the solution being titrated is measured using an automatic titrator, fitted with a Titrode® electrode from Metrohm. The equivalence point in this determination was indicated by a rapid change in potential of the measuring solution.

The reactions taking place were as follows:

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^{-} \quad (3.1)$$

$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{3+} + 7H_2O \quad (3.2)$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} \longrightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+} \quad (3.3)$$

Materials	*Supplied by*
• Deminerlised water	
• $Na_2Cr_2O_7.2H_2O$	Sponsoring company > 99.5 %
• CrO_3	Sponsoring company > 99.6 %
• $Fe_2SO_4.7H_20$ titrant	Previously standardised
• H_3PO_4	Saarchem, 4818040 LC, min. 85 %
• H_2SO_4	Saarchem, 5885060 LP, min. 95 %

Apparatus

- A-grade volumetric flasks and volumetric equipment
- Pipetting equipment or dosing equipment e.g. Metrohm auto-titrators and Dosimat
- 716 / 794 Metrohm auto-titrators and 814 USB Metrohm sample processor.
- Pt Titrode® Electrode from Metrohm
- Tiamo 1.1 Metrohm software

Procedure

- At least three predetermined aliquots of Cr(VI) stock solutions to be evaluated were dispensed into 100 cm^3 beakers
- The samples were placed in position on the 814 USB Metrohm sample processor and the determination started by selection of the appropriate method of analysis

- The sample's analyte concentration was evaluated by the software as per calculation below

The automated method adds water and acid automatically before the determination starts.

Calculation

$$\frac{\text{Titer volume } (cm^3) \text{ x } [FeSO_4] \ (mol/dm^3) \text{ x } 2 \text{ x } M_{(Cr)} \ (g/mol) \text{ x } 1000}{6 \text{ x sample volume } (cm^3)}$$

$$= c_{Cr(VI)} \ (mg/dm^3)$$

3.2 PREPARATION OF SODIUM STOCK SOLUTIONS FOR ION SELECTIVE ELECTRODE MEASUREMENT

Stock solutions of sodium were prepared from sodium chloride (NaCl) crystals in water.

Materials	*Supplied by*
• Ultrapure water,18 MΩ-cm	Mill-Q
• NaCl	Alfa Aesar 99.99 % # 87605
• ISA Solution stock*	Merck > 99.8 % 1.08382.0500

*Ionic strength pH adjusting solution $c_{TRIS} = 1.5$ mol/dm^3
Tris(hydroxymethyl)-aminomethane

Apparatus

- pH / ion meter Metrohm 692
- Dosimat Metrohm 776, magnetic stirrer and exchange unit

- Sodium ion selective electrode Metrohm cat. No. 6.0501.100
- Ag / AgCl reference electrode Metrohm cat. No. 6.0726.107

Procedure

- Approximately 25 g of dried sodium chloride was weighed in a weighing boat, and the mass recorded to 4 decimal places. This was transferred quantitatively into a 1000 cm^3 volumetric flask and made up to the mark with ultra pure water. A mass of 25 421 g NaCl is equivalent to 10 000 mg sodium

- 182 g of Tris (Hydroymethyl)aminomethane was dissolved in 1 dm^3 of ultra pure water. The solution was allowed to adjust to ambient temperature and then made up to the calibrated mark and homogenized

3.3. SPECTROSCOPIC APPROACH WITH THE AIM OF SPECIATION PREDICTION AND QUANTIFICATION

This section provides details of the following information relating to experiments.

- Choice of suitable equipment configurations
- Choice of suitable Cr(VI) concentrations for UV-VIS measurements
- Spectral differences in solutions made from $Na_2Cr_2O_7.2H_2O$ and CrO_3

An Avantes AvaSpec-2048 Optic Spectrometer equipped with an AvaLight-DHS deuterium halogen light source, 50 micro meter slit and transmission dip probe with variable path length was used for absorption measurements.

Absorption measurements of Cr(VI) spectra at different concentrations were recorded in the range 220 – 460 nm at intervals of 1.2 nm at path lengths of 5 and 10 mm respectively. The integration time on the instrument was set such that the maximum counts at the detector over the selected wavelength range were around 14500 counts. The smoothing parameter was initially set at 5 but later set

at a default of 15. The dip probe was initially simply submerged into a sample unprotected from stray light.

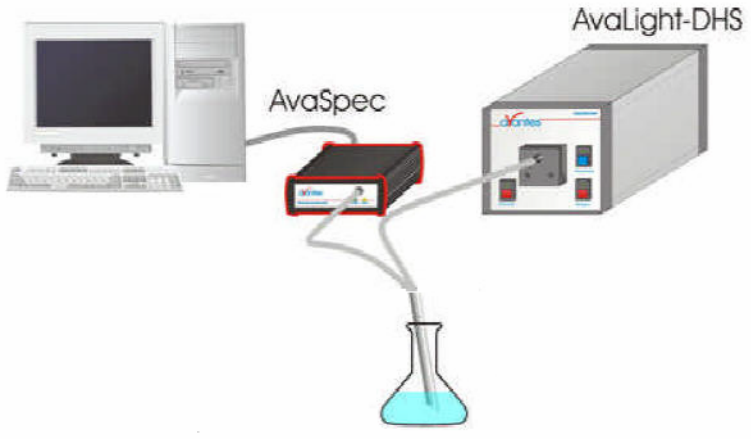

Figure 3.1. UV-VIS Absorbance equipment and its arrangement.

Later it was decided to enclose the dip probe in a “black box” type of an arrangement to measure the effect of the elimination of stray light.

The transmission dip probe was later replaced by a flow-through cell (of fixed path length 1.5 mm), and the system was equipped with a fibre optic switch enabling the spectrometer to reference sample spectra to correct for possible drift.

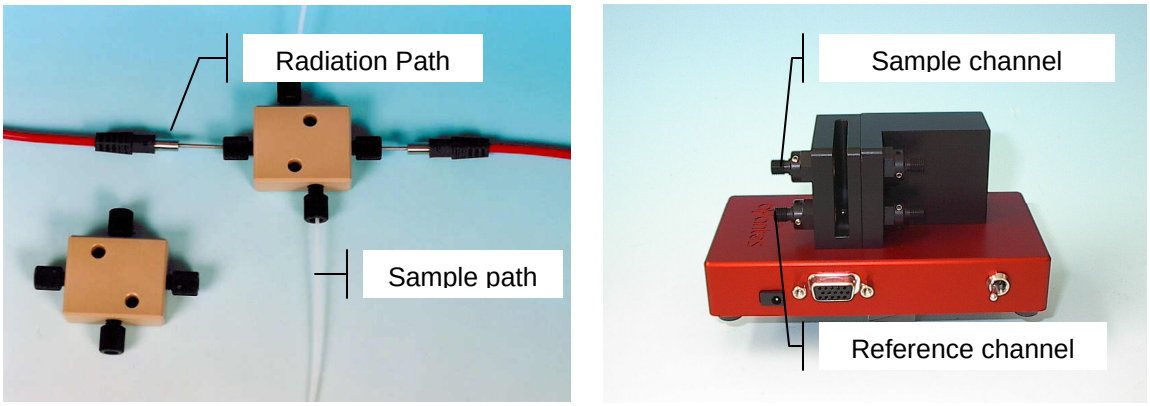

Figure 3.2. Flow through cell and fibre optic switch.

The spectra were measured at room temperature without any specific temperature conditioning of the samples.

Samples of equal concentration of Cr(VI) at 15 and 25 mg/dm^3 were prepared from $Na_2Cr_2O_7.2H_2O$ and CrO_3 to evaluate the differences of their spectra.

Investigation was performed by training neural networks on a series of absorptive scans of various concentrations and ratios of Cr(VI) prepared from $Na_2Cr_2O_7.2H_2O$ and CrO_3 in an effort to measure the effectiveness of using neural networks as a predictive tool in Cr(VI) speciation and quantification. The target error for the training of the neural network was set at 1 % in most cases. A Sigmoidal training function was used with three layers in total – being an input layer, one hidden layer and an output layer. The recorded UV-VIS data was stored in Excel format. This was used to create (i) the calibration matrix of learning sets, and (ii) the test sets. The input layer was defined as the absorbance value per wavelength, and the output was defined as the concentrations of Cr(VI) prepared from $Na_2Cr_2O_7.2H_2O$ and CrO_3.
The software used in this project was WinNN32 1.6,
http://www.nuceng.com/WinNN.htm) by Dr. Yaron Danon [52].

Figure 3.3. Screen shot of the "About" properties of the Artificial Neural Network software used in this project.

3.4 SPECTROSCOPIC APPROACH LINKED TO ION SELECTIVE ELECTRODE MEASUREMENT, WITH THE AIM OF SPECIATION PREDICTION AND QUANTIFICATION

The equipment used for the spectrophotometric determinations is described in section 3.3. A flow cell was used in the place of the transmission dip probe with variable path length.

Absorption measurements of Cr(VI) spectra at different concentrations were recorded in the range 220 – 460 nm at intervals of 1.2 nm at a path length of 1.5 mm. The samples and standards were adjusted by adding TRIS such that the pH of the sample was greater than 6. This was achieved by making samples and standards 0.03 M in TRIS. The spectra were measured at room temperature without any specific temperature conditioning of the samples. Samples were diluted 25000 times to fall within the calibration range. Calibration samples were prepared from a previously standardised sodium dichromate solution in the range 5 – 30 mg/dm^3 Cr(VI).

For the ion selective electrode measurements, a standard addition technique was used, by dosing predefined volumes of a stock solution of sodium to the samples. The ionic strength and pH of the sample were adjusted. Samples were made 1 M in TRIS and 0.1 M in HCl such that the measured sample had a pH of between 9 and 10. Samples were diluted to fall within the linear response range of the sodium glass electrode.

Samples were diluted twice to yield a total dilution of 1428 times. 1 cm^3 of sample was diluted to 100 cm^3 in water (to yield a dilution factor of 100 times). 7 cm^3 aliquot of this diluted sample was added to a 100 cm^3 volumetric flask, 66.7 cm^3 1.5 M TRIS and 1 cm^3 10 M HCl were also added and topped to the mark with water. A 40 cm^3 aliquot was analysed by a standard addition technique by adding 0.1, 0.2, 0.3 and 0.4 cm^3 of a stock solution of sodium. The addition of the sodium stock solution represents *approximately* 50, 100, 150 and 200% of the sodium content in the diluted sample analysed. The potential was measured after each addition, and the ion meter calculated the results automatically.

3.5 A TITRIMETRIC APPROACH WITH THE AIM OF DIRECT SPECIATION ANALYSIS AND QUANTIFICATION

The equipment used in the laboratory study for a titrimetric technique for the analysis of chromic acid and sodium dichromate mixtures were as follows,

Dosing of Cr(VI) stock solutions

- Titrando 836 from Metrohm fitted with two 800 Dosinos of 5 and 10 cm^3 burette volume
- Tiamo 1.1 Metrohm software

Titration equipment

- 716 DMS Titrino fitted with a 50 cm^3 burette, from Metrohm
- pH electrode 6.0262.100 from Metrohm
- Tiamo 1.1 Metrohm software

3.5.1 Standardisation of sodium hydroxide titrants

Materials	*Supplied by*
• Ultrapure water, 18 MΩ-cm	Mill-Q
• Potassium hydrogen phthalate (KHP)	Merck 99.95% # 1.04874.0250

Procedure

- Approximately 6 g of previously dried and cooled KHP was placed in a 100 cm^3 beaker, and the mass was recorded to 4 decimal places. ca. 30 cm^3 water was added

- These solutions were titrated with freshly prepared 1 M sodium hydroxide solution to the first equivalence-point according to the following parameters using a *monotonic* titration technique. Start volume 18 cm^3, start delay of 60 seconds, signal drift of 20 mV min^{-1}, waiting time 38 seconds, volume increment 0.1 cm^3 and a maximum dosing rate 50 cm^3 min^{-1}

Calculation

$$\frac{\text{Mass KHP (g) x 1000}}{M_{(\text{KHP})}(\text{g/mol}) \text{ x titer volume } (\text{cm}^3)}$$

$$= c_{\text{NaOH}} \ (\text{mol/dm}^3)$$

3.5.2 Preparation, standardisation of Cr(VI) stock solutions and titration of mixtures

Stock solutions of Cr(VI) were prepared from sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$) crystals (approximately 200 g/dm^3) and chromium(VI) oxide crystals (CrO_3) (approximately 100 g/dm^3) in water. These solutions were standardised against Iron(II) Sulphate solutions. See Appendix 1 for the standardisation of the Iron(II) Sulphate titrant.

Quantities of Cr(VI) were dispensed in various ratios, diluted with approximately 50 cm^3 of water and titrated against a previously standardised sodium hydroxide titrant according to the following parameters using a *dynamic* titration technique to two equivalence-points. Start volume 0 cm^3, start delay 0 seconds, signal drift 20 mV min^{-1}, waiting time 38 seconds, minimum volume increment 0.01 cm^3 and dosing rate of 20 $cm^3\,min^{-1}$.

The reactions taking place were as follows: *(see discussion in section 4.5 of Chapter 4)*

Equivalence-point 1:

$$H_2CrO_4 + OH^- \rightleftharpoons HCrO_4^- + H_2O \qquad (3.4)$$

Equivalence-point 2:

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O \qquad (3.5)$$

Calculation

Equivalence-point 1

$$\left(\frac{\text{Titer volume } (cm^3) \text{ x } c_{NaOH} \text{ } (mol/dm^3) \text{ x } M_{(Cr)} \text{ } (g/mol)}{1000} \right) \text{ x } 1000$$

$$= \text{mass Cr(VI) (mg) (from chromic acid)} \qquad \{1\}$$

1 mol Cr(VI) from Chromic acid (H_2CrO_4) is equivalent to 1 mol $HCrO_4^-$ which is equivalent to ½ mol of $Cr_2O_7^{2-}$ *which is formed when* $HCrO_4^-$ *dimerises.*

Calculation

Equivalence-point 2

$$\left(\frac{\left(\text{ Titer vol. EP2 } (cm^3) - \text{Titer vol. EP1 } (cm^3) \right) \text{ x } c_{NaOH} \text{ } (mol/dm^3) \text{ x } M_{(Cr)} \text{ } (g/mol)}{1000} \right) \text{ x } 1000$$

= mass Cr(VI) (mg) (from chromic acid and dichromate)

{2}

Therefore {2} – {1}

= Cr(VI) (mg) (from dichromate)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 ON-LINE ANALYSER DESIGN REQUIREMENTS

The following sets of requirements were stipulated by the sponsoring company as the minimum criteria to be met by an on-line measurement.

The analyser should be capable of measuring a sample from the latter stages of the electrolytical production plant. The analyser should be capable of measuring the sample's chromic acid and sodium dichromate content, and the expression of this data in a convention (or nomenclature) used routinely in the electrolytical production plant.

The rate at which the analysis should be reported should range between 10 to 30 minutes per set of result -10 minutes being acceptable for the electrolytical production plant process manipulation and allowance for operating personnel to use this information accordingly.

The accuracy of the analytical data should be better than or equal to 1 %.

4.2 HISTORICAL DATA AND NOMENCLATURE USED

The following expression of data is used at the sponsoring company.

The concentrations of CrO_3 (CA) and $Na_2Cr_2O_7.2H_2O$ (SDC) may be calculated on a *m/v* (e.g. g/dm^3) or a *m/m* (e.g. g/kg) basis. Sodium dichromate is expressed as $Na_2Cr_2O_7.2H_2O$, ($M_{(SDC)}$ 298 g/mol). Chromic acid ($M_{(CA)}$ 100 g/mol) is also expressed as $Na_2Cr_2O_7.2H_2O$.

From the above two statements it is clear that a sample's Cr(VI) content, whether this is contributed from the sample's dichromate content or it's chromic acid

content, is expressed as $Na_2Cr_2O_7.2H_2O$ and is simply termed as “sodium dichromate equivalence”.

A term used in the electrolytical production plant called “acidification” is a ratio of CrO_3 to $Na_2Cr_2O_7.2H_2O$ as in the calculations that follow:

$$\frac{c_{CA}\ (g/dm^3)\ \text{expressed as}\ c_{SDC}\ (g/dm^3)\ \text{x}\ 100}{\left(c_{CA}\ (g/dm^3 \text{expressed as}\ c_{SDC}\ (g/dm^3)\right)\ +\ c_{SDC}\ (g/dm^3)}$$

$$\frac{c_{CA}\ (g/dm^3)\ \text{x}\ 1.49^{*}\ \text{x}\ 100}{\left(c_{CA}\ (g/dm^3)\ \text{x}\ 1.49\right)\ +\ c_{SDC}\ (g/dm^3)}$$

*1 g CrO_3 is equivalent to 1.49 g $Na_2Cr_2O_7.2H_2O$

Data from the process’ database (*Ref. 1 on attached CD*) shows that the total Cr(VI) content in a final stage process stream fluctuates between 481 and 557 g/dm^3. The contribution of the chromic acid content to the *total* Cr(VI) content fluctuates between 288 – 349 g/dm^3. The contribution of the sodium dichromate content to the total Cr(VI) content fluctuates between 169 – 227 g/dm^3.

The information from Figure 4.1 became the basis for the development of the analytical working range to be measured in an on-line application.

4.3 SPECTROSCOPIC APPROACH, WITH THE AIM OF SPECIATION PREDICTION AND QUANTIFICATION

The original scope of the project called for a spectroscopic detection tool, as the basis of the development of the analyser. The company Avantes - (www.avantes.com) was identified as the most suitable supplier of appropriate equipment. This equipment comes as a modular system that can be designed, modified, expanded, etc. according to the needs of the experiment.

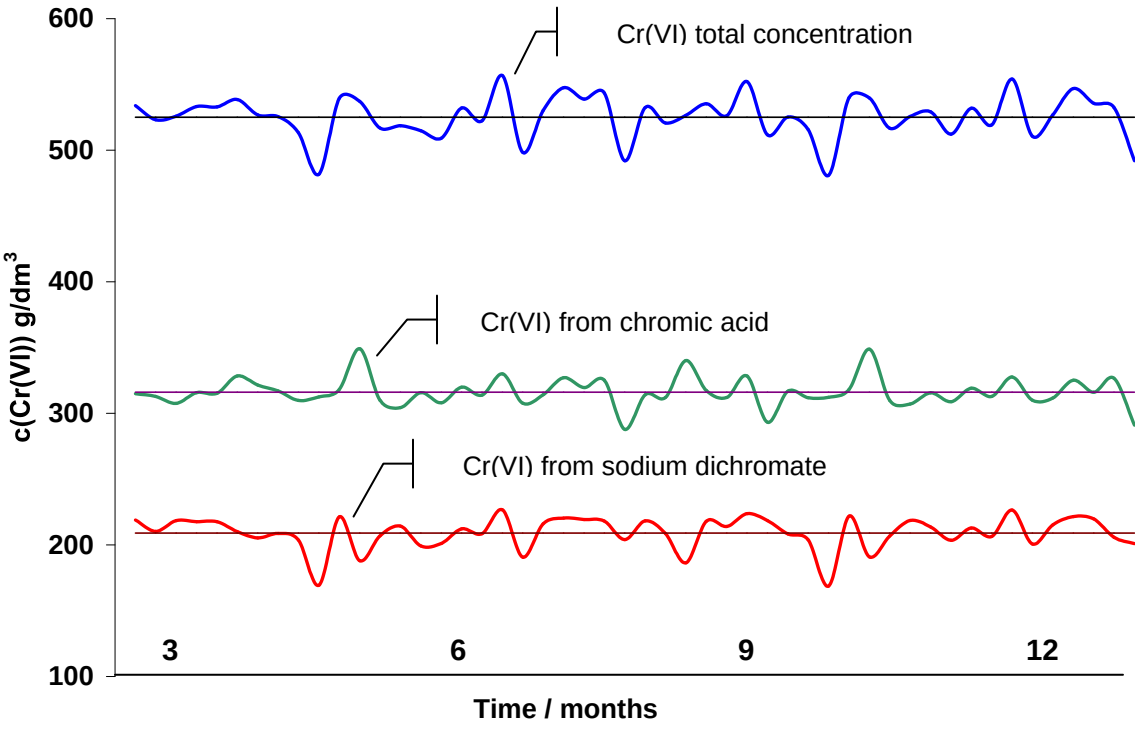

Figure 4.1. Historical data of Cr(VI) content from chromic acid and sodium dichromate in final stage process stream.

4.3.1 Choice of suitable equipment configuration

Development of the on-line instrument was started by investigation of the analytical measuring device. The spectrophotometer was equipped with a transmission dip probe of variable path length.

Samples of Cr(VI) prepared from *sodium dichromate* in the range of *1 mg/dm^3* to *400 g/dm^3* were used for testing purposes. The absorptive scans (*Ref. 2 on attached CD*) were evaluated for details of useable working ranges and consistency in overall appearance. A second purpose of the evaluation in the above mentioned ranges was to determine at what concentrations an absorbance maximum of ca. 1 unit was exceeded. The path length was initially set at 10 mm. A smoothing parameter (See appendix 2 for definition) of 5 was

applied. A *selection* of the spectra in the prepared concentration ranges is shown in Figures 4.2 and 4.3 respectively.

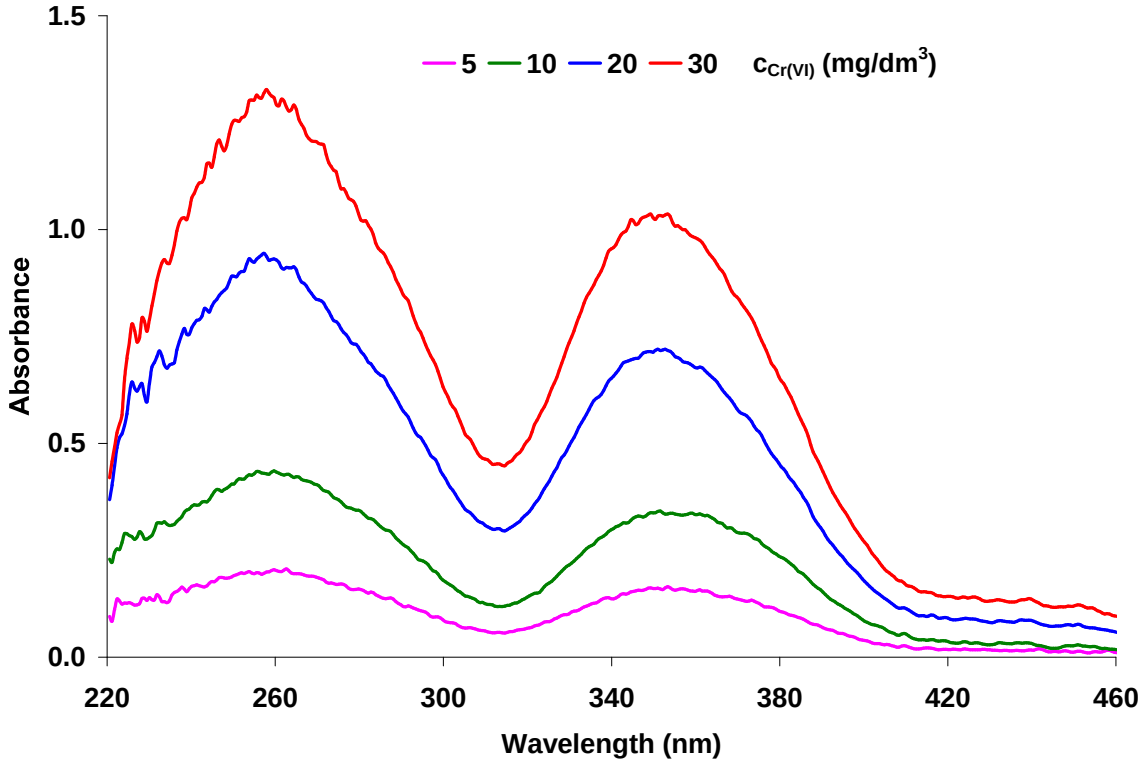

Figure 4.2. Change in absorbance for diluted Cr(VI) solutions; a 10 mm dip probe was used. The samples were prepared from sodium dichromate.

From the information seen in Figures 4.2 and 4.3 it became evident that a useable concentration range should not exceed ca. 30 to 40 mg/dm^3. Distortion of the data occurs at higher Cr(VI) concentrations (> 50 mg/dm^3) and the curves are not smooth as expected.

As mentioned above, the total Cr(VI) content in a final stage process stream ranges between 481 and 557 g/dm^3 (an average of 525 g/dm^3) which would thus require a dilution of ca. 15 000 times, to bring this sample into an acceptable concentration range as to prevent absorption units exceeding ca. 1.

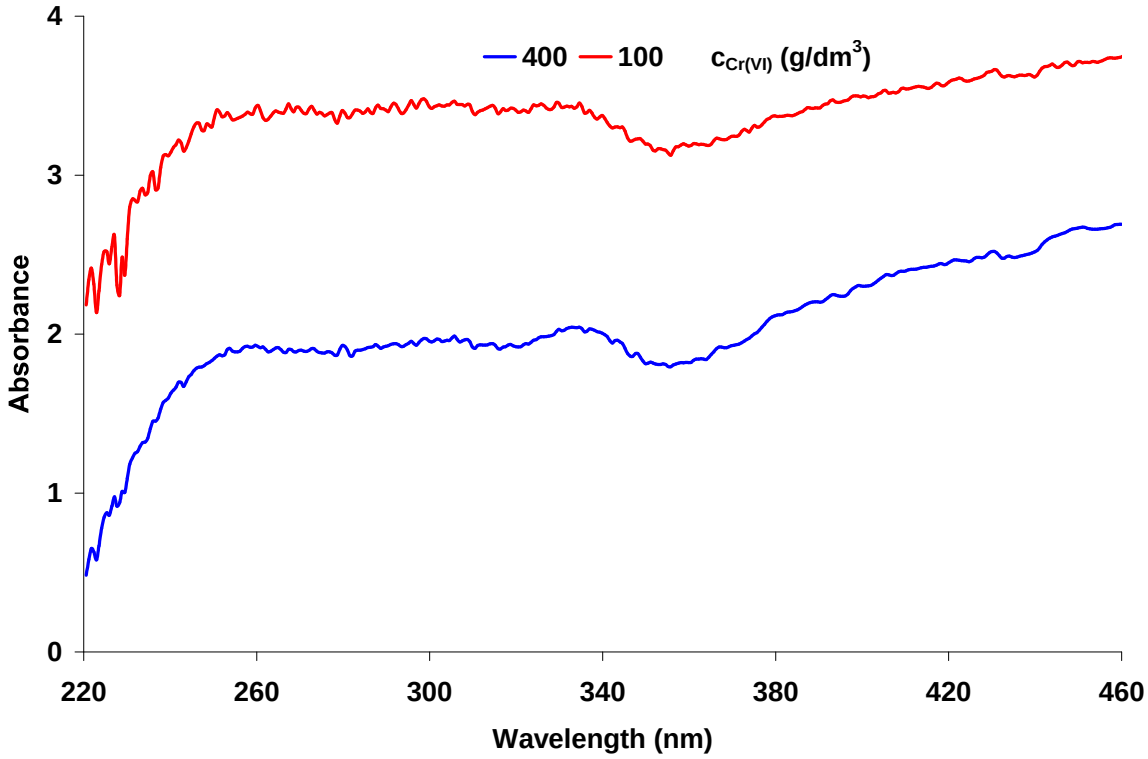

Figure 4.3. Change in absorbance for concentrated Cr(VI) solutions; a 10 mm dip probe was used. The samples were prepared from sodium dichromate.

Manipulation of the *individual* contribution of Cr(VI) from chromic acid and sodium dichromate in this process stream, together with the determined dilution factor (ca. 15 000) yielded an average Cr(VI) content from chromic acid of 21 mg/dm^3 and Cr(VI) content from sodium dichromate of 13 mg/dm^3.

A set of samples was prepared to bracket the expected concentrations of 21 and 13 mg/dm^3 of chromic acid and sodium dichromate respectively. These ranged from 16 to 26 mg/dm^3 for Cr(VI) prepared from chromic acid, and 8 to 18 mg/dm^3 for Cr(VI) prepared from sodium dichromate. See Table 4.1.

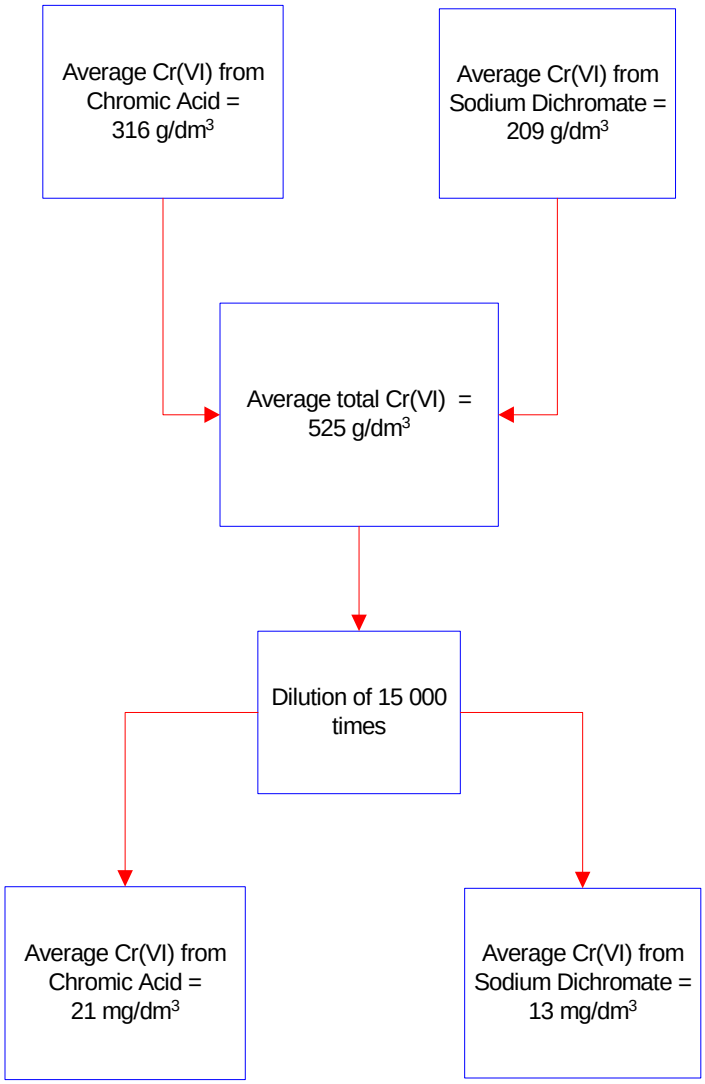

Figure 4.4. Dilution requirements for a process stream sample according to the data points in Figure 4.1.

A selection of solutions (in bold below) were measured with a path length of 5 mm and smoothing parameter of 5 and 15 respectively. A smoothing parameter of 15 was applied with the aim of obtaining smoother and more reproducible curves. A light shield was used to protect the dip probe from stray radiation.

Solution no	$c_{Cr(VI)}$ Chromic acid (mg/dm^3)	$c_{Cr(VI)}$ Sodium dichromate (mg/dm^3)	$c_{Cr(VI)}$ Total (mg/dm^3)
1	**16.0**	**8.0**	**24.0**
2	18.5	8.0	26.5
3	21.0	8.0	29.0
4	23.5	8.0	31.5
5	**26.0**	**8.0**	**34.0**
6	16.0	10.5	26.5
7	18.5	10.5	29.0
8	21.0	10.5	31.5
9	**23.5**	**10.5**	**34.0**
10	26.0	10.5	36.5
11	16.0	13.0	29.0
12	18.5	13.0	31.5
13	**21.0**	**13.0**	**34.0**
14	23.5	13.0	36.5
15	26.0	13.0	39.0
16	16.0	15.5	31.5
17	**18.5**	**15.5**	**34.0**
18	21.0	15.5	36.5
19	23.5	15.5	39.0
20	26.0	15.5	41.5
21	**16.0**	**18.0**	**34.0**
22	18.5	18.0	36.5
23	21.0	18.0	39.0
24	23.5	18.0	41.5
25	**26.0**	**18.0**	**44.0**

Table 4.1. Samples prepared to bracket the required concentrations of chromic acid and sodium dichromate.

The absorptive scans (*Ref. 3 on attached CD*) shows that a smoothing parameter of 15, with a light shield yields the best quality of a scan. A *portion* of the scan is shown below, detailing this improvement. By decreasing the path length to 5 mm the absorbance value is also decreased compared to 10 mm, for similar concentrations of Cr(VI), as expected from Beer's law. This has its advantage in keeping the absorbance data below 1 unit, and will therefore be in an accurate range of measurement.

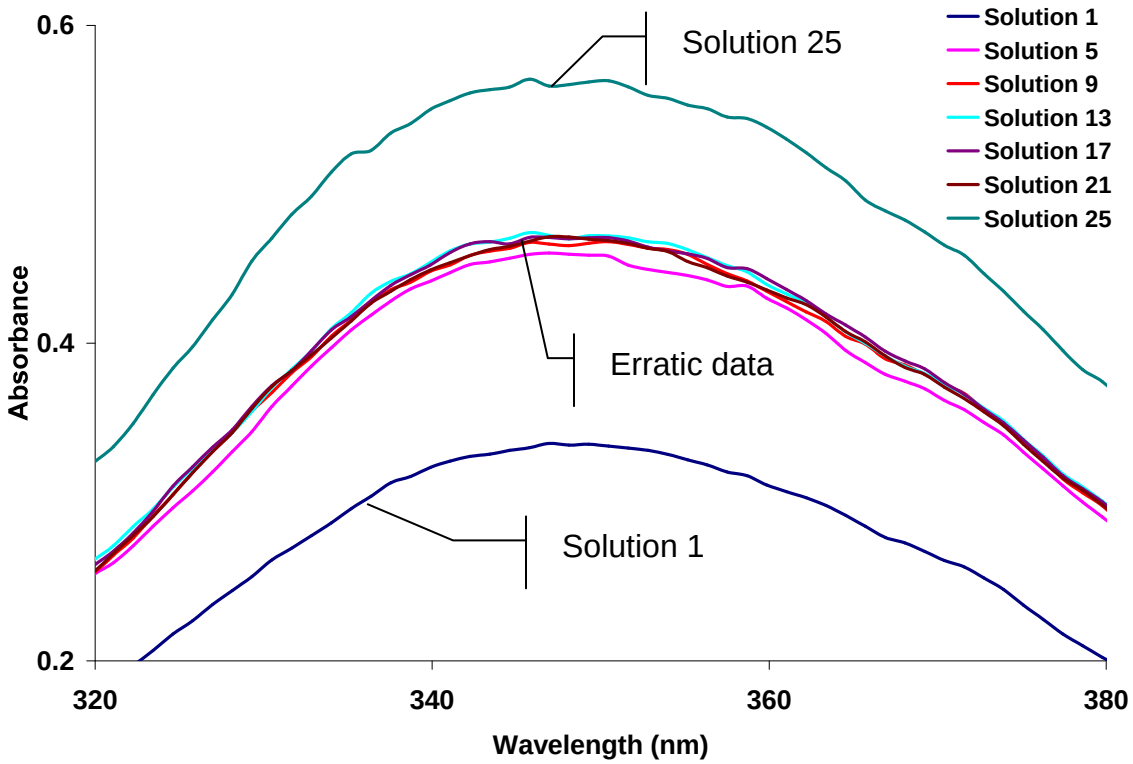

Figure 4.5. Smoothing parameter of 5 applied to data measurements. The curves are inconsistent from one concentration step to the next.

The best suited operating conditions in hardware and software configurations at this stage of the investigation were thus:

- A path length setting of 5 mm
- A smoothing parameter of 15, and
- Light shield installed

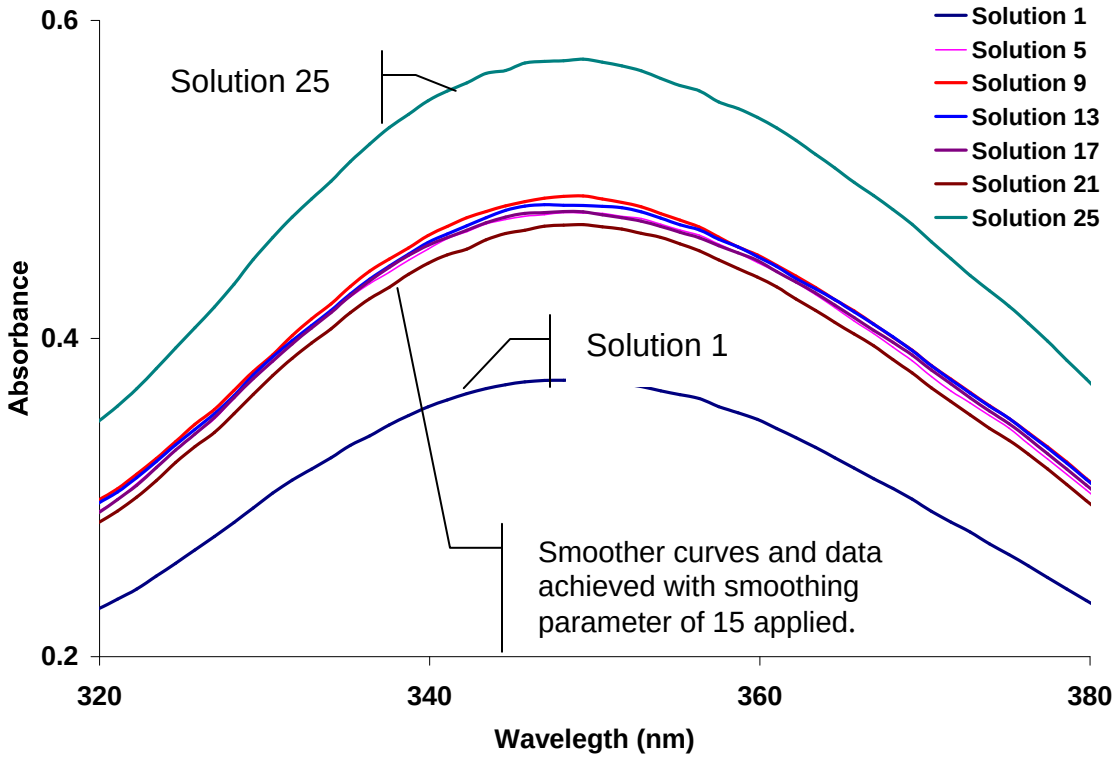

Figure 4.6. Comparison of data in changing the smoothing parameter from 5 to15.

4.3.2 Investigation of changes in absorptive spectra with sodium dichromate and chromic acid at constant Cr(VI) concentrations.

Dilute solutions prepared from $Na_2Cr_2O_7.2H_20$ and CrO_3 suggest that a spectral shift is evident for equal hexavalent chromium concentrations. Figure 4.7 shows that sodium dichromate absorbs radiation at approximately 2 to 5 nm on the longer wavelength side than that of chromic acid. This is known as a bathochromic or red shift. (*Ref. 4 on attached CD*)

Similarly, the absorption maxima are different. As an example at λ_{350} the shift is 0.03 and 0.01 absorption units for a 25 mg/dm^3 and 15 mg/dm^3 Cr(VI) concentration respectively.

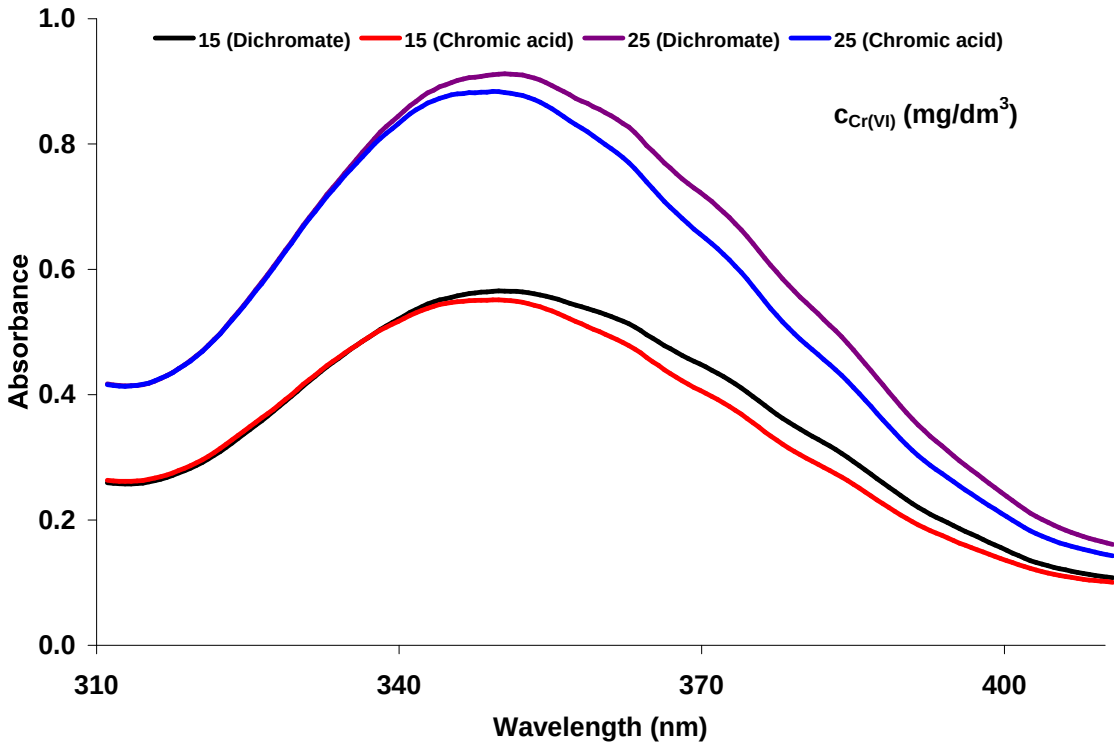

Figure 4.7. Comparison of data of equal Cr(VI) content prepared form chromic acid and sodium dichromate.

Cleary the spectra of solutions of $Na_2Cr_2O_7.2H_20$ and CrO_3 at equal Cr(VI) concentrations are different. Cruywagen et al.'s [4] data showed a similar trend. The most likely explanation for this would be a change in pH at equal Cr(VI) concentration.

Measured data (*Ref. 5 on attached CD*) confirms this trend. Samples prepared from chromic acid were more acidic than those prepared from sodium dichromate.

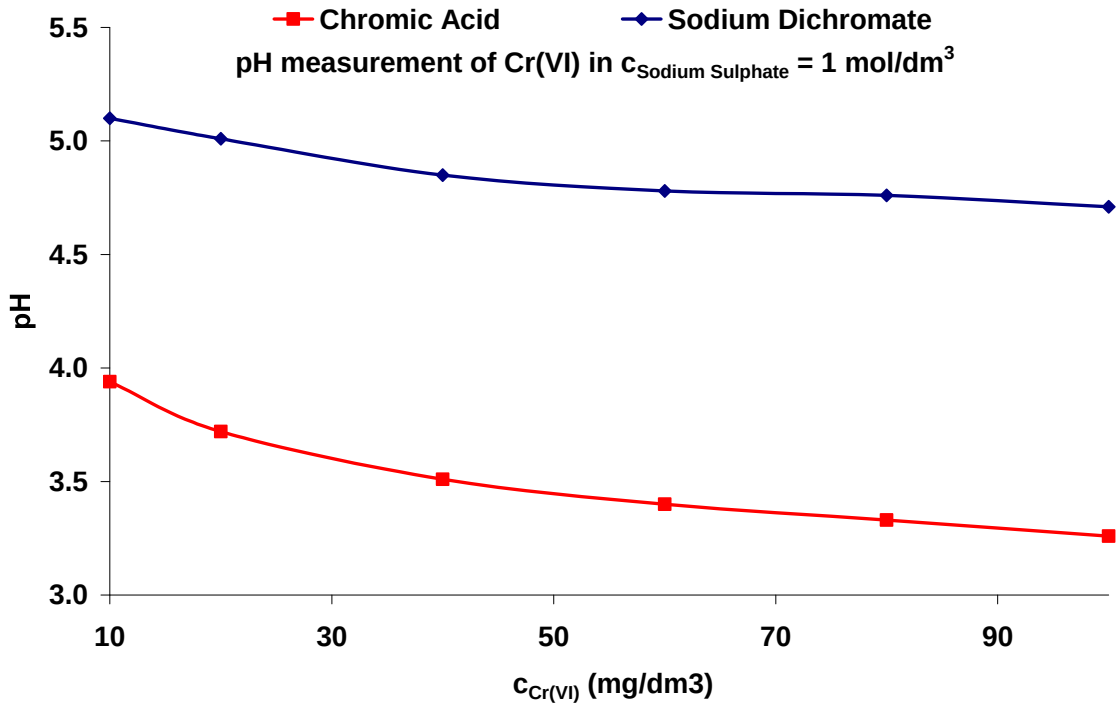

Figure 4.8. Comparison of pH of equal Cr(VI) content prepared form chromic acid and sodium dichromate. The analysis was performed in a solution of sodium sulphate of constant ionic strength.

4.3.3 Simultaneous spectrophotometric determination of $Na_2Cr_2O_7.2H_20$ and CrO_3.

Two approaches were taken in the attempt to quantitatively measure solutions that were known to have a Cr(VI) contribution from both $Na_2Cr_2O_7.2H_20$ and CrO_3. In the first technique, the two analytes were quantified simultaneously by spectrophotometric measurement, and applying Beer's law. A provision for Beer's law to hold true for simultaneous measurement, is that there is no reaction [53] between the solutes. Absorptions at two wavelengths are measured and Beer's law is solved for each species. (These absorbances are additive at the measured wavelength). The well-known simultaneous determination of dichromate and permanganate served as an example for the quantification of $Na_2Cr_2O_7.2H_20$ and CrO_3.

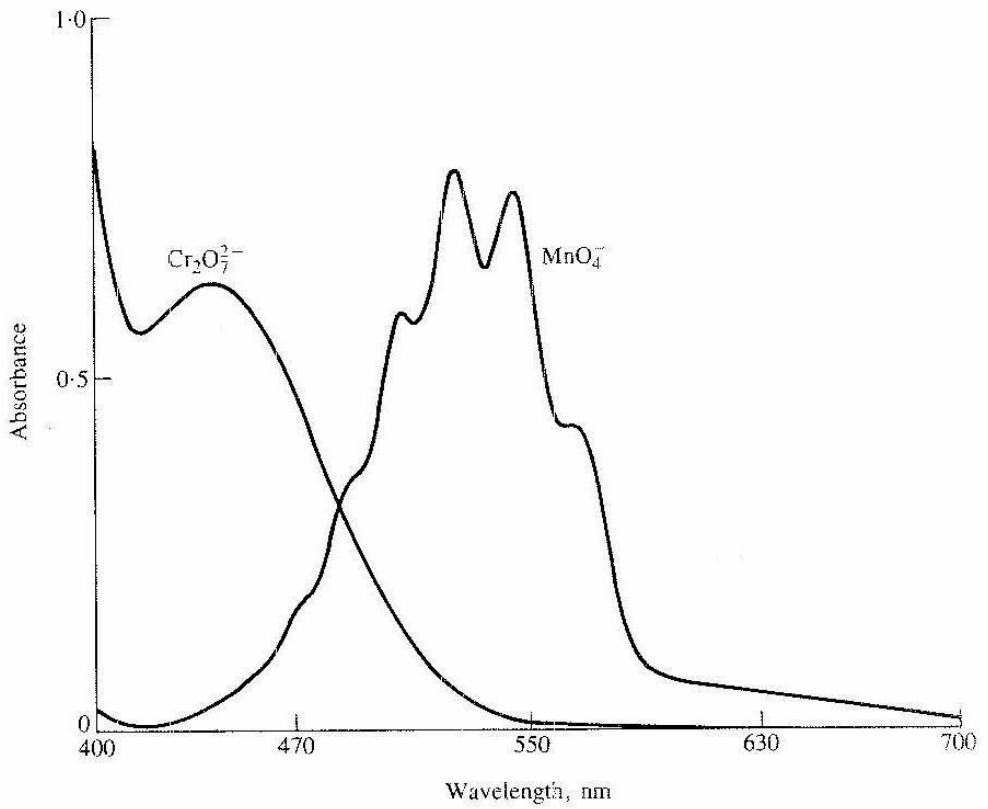

Figure 4.9. The example for the simultaneous measurement of dichromate and permanganate was applied to the measurement of $Na_2Cr_2O_7.2H_20$ and CrO_3 [53].

Work completed on 12 synthetic samples at two sets of wavelengths (*Ref. 6 on attached CD*) shows that the accuracy (see Figure 4.10) of this method is not acceptable. The recovery is significantly spread from a target value of 100 %.

The method for the evaluation of two solutes simultaneously by spectrophotometric measurement does not yield useable information for the quantification of samples prepared from $Na_2Cr_2O_7.2H_20$ and CrO_3.

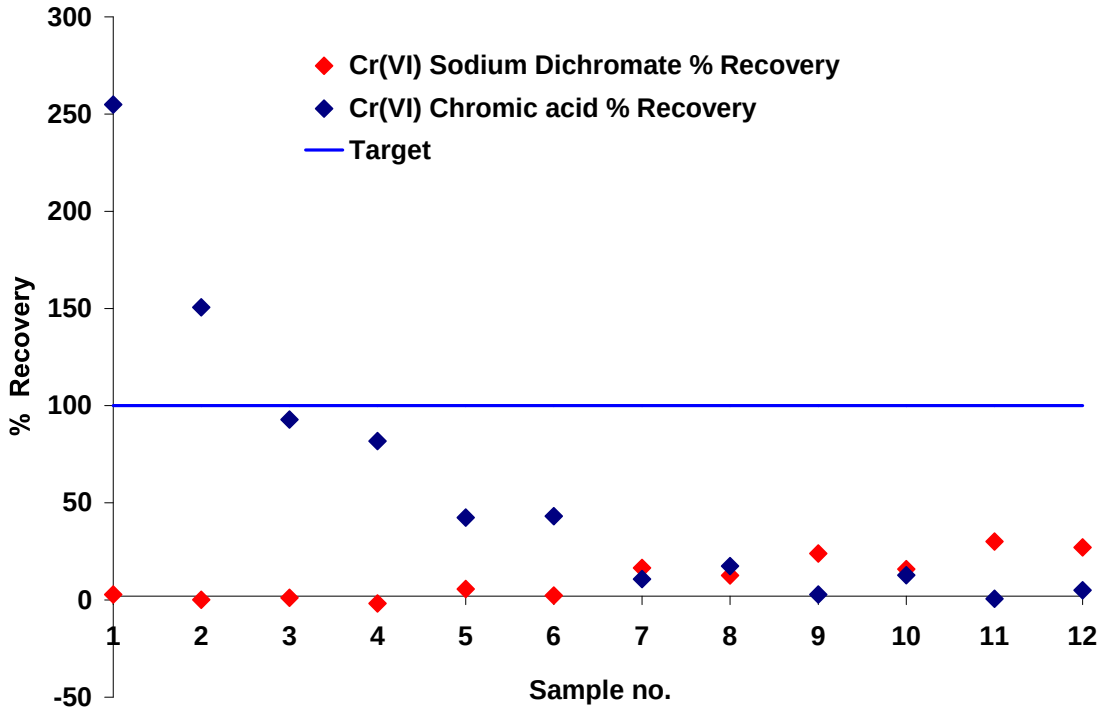

Figure 4.10. Data expressing recovery % of determined $Na_2Cr_2O_7.2H_20$ and CrO_3 using Beer's law and simultaneous equations.

In the second technique, spectrophotometric measurements were used to train *artificial neural networks* with the aim of using this tool to predict the concentration of $Na_2Cr_2O_7.2H_20$ and CrO_3 in samples.

A calibration matrix for the simultaneous determination of Cr(VI) from two sources was constructed using an experimental design based on Figure 4.4 and Table 4.1, composed of two factors and five levels. *Selected* spectra recorded for the training set are shown in Figure 4.12. (Full data set can be seen in *Ref. 8 on attached CD).*

These spectra were recorded with a path length of 5 mm, a smoothing parameter of 15 and a light shield installed. A target error of 1 % was used for the training, with 1 hidden layer for the architectural design of the network. Wavelengths between 260 to 400 nm, at an interval of 1.2 nm were used for training.

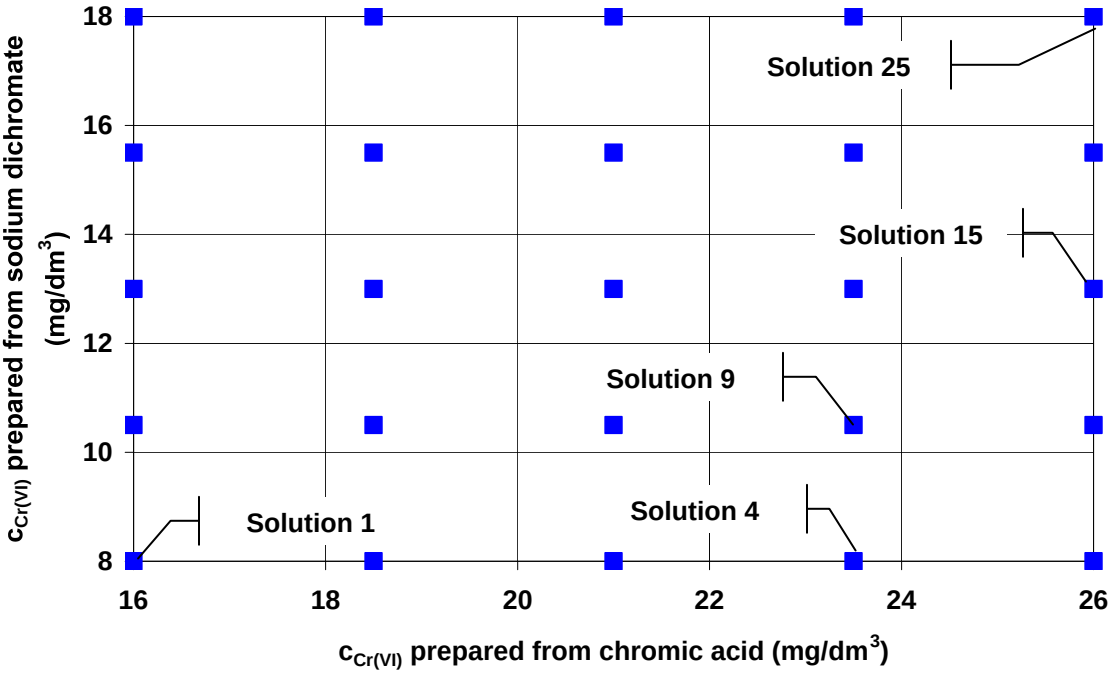

Figure 4.11. Experimental factorial design 5^2 (training points are seen as blue squares) (*Ref. 7 on attached CD*)

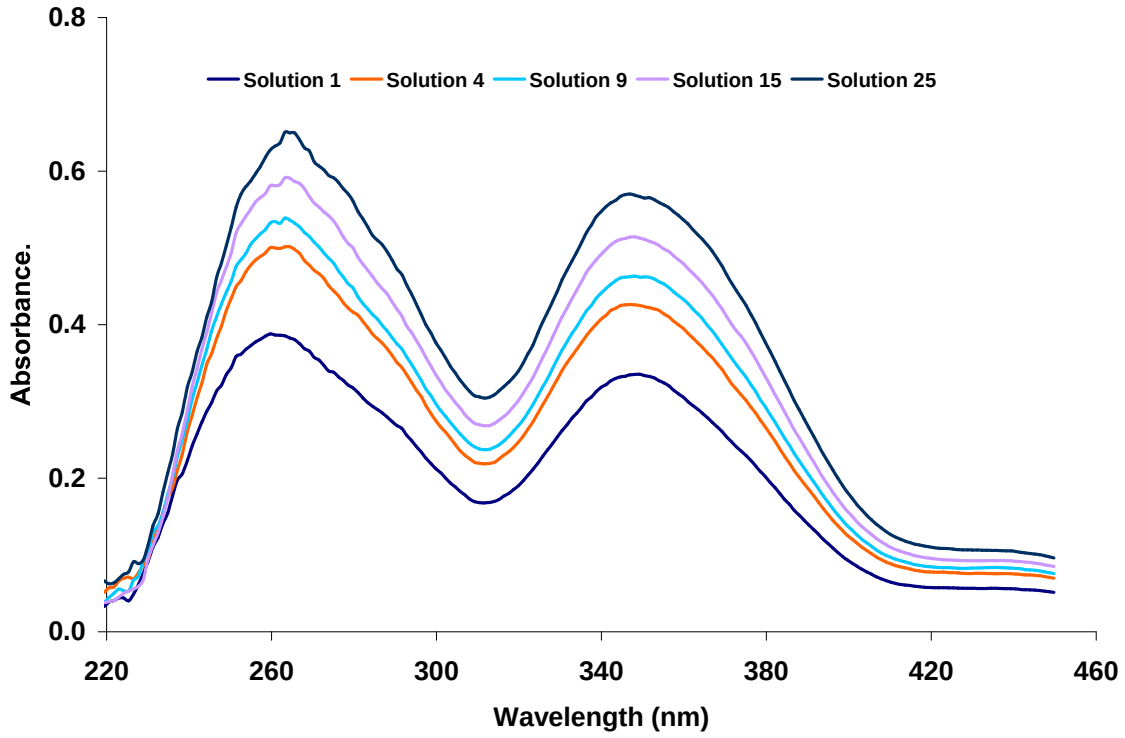

Figure 4.12. *Selected* spectra recorded for the training set are shown. Solution descriptions are tabulated in Table 4.1.

The results of the testing points are given in Figure 4.13. The correlation between the actual and computed results was not satisfactory. Agreement was not found. The average computed error for the predicted Cr(VI) content in the chromic acid preparation was found to be 19.6 % (ranging from 6.2 to 36.8 %), with a standard deviation of 11.2 %.

The average computed error for the predicted Cr(VI) content in the sodium dichromate preparation was found to be 30.4 % (ranging from 3.1 to 69.9 %), with a standard deviation of 20.6 %.

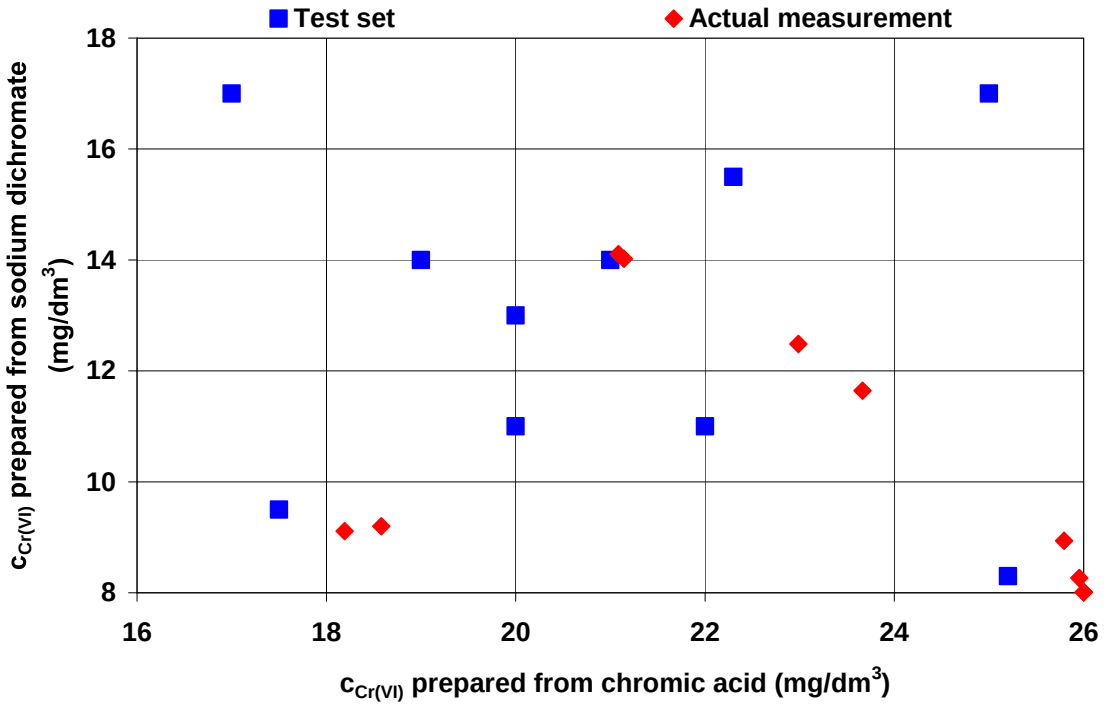

Figure 4.13. Data obtained in the test set after training on neural network. Actual test points are indicated in blue. Predicted test data are indicated in red.

In an attempt to force and shift the equilibrium of the spectra measured in a water medium, the solutions prepared previously as per the matrix described in Figure 4.11 where prepared in c_{H+} = 0.1 mol/dm^3 medium. (The sample preparation is documented in *Ref. 9 on attached CD*). *Selected* spectra recorded for the training set in acidic medium are shown in Figure 4.14. (The full data set can be seen in *Ref. 10 on attached CD).* These spectra were recorded with a path length of 5 mm, a smoothing parameter of 15 with a light shield installed. A target error of 1 % was used for the training, with 1 hidden layer for the architectural design of the network. Wavelengths between 260 to 400 nm, at an interval of 1.2 nm were used for training.

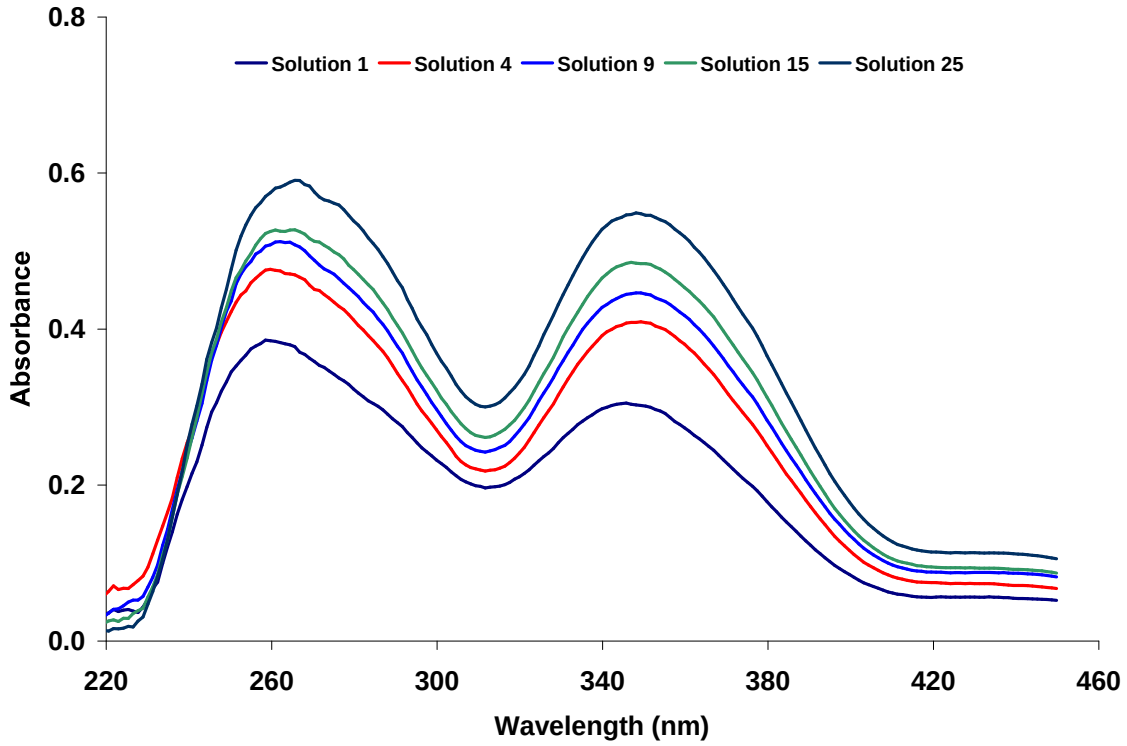

Figure 4.14. *Selected* spectra recorded for the training set in acid medium are shown. Solution descriptions are tabulated in Table 4.1.

As expected the spectra in acidic medium shifted to a shorter wavelength compared to spectra in a water medium at equivalent Cr(VI) concentrations. This is known as hypsochromic (blue) shift. Absorption maxima also decreased due to the increase in acidity; one is example is shown in Figurer 4.15.

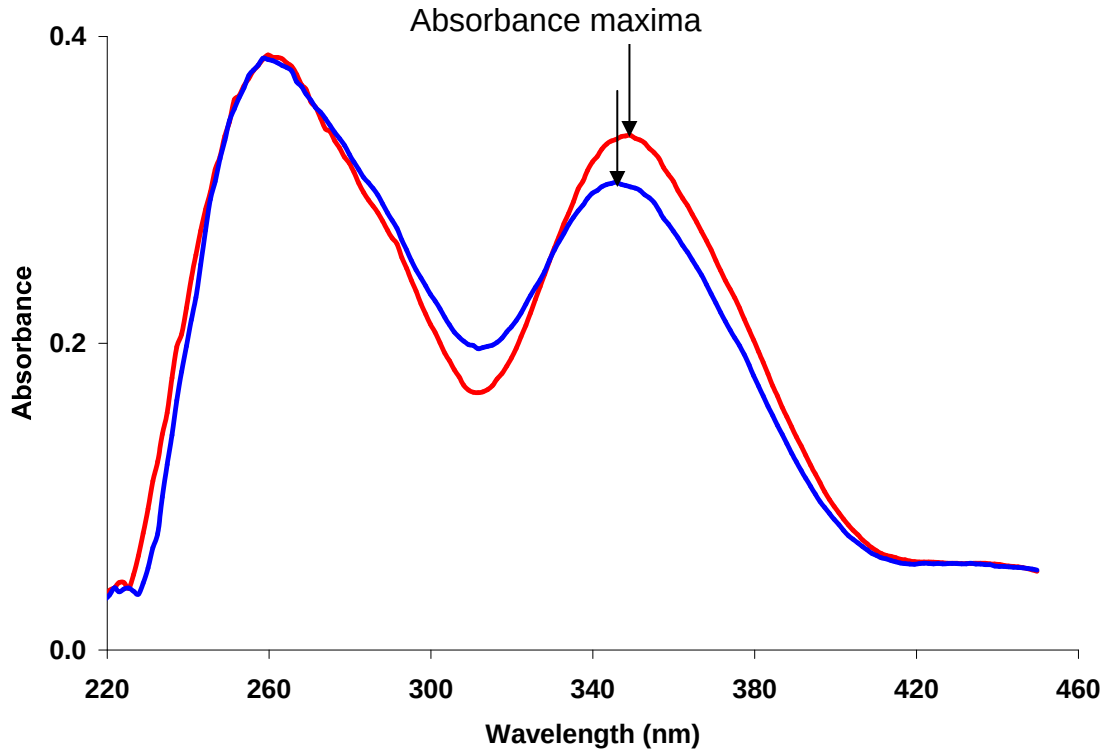

Figure 4.15. Evidence of the hypsochromic shift of spectra of equal Cr(VI) concentrations prepared from chromic acid and sodium dichromate in water (red curve) and acid medium (blue curve). Solution 1 is used as an example. The spectra in acidic medium shifted to a shorter wavelength and absorption maxima decreased.

The results of the testing points are given in Figure 4.16. The correlation between the actual and computed results was not satisfactory. Agreement was not found. The average computed error for the predicted Cr(VI) content in the chromic acid preparation was found to be 16.7 % (ranging from 0.4 to 44.7 %), with a standard deviation of 15.7 %. The average computed error for the predicted Cr(VI) content in the sodium dichromate preparation was found to be 31.6 % (ranging from 3.6 to 59.9 %), with a standard deviation of 17.4 %.

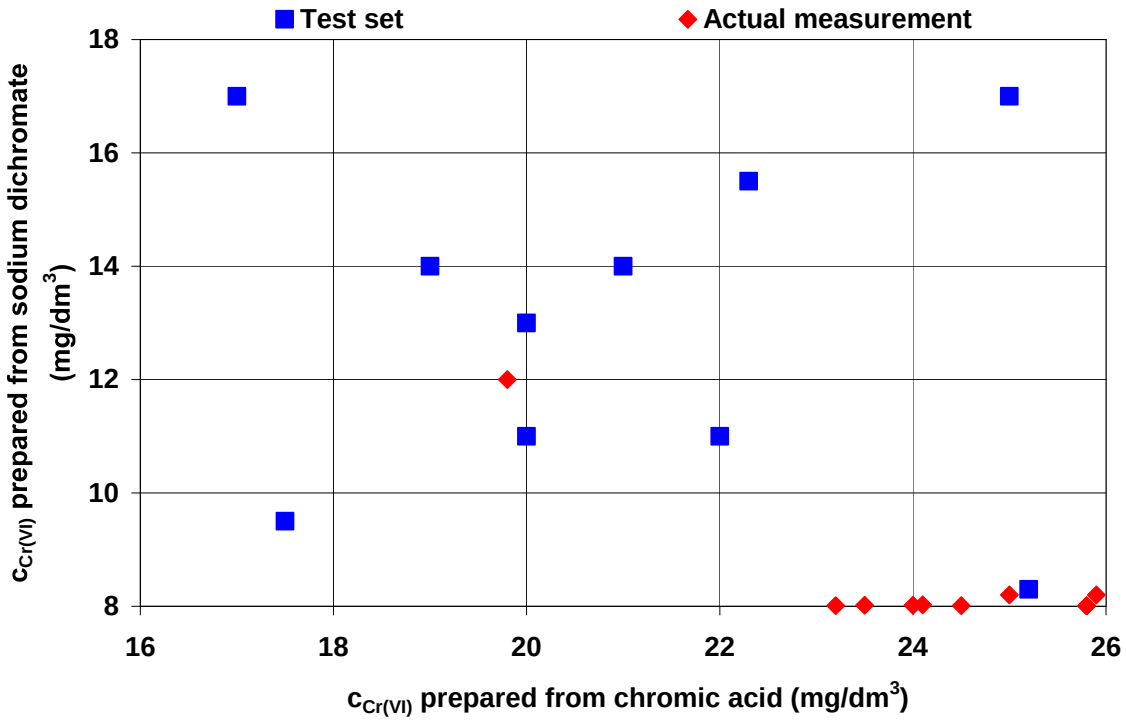

Figure 4.16. Data obtained in the test in acid medium after training on neural network. Actual test points are indicated in blue. Predicted test data are indicated in red.

At this stage of the investigation it became evident that neither samples prepared from chromic acid and sodium dichromate in water or in c_{H+} = 0.1 mol/dm^3 medium were of any value for the purpose of this project.

One further attempt to train a neural network to yield acceptable accuracy in chromic acid and sodium dichromate content, was to combine the spectrophotometric data of water medium *and* c_{H+} = 0.1 mol/dm^3 medium in one procedure and training session. By forcing change in *one* training session, it was anticipated that one would gain accuracy and useable prediction capabilities.

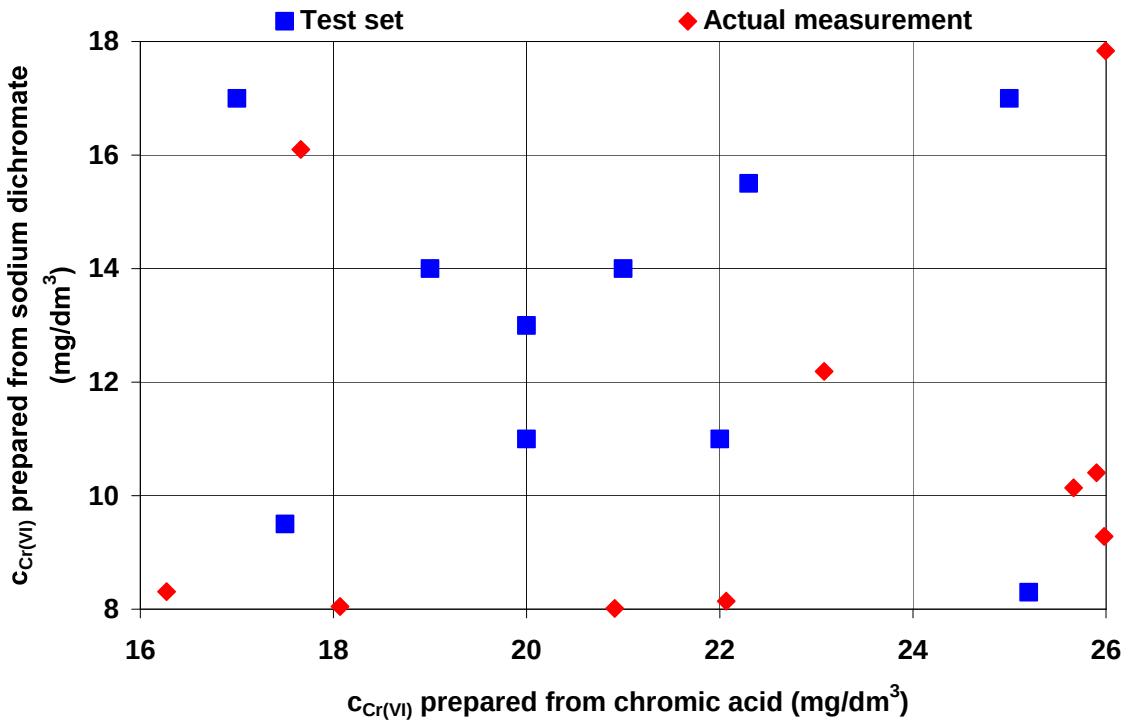

Figure 4.17. Data obtained in the test patterns in training a neural network on two sets of spectrophotometric combinations – water and acidic medium. Actual test points are indicated in blue. Predicted test data are indicated in red.

The results of the testing points are given in Figure 4.17. The correlation between the actual and computed results was not satisfactory. Agreement was not found. The average computed error for the predicted Cr(VI) content in the chromic acid preparation was found to be 21.1 % (ranging from 4 to 35.7 %), with a standard deviation of 11.9 %. The average computed error for the predicted Cr(VI) content in the sodium dichromate preparation was found to be 32.5 % (ranging from 4.9 to 93.9 %), with a standard deviation of 23.6 %.

Another avenue investigated was to change the ranges of chromic acid and sodium dichromate in the spectrophotometric training set. Previously, in both the water and acidic medium, the concentration of Cr(VI) contributed from chromic and sodium dichromate was collectively a maximum of 24 mg/dm^3 (Solution 1) to 44 mg/dm^3 (Solution 25). The total Cr(VI) concentration was increased to

81 mg/dm^3 (solution 1) and to 149 mg/dm^3 (solution 25), representing a step change of 3.4 times the original concentrations used according to Table 4.1. These spectra were recorded with a path length of 1.5 mm in a *flow cell* arrangement and a smoothing parameter of 15. A target error of 1 % was used for the training, with 1 hidden layer for the architectural design of the network. Wavelengths between 209 to 449 nm, at an interval of 1.2 nm were used for training. (The full data set of information is available as *Ref. 11 on attached CD*)

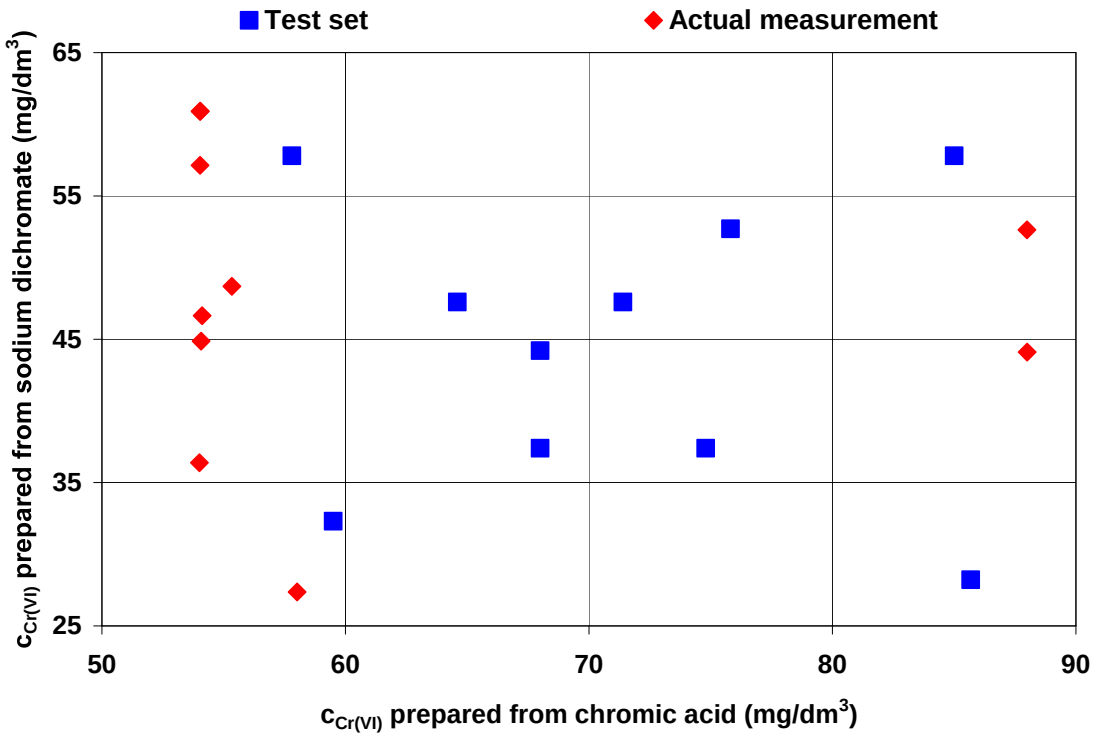

Figure 4.18. Data obtained in the test patterns in training a neural network on larger concentration combinations of chromic acid and sodium dichromate. Actual test points are indicated in blue. Predicted test data are indicated in red.

The average computed error for the predicted Cr(VI) content in the chromic acid preparation was found to be 17.5 % (ranging from 3.5 to 35.4 %), with a standard deviation of 9.4 %. The average computed error for the predicted Cr(VI) content in the sodium dichromate preparation was found to be 21.5 % (ranging from 0.1 to 72.6 %), with a standard deviation of 20.8 %.

The only conclusion that could be reached in the investigations thus far, was that neural network applications were not suitable for prediction of Cr(VI) in mixtures of preparations of chromic acid and sodium dichromate in the ranges and conditions as described above. None of the combinations meet the requirements of an accuracy of less than 1 %. Real samples from the production plant were not measured in this part of the investigation because of the poor correlation found of known versus predicated data of synthetic samples via the neural network technique.

4.4 SPECTROSCOPIC APPROACH LINKED TO ION SELECTIVE ELECTRODE MEASUREMENT, WITH THE AIM OF SPECIATION PREDICTION AND QUANTIFICATION

4.4.1 Introduction

Mixtures of chromic acid and sodium dichromate, irrespective of the species under the conditions of these mixtures, contribute a hexavalent chromium and sodium content to these mixtures.

With some manipulation of this information, it is possible to calculate the relative concentrations of the individual species, and to express these as sodium dichromate and chromic acid. Refer to section 4.2 for definitions and nomenclature used. The process described here, will take place in three steps:

Step 1 Measure the sodium content in the sample, and express this as $Na_2Cr_2O_7.2H_20$ (a)

Step 2 Measure the total Cr(VI) content in the sample, and express this as $Na_2Cr_2O_7.2H_20$ (b)

Step 3 Subtract (a) from (b) and express as CrO_3

Two measurements are able to yield information on a sample's $Na_2Cr_2O_7.2H_20$ and CrO_3 content, and this is useful in determining their ratios to each other, previously defined as "acidification" in section 4.2.

4.4.2 Determination of hexavalent chromium concentrations

From the investigations completed in section 4.3, it became evident that good linearity existed by comparing absorption and total Cr(VI) concentrations. The only proviso for this to hold true, is to make sure that all the Cr(VI) species in solution are either in the form of H_2CrO_4 or CrO_4^{2-}. One would most likely introduce error into the measurement if mixtures of H_2CrO_4 and $HCrO_4^-$ or $HCrO_4^-$ and CrO_4^{2-} were simultaneously quantified. Only one specie of hexavalent chromium should be measured. This is achieved by making sure that the pH of the solutions [7] is less than 1 or greater than 6 respectively.

Tris(hydroxymethyl)-aminomethane (TRIS), was added to Cr(VI) solutions prepared from sodium dichromate to adjust the pH significantly above 6. The advantage of TRIS, is that it is pure (of primary standard quality), has a strong buffering capacity and does not have a UV–VIS footprint in the analytical measuring range of 220 – 460 nm.

Smaller concentrations of Cr(VI) need to be measured (so as not to exceed the one unit absorption maximum used as guideline) because of the hypsochromic shift and consequent increase of absorption maxima as a result of the increase in pH of the adjusted sample. As an example, a 10 mg/dm^3 Cr(VI) solution is adjusted to pH 10.5 (curve (a)) and 1.5 (curve (b)) in Figure 4.19 to demonstrate this phenomenon. Note that the ionic strength of the two solutions is not constant.

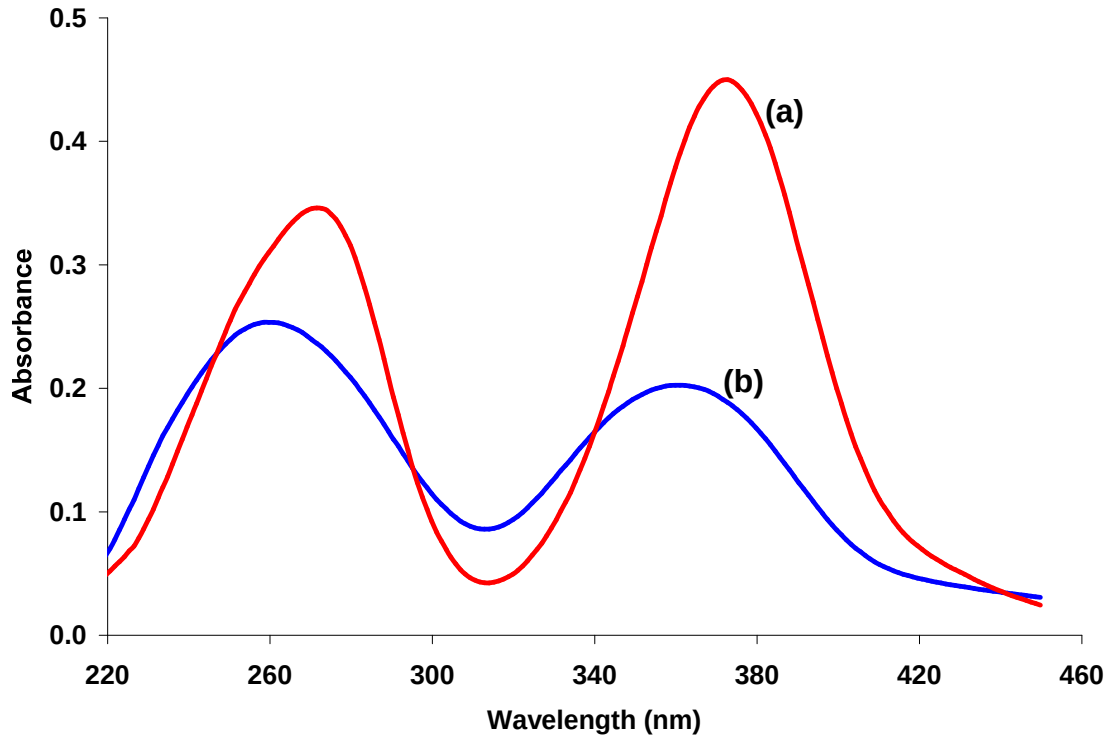

Figure 4.19. 10 mg/dm^3 Cr(VI) solution is adjusted to pH 10.5 (a) and 1.5 (b) respectively, demonstrating the effect of pH.

An example of the achieved correlation of absorption vs. Cr(VI) concentration at pH 10.5 in the analytical wavelength range of 220 – 460 nm is shown in Figure 4.20. Correlation coefficients greater than or equal to 0.999 are found in the wavelength regions of 247 – 291 and 337 – 413 nm, and these correspond to the maxima of the absorption versus wavelength data points. In other words the best achieved sensitivity for quantification of Cr(VI) is measurable at these wavelength regions (and concentrations), and can thus be used as a tool for analysis of total Cr(VI) in samples with suitable dilution regimes.

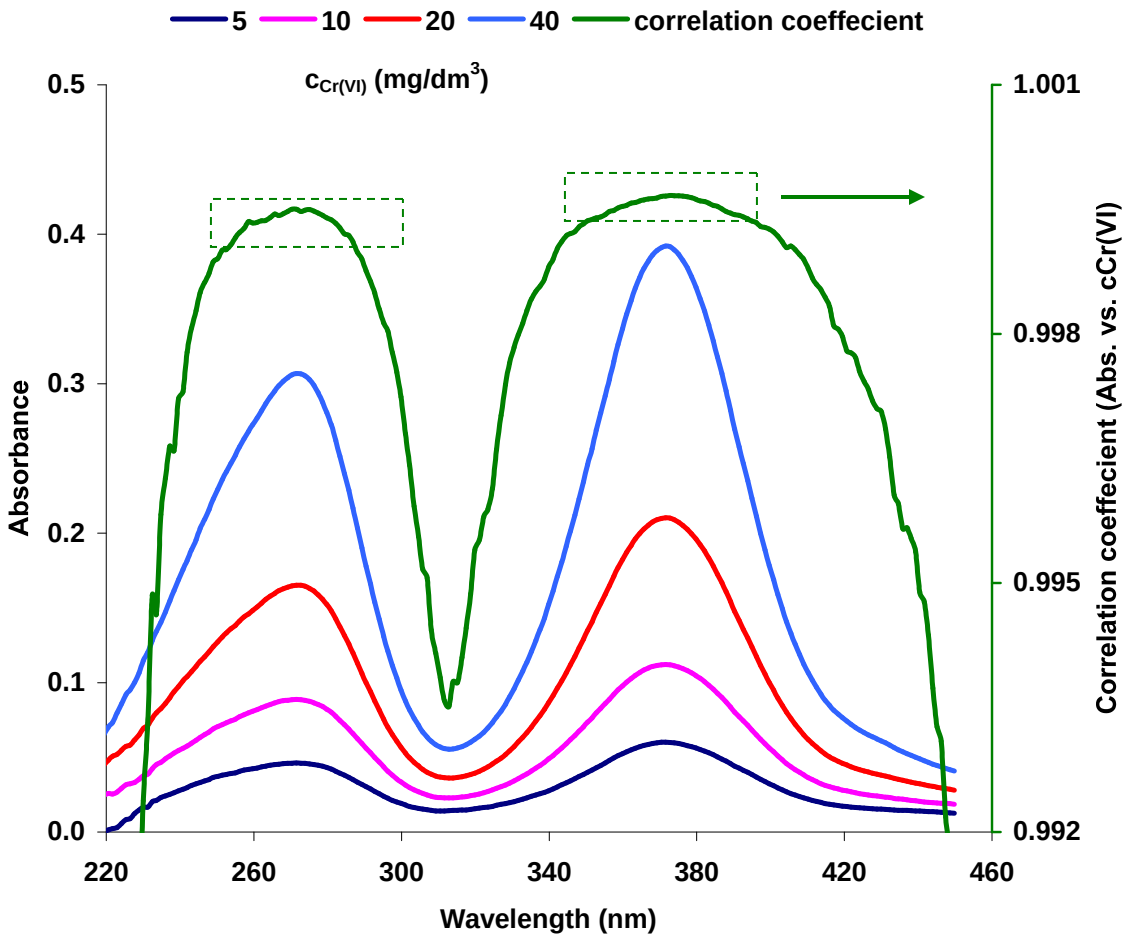

Figure 4.20. Spectrophotometric data demonstrating the linear relationship of absorption and Cr(VI) concentration at alkaline conditions of pH 10.5.

4.4.3 Determination of sodium concentrations

The reported measuring range of the sodium glass electrode is between 1 x 10^{-5} and 1 mol/dm^3 Na^+ (0.23 mg/dm^3 to 22.99 g/dm^3 Na^+). The condition of the measuring electrode used in these experiments was tested to evaluate the best suited practical range of use. The test solutions' ionic strength was adjusted to 1 M in TRIS and 0.1 M in HCl. A double-junction reference electrode filled with TRIS in the outer chamber was used. The pH of the measured solutions was approximately 9.2. The best working range for this electrode was evaluated to be between 5.62 x 10^{-5} ($10^{-4.25}$) and 1.97 x 10^{-1} ($10^{-0.71}$) mol/dm^3 Na^+, where the

correlation coefficient was found to be r^2 = 0.999975. (Full data set may be seen on *Ref. 12 on attached CD*).

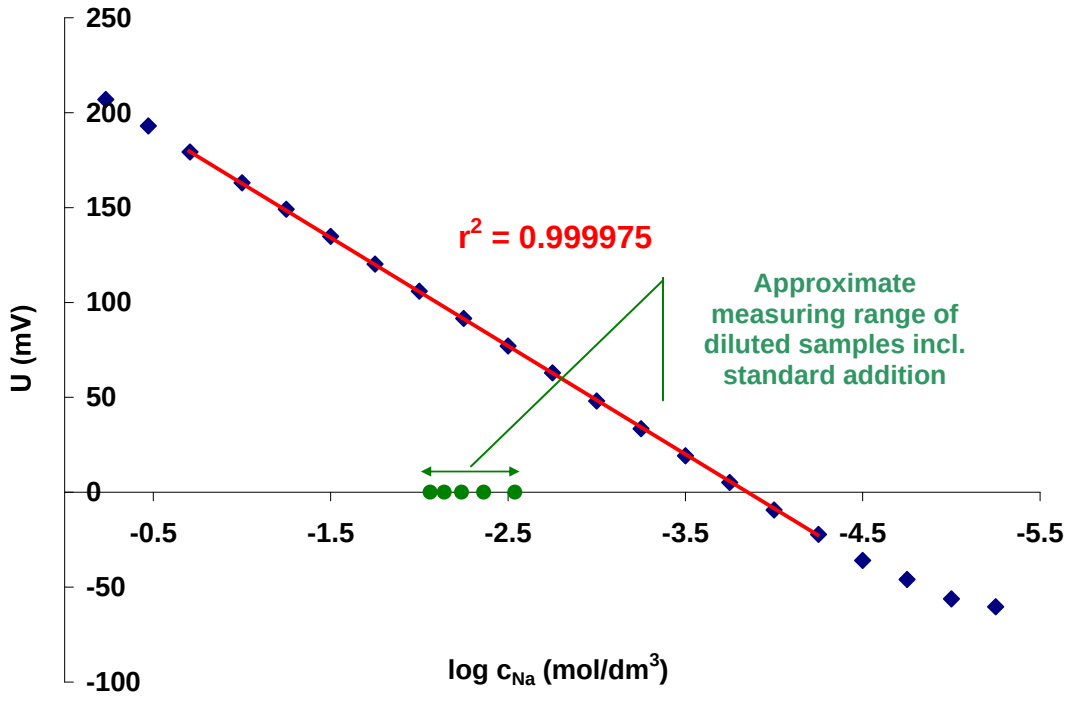

Figure 4.21. Determination of the useable working range of the sodium glass electrode.

4.4.4 Indirect speciation analysis linked by total hexavalent chromium concentrations and sodium concentrations

As previously mentioned in section 4.2, data from the process' database (Ref. 1 on attached CD) shows that the Cr(VI) content in a final stage process stream lies between 481 and 557 g/dm^3 (average of 525 g/dm^3). The contribution of the sodium from the sodium dichromate content was calculated to be between 75 and 100 g/dm^3 (average of 93 g/dm^3). Suitable dilution was therefore needed to measure the Cr(VI) content and sodium content of real samples, such that these were measured within the calibration ranges for spectroscopic determination and linear response for the ion selective electrode determination respectively.

The best working range of the sodium glass electrode used was found to be between 1.3 to 4521 mg/dm^3 Na^+ in artificially prepared calibration solutions. Real samples would therefore *ideally* have to be diluted approximately 1300 times to a Na^+ concentration of $10^{-2.5}$ M (the mid point of the linear response range of the electrode used).

The UV–VIS. calibration range of the total Cr(VI) measurement was prepared between 5 and 30 mg/dm^3 – such that the absorption data did not significantly exceed an absorption value of one unit.

A sample from the process was analysed in the laboratory using the usual methods prescribed for this sample i.e. a titrimetric acid base technique was used to quantify the chromic acid and sodium dichromate content. *This method was taken as the reference or standard method as described further in this discussion.* This data was manipulated in the typical manner to express the information in terms of sodium and Cr(VI) content.

Analysis no.	**c_{Na} (g/dm^3)**	**$c_{Cr(VI)}$ (g/dm^3)**
1	92.57	541.99
2	92.71	541.99
3	92.48	541.63
4	92.48	541.75
5	92.09	540.89
6	92.57	541.99
7	92.82	542.49
8	92.48	541.75
9	92.65	542.18
Mean	92.54	541.85
Standard deviation	0.20	0.44
Spread	0.72	1.60
Minimum	92.09	540.89
Maximum	92.82	542.48

Table 4.2. A sample from a final process stream is analysed to measure the sodium and Cr(VI) content using the prescribed methods at the sponsoring company's laboratory.

This information was used as a basis for the determination of sodium by ion selective electrode measurements. Three determinations using the sample preparation described in chapter 3 (section 3.4), yielded 94.9, 95.3, and 93.5 g/dm^3. The samples were diluted 1428 times. The mean result was 94.6 g/dm^3 with a standard deviation of 0.95 g/dm^3.

Although only three determinations were completed the aim was simply to measure if this was a viable strategy to follow at this point of the investigation.

An F-test had to be applied to the data to measure whether there was a significant difference in the random error of the two sets of data.

$$F' = {s_1}^2 \Big/ {s_2}^2 = 0.95^2 \Big/ 0.20^2 = 21.50$$

where, s_1 is the standard deviation of the ion selective electrode measurement

s_2 is the standard deviation of the standard measurement

F' Critical value of F' according to F test

F' determined is greater than F' critical 4.46 (P = 0.05), and therefore it was found that ion selective electrode technique was less precise than the standard method. The comparison of the two experimental means to test the ion selective electrode method against the standard method, to measure whether the two techniques differ significantly was applied (unequal variance in the methods was proved above).

$$t = \frac{\left(\bar{x}_1 - \bar{x}_2\right)}{\sqrt{\frac{{s_1}^2}{n_1} + \frac{{s_2}^2}{n_2}}} = 3.69^*$$

where, s_1 is the standard deviation of the ion selective electrode measurement

s_2 is the standard deviation of the standard measurement

$\bar{x}_1$ is the mean of the ion selective electrode measurement

$\bar{x}_2$ is the mean of the standard measurement

n_1 is the degree of freedom for the ion selective electrode measurement

n_2 is the degree of freedom for the standard measurement

t determined (3.69*) was less than t critical 4.30* (P = 0.05), and therefore it was found that ion selective electrode technique was not significantly different from the standard method. Statistical analysis confirms that there is no significant difference between the ion selective electrode measurements compared to the calculated data by the prescribed analytical method, although the precision of the former method is worse than the standard method. * Data obtained from Excel

Similarly then the Cr(VI) content was evaluated. The information in Table 4.2 was used as a basis for the determination of Cr(VI) by spectrophotometric measurements. Duplicate analysis was used to calculate the Cr(VI) content based on wavelength range of 370 – 372 nm (the most linear portion of the absorbance vs. concentration data). Six results using the sample preparation described in chapter 3, yielded a mean result is 534.55 g/dm^3 with a standard deviation of 4.60 g/dm^3.

An F-test had to be applied to the data to measure whether there was a significant difference in the random error of the two sets of data. F' determined (108.0) is greater than F' critical 3.69 (P = 0.05), and therefore it was found that spectrophotometric technique was less precise than the standard method.

The comparison on the two experimental means to test the spectrophotometric method against the standard method, to measure whether the two techniques differ significantly was applied (unequal variance in the methods where proved above). t determined (3.87*) is greater than t critical 2.57* (P = 0.05), and therefore it was found that spectrophotometric technique was significantly different from the standard method. * Data obtained from Excel. Although the results of the spectrophotometric method yielded a statistical bias, this evidence was sufficient to move ahead and investigate further on a range of real samples the applicability of this type of measurement for development into an on-line instrument.

The same methodology was followed in these tests as the one above (Full data set may be seen on *Ref. 13 on attached CD*).

Sodium analysis was completed in *triplicate* determinations using a standard addition technique such the measuring range of the sample fell within the linear response range of the electrode.

The Cr(VI) measurements were completed in *triplicate* determinations, and suitably diluted to fall within the calibration range (5 – 30 mg/dm^3).

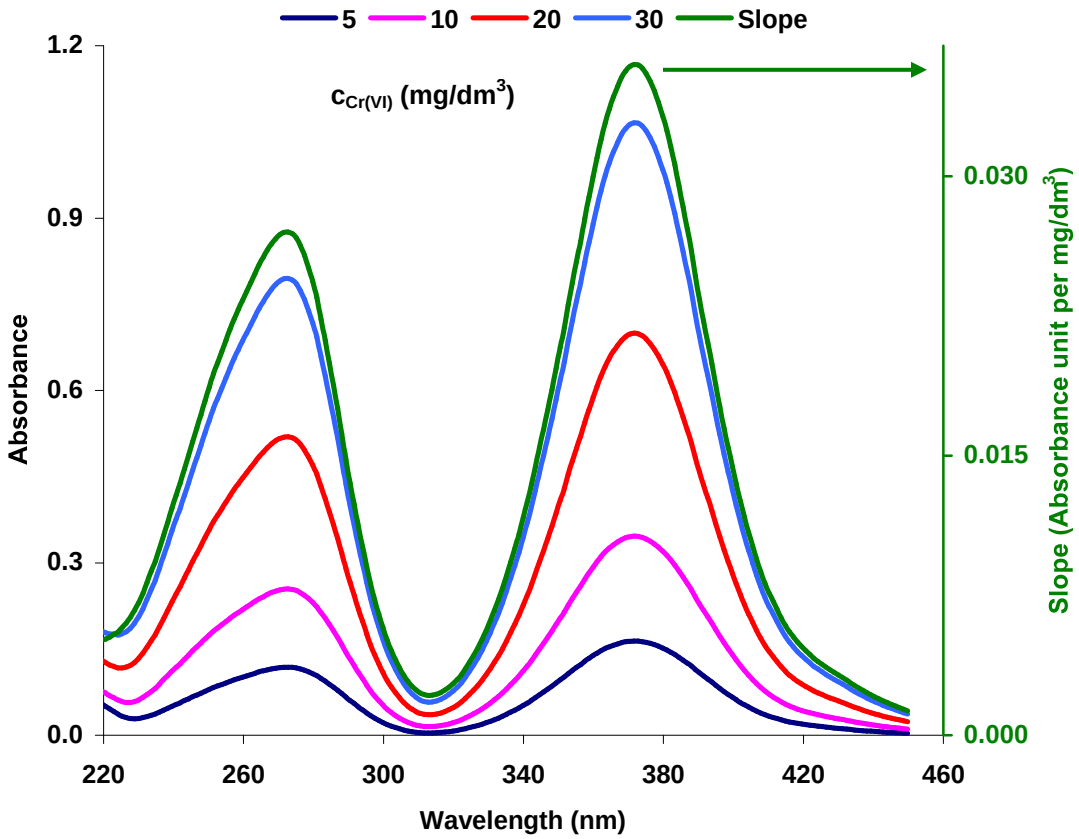

Figure 4.22. Determination of the best suited wavelength at which to measure Cr(VI), evaluated at the highest sensitivity (slope) and found to be between 370.4 and 372.7 nm.

The samples were diluted 25 000 times, with an addition of TRIS, such that the pH measured was significantly greater than 6. The results were calculated from the calibration curve at the most *sensitive* wavelength. (This was evaluated by plotting the absorption versus concentration data i.e. slope against wavelength, and determining the maxima). The most sensitive wavelength portion of the spectrum lies between 370.4 and 372.7 nm, which corresponds to the absorption maxima at these conditions of concentration and pH. An example of this is seen in Figure 4.22.

The following results (Table 4.3) were obtained for the sodium determination.

Sample 7 and 10 (minimum and maximum deviations from target difference of zero) were tested as outliers according to Grubbs' test,

$$G = \frac{\left| suspect \quad value - \bar{x} \right|}{s}$$

where, G is the determined value

$\bar{x}$ is the average of the determined series including the suspected value(s)

s is the standard deviation of the determined series including the suspected value(s)

G critical (11 determinations) = 2.352, and therefore no values were rejected. (G determined (sample 7) = 1.224 and G determined (sample 10) = 2.143).

Sample no	Sample description	Standard procedure c_{Na} (g/dm^3)	ISE c_{Na} (g/dm^3)	Delta (g/dm^3)	|Error| (%)
Sample 1	Cell 13	98.34	96.83	-1.50	1.5
Sample 2	Cell 14	98.52	95.30	-3.22	3.3
Sample 3	Cell 15	97.14	98.47	1.32	1.4
Sample 4	Cell 16	96.63	92.33	-4.29	4.4
Sample 5	Stage 5	103.21	101.35	-1.86	1.8
Sample 6	Stage 6	100.49	99.43	-1.06	1.1
Sample 7	Stage 7	99.80	100.40	0.60	0.6
Sample 8	Stage 8	97.53	101.00	3.47	3.6
Sample 9	Cell 14	100.01	97.45	-2.54	2.5
Sample 10	Anolyte Product	89.64	95.63	5.99	6.7
Sample 11	Anolyte Product	96.61	100.60	3.99	4.1
				Spread	6.1
				Minimum	0.6
				Maximum	6.7
				Average	2.8

Table 4.3 A range of samples from a final process stream is analysed to measure the sodium content using the prescribed methods and the proposed ISE measurement.

The test for comparing two means is not appropriate in this case, since different samples were analysed which contained different ranges of analyte. (The methods are subject to random error and there are differences in samples). The problem is overcome though by evaluating the differences between sets of data and making the assumption (or rather testing the assumption) that those differences are zero. The *paired* t-test was thus applied.

$$t = \bar{d}\sqrt{n / s_d}$$

where, $\bar{d}$ and s_d are the mean and standard deviation respectively of d, the difference between paired values.

t determined (0.080*) was less than t critical 2.228* (P = 0.05), and therefore it was found that ion selective electrode technique was not significantly different

from the standard method across a range of sample types and analyte concentrations.

However, the measured *average* error (2.8 %) against the standard method did not meet the required accuracy of 1 % as stipulated in section 4.1.

The following results were obtained for the Cr(VI) determination.

Sample no	Sample description	Standard procedure $c_{Cr(VI)}$ (g/dm^3)	UV–VIS $c_{Cr(VI)}$ (g/dm^3)	Delta (g/dm^3)	|Error| (%)
Sample 1	Cell 13	533.01	534.09	1.09	0.2
Sample 2	Cell 14	536.98	555.74	18.76	3.5
Sample 3	Cell 15	541.99	557.29	15.30	2.8
Sample 4	Cell 16	538.62	516.20	-22.42	4.2
Sample 5	Stage 5	526.07	510.52	-15.55	3.0
Sample 6	Stage 6	526.36	515.50	-10.86	2.1
Sample 7	Stage 7	535.57	520.52	-15.05	2.8
Sample 8	Stage 8	539.02	533.47	-5.55	1.0
Sample 9	Cell 14	540.83	538.44	-2.39	0.4
Sample 10	Anolyte Product	498.43	511.88	13.45	2.7
				Spread	4.0
				Minimum	0.2
				Maximum	4.2
				Average	2.3

Table 4.4. A range of samples from a final process stream is analysed to measure the Cr(VI) content using the prescribed methods and the proposed UV–VIS measurement.

Sample 1 and 4 (minimum and maximum deviations from target of zero) were tested as outliers according to Grubbs' test. G critical (10 determinations) = 2.289. Sample 1 was not rejected. (G determined (sample 1) = 1.55. Sample 4 was not rejected. (G determined = 1.45).

The comparison on the differences of the spectrophotometric method against the standard method, to measure whether the two techniques differ significantly was

applied according to the *paired* t-test. t determined (0.513*) is less than t critical 2.262* (P = 0.05), and therefore it was found that spectrophotometric technique was not significantly different from the standard method across a range of sample types and analyte concentrations. * Data obtained from Excel

However, the measured *average* error (2.3 %) against the standard method did not meet the required accuracy of 1 % as stipulated in section 4.1.

Notwithstanding the evidence seen in the analytical measurement, attention needed to be focused on the sample preparation needed to establish an on-line technique. The preparation step needed to be capable of diluting a viscous and highly aggressive sample. At the same time, the pH and ionic strength adjustment were needed for sodium determination and pH for the Cr(VI) determination. Highly accurate dilutions were required to improve on laboratory accuracy i.e. to meet the requirement of 1 % accuracy.

Although there are numerous advantages to using UV–VIS measurements for quantitative applications, disadvantages or challenges need some consideration. Firstly, it is a comparative technique which requires a referencing data set. A standard calibration is usually used as a reference. A standard addition technique, in which known amounts of analyte are added to the sample, is an alternative to a reference data set. This would be required to be built into an on-line analysing system. Secondly, it is prone to drift. The drift is due to instrumental noise, temperature fluctuations and other non-specific reasons. Usually this is compensated for by a referencing channel which determines the ratio of change in absorption of a standard spectrum in time, and applies this change to the sample spectrum. Alternatively, a reference sample may be used as a check on drift or system performance. Building this type of compensation into an on-line technique makes for complicated control and skill needed in operation of such a system – something which is not easily achievable in an environment where artisan / technical staff are responsible for analytical

equipment and not chemists (as this instrument will be in a production environment).

Ion selective electrode measurements are excellent tools for quantification down to low analyte concentrations, typically 1.3 mg/dm^3 Na ($10^{-4.25}$ M). However, long-term stability of this electrode in this type of matrix is questionable and was not probed in this investigation. From experience gained in the use of the electrode, it become necessary to periodically “re-charge” the glass membrane by immersing the electrode in a concentrated sodium solution, typically 1 M. Evidence of the electrode loosing its sensitivity was seen by a drift of the response slope of the ISE outside acceptable limits of between 57 and 60 mV. This, as in the case above, maybe compensated for by a check sample of known sodium content. Building this type of compensation into an on-line technique makes for complicated control and skill needed in the operation of this type of on-line measurement.

Careful consideration was paid to a conceptual design of a sodium and chromium analyser, capable of highly accurate dilutions and sample preparation, using the guidelines of chapter 1, section 1.4. Although cost was not a requirement in the initial scope of this project, in a competitive commercial environment, attention needed to be given to capital investment.

Consideration requirements	Comment	Challenge
Selection of the process variable.	Information gained could be used to operate the process more efficiently. (Chromic acid and sodium dichromate content)	None.
Quantitative relation between the measured and controllable properties.	Sodium and hexavalent chromium content in sample.	Sophisticated techniques for a process analyser although regarded as standard analytical techniques.
Places of sampling.	Final stage of electrolysis production.	None.
Frequency of the measurements.	A result frequency of 10 minutes between reporting was required.	Guidelines of reporting of data between 10 to 30 minutes may be exceeded.
Time duration of the measurements.	Large dilutions and sample preparation delays reporting of data. Estimated time for two two-stage dilutions with pH and / or ionic strength adjustment ca. 15 minutes. Decontamination of measuring cells takes time. Small sample	Proper decontamination or sample carry-over will delay reporting of results.

	aliquots need larger flushing time of sample lines.	
Tolerance limits.	Guideline of 1 % accuracy stipulated by the sponsoring company.	Large dilutions may result in significant error of final calculations. Non-ideal behavior of analytical tools must be controlled.
Selection of sensing or analysing instrument(s).	Two independent measurements needed.	Extensive sample preparation to enable ISE and UV–VIS analysis.
Cost.	On-line dilutors (two two-stage) @ ca. R80 k each. ISE / Meter ca. R30 k. UV–VIS spectrometer ca. R70 k. CPU and peripherals ca. R10 k. Installation costs ca. R10 k.	Excessive capital investment of ca. R500 k.
Maintenance of instruments.	Dilutors may require routine maintenance.	Costly skilled personnel required for maintenance. ISE and UV–VIS analysis are fairly dependable techniques commercially available.
Calibration frequency of the instruments used.	Not investigated, but known to have drift, and	Comparative techniques requiring excessive

	therefore needs compensation. On-line dilutors need checks.	control.
Total cost of measurements.	Reagents costly especially TRIS, although inexpensive compared to laboratory based determinations.	Consumable budget will have to be optimized. Low cost to reliable results is always first priority.
Reliability, ease of operation and simplicity.	Questionable.	Not easily achievable in an environment where technical staff are responsible for analytical equipment and not chemists

Table 4.5. Summary of considerations for the development of an ISE and UV–VIS technique for on-line application.

From the information and rationale derived from Table 4.5 it became clear that there where too many challenges in the conceptual design of an ISE and UV–VIS technique for on-line application. Costs were also excessive and the integration of two independent measurements (instruments) was too complicated for a process instrument. The standard method for this analysis was now considered for an on-line application development.

4.5 TITRIMETRIC ACID BASE ANALYSIS

Dissolved CrO_3, as H_2CrO_4, reacts with hydroxide ions to form $HCrO_4^-$ (Reaction 4.2). $HCrO_4^-$ dimerises (resulting in the removal of water) provided that the concentration of chromium exceeds approximately 1 g/dm^3 to $Cr_2O_7^{2-}$ (Reaction 4.1).

Dichromate ions react with hydroxide ions to form $HCrO_4^-$ (Reaction 4.3) (these also form dimers to give way to the formation of $Cr_2O_7^{2-}$) to yield chromate ions. (Reaction 4.4)

The concept of evaluating mixtures of chromic acid and sodium dichromate needed to be validated based on the following reactions,

$$2H_2CrO_4 + 2OH^- \rightleftharpoons 2HCrO_4^- + 2H_2O \quad (4.2)$$

and

$$2Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2HCrO_4^- + 2CrO_4^{2-} \quad (4.3)$$

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O \quad (4.4)$$

1 M sodium hydroxide solutions were prepared and standardised against potassium hydrogen phthalate (KHP) and used as titrants. See appendix 3 for details. An example of a titration curve is detailed in Figure 4.23. The equivalence-point is determined by a rapid change in pH versus added titrant and evaluated by the calculated maximum of the first derivative of volume added against pH measured.

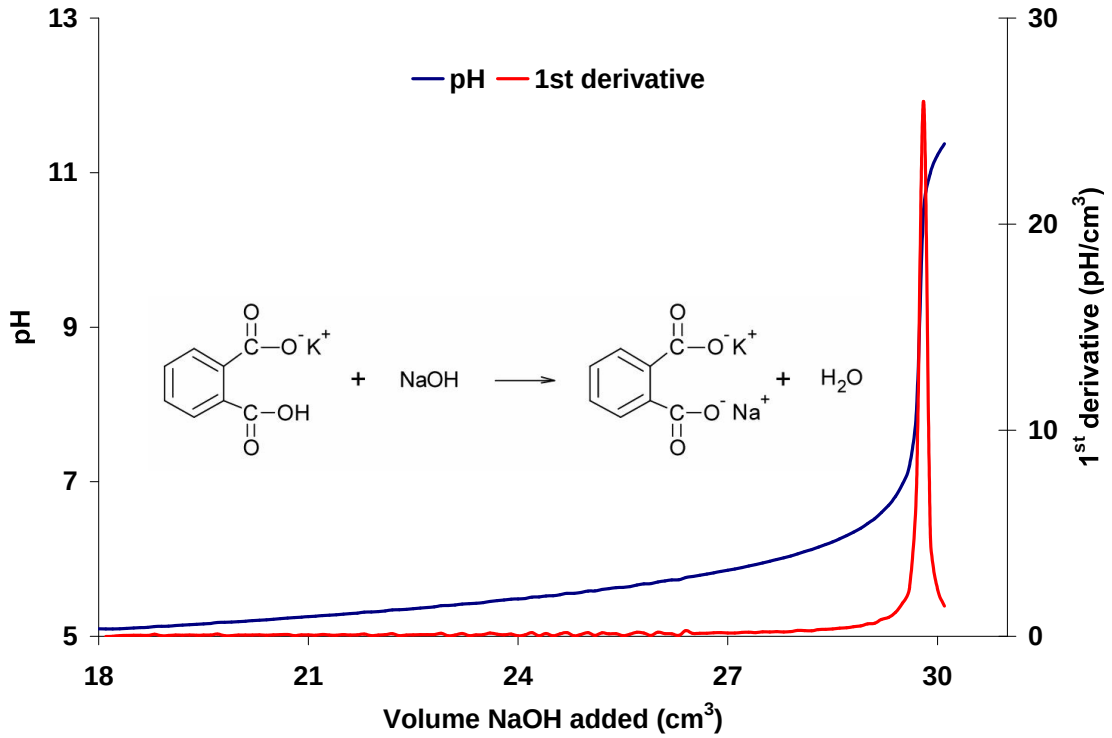

Figure 4.23. Determination of molar concentration of sodium hydroxide against a known mass of potassium hydrogen phthalate, yields a clear and well-defined equivalence-point. The equivalence-point is determined from the rapid change in pH against volume of titrant added.

Further data is available on all sodium hydroxide solutions standardised in these determinations described later. (Full data set may be seen on *Ref. 14 on attached CD*).

A matrix for the *simultaneous determination of Cr(VI)* from two sources was constructed using an experimental design based on a range of Cr(VI) quantities such that a burette volume of 50 cm^3 was utilised between approximately 1 cm^3 and 40 cm^3 (or rather 2 – 80 % of total volume based on a 1 M NaOH titrant). The assumptions of equations 4.2 and 4.4 holding true against a pre-standardised sodium hydroxide titrant were tested. Quantities of Cr(VI) prepared from chromic acid and sodium dichromate were dispensed from solutions pre-standardised against a ferrous titrant.

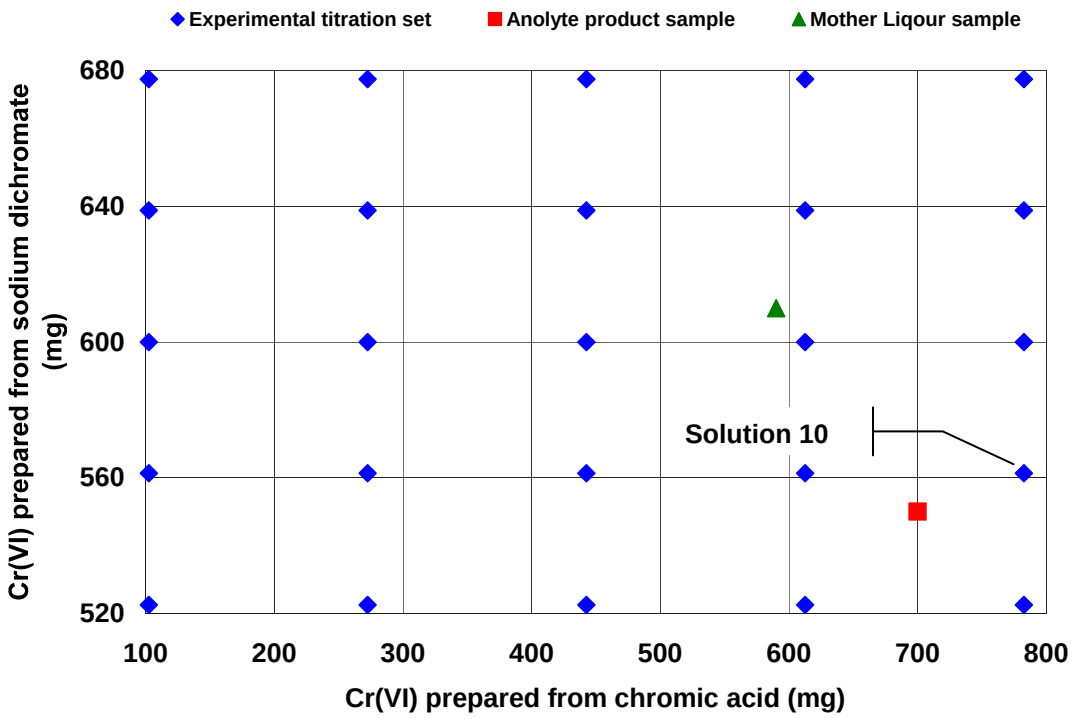

Figure 4.24. Experimental factorial design 5^2 for the simultaneous determination of two sources of Cr(VI) from chromic acid and sodium dichromate. Two real sample points are indicated for reference. (*Ref. 15 on attached CD*)

For reference, two points indicated on the graph (green triangle and red square) represent approximate expected contributions of Cr(VI) from chromic acid and sodium dichromate in a Mother Liqour and Anolyte Product sample respectively. These points are dependant on the ratio of Cr(VI) in real samples, and also dependant on the sample mass taken for analysis. Usually about 3 g of sample is used in the standard method used at the sponsoring company's laboratory. It must be emphasized that these points may thus shift from sample to sample, and analysis to analysis, and that the two points are for reference only. They are not intended to indicate an absolute position on the constructed matrix.

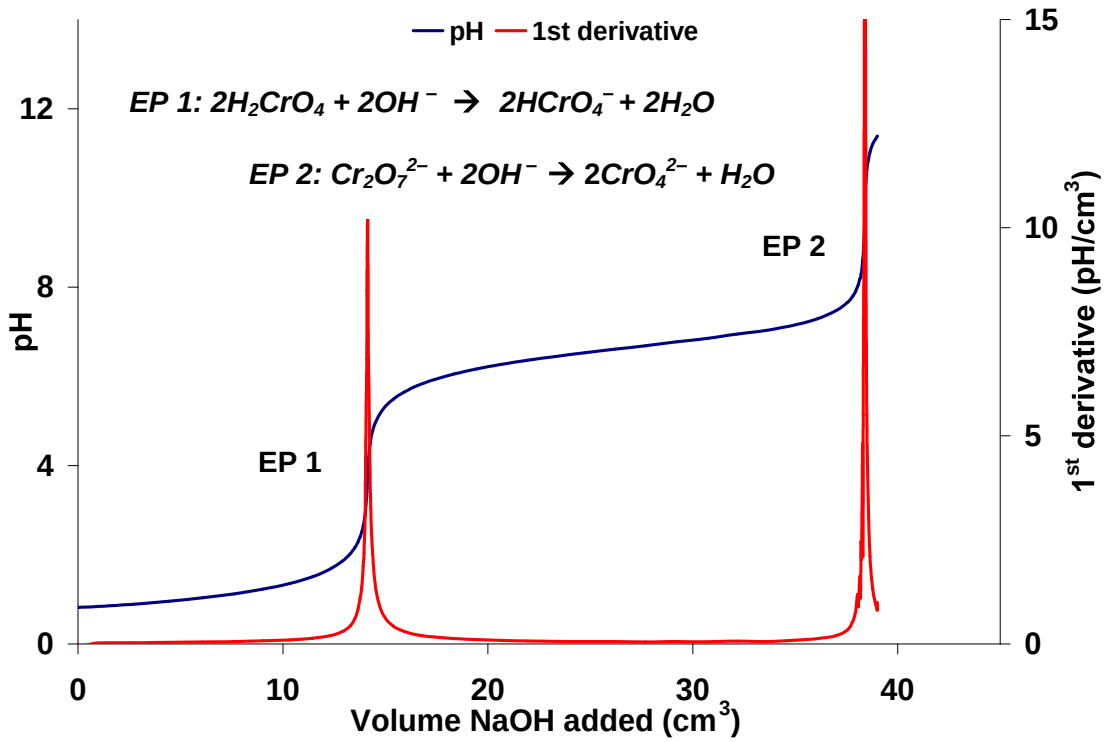

Figure 4.25. Simultaneous determination of the concentration of dissolved chromic acid and sodium dichromate using sodium hydroxide as titrant yields two clear and well-defined equivalence-points.

An example of a titration curve (solution 10) for the *simultaneous determination dissolved chromic acid and sodium dichromate* is detailed in Figure 4.25.

The equivalence-point is determined by a rapid change in pH versus added sodium hydroxide titrant and evaluated by the calculated maximum of the first derivative of volume added against pH measured.

The following results were obtained for the determination of chromic acid in a simultaneous titration to two equivalence points according to Figure 4.24. The full data set may be seen on Ref. 15 on the attached CD.

Solution no.	Cr(VI) added from chromic acid (mg)	Cr(VI) measured (mg)	Delta (mg)	|Error| (%)
1	102.5	102.8	0.3	0.3
2	272.5	271.1	-1.4	0.5
3	442.5	439.7	-2.8	0.6
4	612.5	608.9	-3.6	0.6
5	782.5	776.9	-5.6	0.7
6	102.5	103.1	0.6	0.6
7	272.5	271.2	-1.3	0.5
8	442.5	440.2	-2.3	0.5
9	612.5	609.4	-3.1	0.5
10	782.5	779.7	-2.8	0.4
11	102.5	102.8	0.3	0.3
12	272.5	271.2	-1.3	0.5
13	442.5	439.3	-3.2	0.7
14	612.5	608.4	-4.1	0.7
15	782.5	776.8	-5.7	0.7
16	102.5	103.2	0.7	0.7
17	272.5	271.3	-1.2	0.4
18	442.5	440.3	-2.2	0.5
19	612.5	608.6	-3.9	0.6
20	782.5	776.8	-5.7	0.7
21	102.5	102.8	0.3	0.3
22	272.5	271.2	-1.3	0.5
23	442.5	439.9	-2.6	0.6
24	612.5	608.2	-4.3	0.7
25	782.5	776.9	-5.6	0.7
			Spread	0.5
			Minimum	0.3
			Maximum	0.7
			Average	0.56

Table 4.6. Cr(VI) is added in known quantities from a chromic acid stock solution and determined via sodium hydroxide titration, testing the validity of equation 4.2.

In this case it is inappropriate to use the paired t-test since its validity rests on the assumption that any errors are independent of concentration (or is the case above quantity measured). An alternative method is to use linear regression analysis. The output shows that the r-value is 0.999996925*, and the slope of the plotted added vs. measured chromic acid content is 1.008022453*,

demonstrating near perfect correlation. *Data obtained from Excel. The measured maximum error of 0.7 % meets the requirements of less than 1 % as stipulated in section 4.1. This method is acceptable for the determination of chromic acid.

The following results (Table 4.7) were obtained for the determination of sodium dichromate. The full data set may be seen on Ref. 15 on the attached CD.

Sample 8 (highest error) was tested as an outlier according to Grubbs' test. G determined = 3.150 is greater than G critical (25 determinations) = 2.783, and was therefore rejected from the data set. Sample 5 (second highest error) was tested as an outlier according to Grubbs' test. G determined = 2.992 is greater than G critical (24 determinations) = 2.765, and was therefore rejected from the data set.

Solution no.	Cr(VI) added from sodium dichromate (mg)	Cr(VI) measured (mg)	Delta (mg)	|Error| (%)
1	522.50	518.7	-3.8	0.7
2	522.50	518.9	-3.6	0.7
3	522.50	525.8	3.3	0.6
4	522.50	530.6	8.1	1.6
5*	**522.50**	**537.6**	**15.1**	**2.9**
6	561.30	571.3	10.0	1.8
7	561.30	559.4	-1.9	0.3
8*	**561.30**	**582.5**	**21.2**	**3.8**
9	561.30	564.7	3.4	0.6
10	561.30	559.0	-2.3	0.4
11	600.00	593.7	-6.3	1.0
12	600.00	594.7	-5.3	0.9
13	600.00	597.8	-2.2	0.4
14	600.00	599.3	-0.7	0.1
15	600.00	609.6	9.6	1.6
16	638.80	633.2	-5.6	0.9
17	638.80	636.3	-2.5	0.4
18	638.80	636.1	-2.7	0.4
19	638.80	639.0	0.2	0.0
20	638.80	650.9	12.1	1.9
21	677.50	678.7	1.2	0.2
22	677.50	673.9	-3.6	0.5

23	677.50	680.4	2.9	0.4
24	677.50	676.8	-0.7	0.1
25	677.50	678.4	0.9	0.1

Spread (Excl. rejected data points)	1.9
Minimum (Excl. rejected data points)	0
Maximum (Excl. rejected data points)	1.9
Average (Excl. rejected data points)	0.67

Table 4.7. Cr(VI) is added in known quantities from a stock solution of sodium dichromate and determined via sodium hydroxide titration, testing the validity of equation 4.4. ***Samples 5 and 8 were rejected from the data set based on them being evaluated against a Grubbs' test.**

In this case it is also inappropriate to use the paired t-test. An alternative method is to use linear regression analysis. The output shows that the r-value is 0.995508897*, and the slope of the plotted added vs. measured sodium dichromate content is 0.990939875*, demonstrating good correlation, however not as near perfect as that seen in the chromic acid determination. *Data obtained from Excel. The measured maximum error of 1.9 % does not meet the requirements of less than 1% as stipulated in section 4.1. However, 82.6% of the results still meet this requirement.

Based on the evidence seen in Tables 4.6 and 4.7, it became clear that the way forward in the development of an on-line technique was to base this on a titrimetric determination. The technique is simple, and best suited to the ranges of Cr(VI) measured in electrolytical plant samples. The advantage of this type of technique is that it is a direct (not a comparative) technique (as opposed to e.g. a UV–VIS method). Another advantage of the method is that it is not pH sensitive, in that the method is not dependant upon an absolute or specific pH value, but rather two changes (two equivalence points) in pH values. Even if drift of the measuring electrode occurs with the pH measurement, this will not affect the determination.

Specific dilution considerations are not essential for this determination, i.e. the quantity of water used for dilution does not matter in the analysis since the chemistry that takes place is between chromic acid, dichromate ions and hydroxide ions directly. The only important consideration is that the solution being titrated is sufficiently concentrated in Cr(VI) ions [6] (greater than 1 g/dm^3) so that reactions 4.2 and 4.4 hold true as tested and proved above. The Cr(VI) content in the test samples of Tables 4.6 and 4.7 above, varied between about 17 (sample 1) and 42 g/dm^3 (sample 25). The Cr(VI) content in the electrolytical plant samples as seen from Figure 4.1 shows that in a final stage process stream this fluctuates between 481 and 557 g/dm^3.

In the standard method used in the sponsoring company's laboratory the norm is to take approximately 3 g of liquid sample and to dilute this with approximately 35 cm^3 of water at the start of the titrimetric method. This equates to a rough dilution factor of 12 times. The Cr(VI) concentration at the start of the titration is thus about 40 g/dm^3, well within the limit of having to be greater than 1 g/dm^3.

Consideration was paid to a conceptual and practical design for a titrimetric on-line analyser based on Figure 4.26.

A more comprehensive description with photographs of the individual equipment is available as Appendix 4.

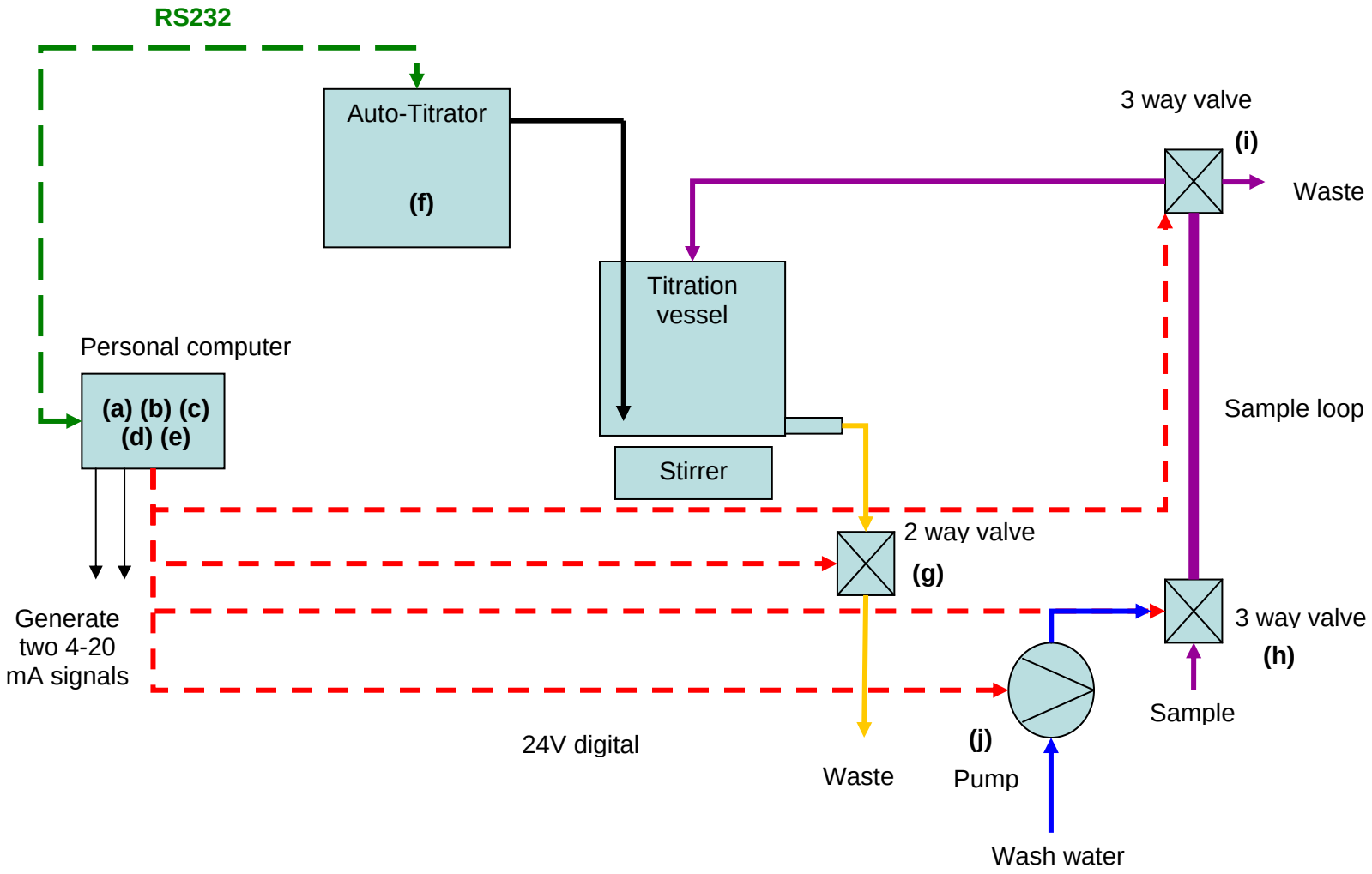

Figure 4.26. Conceptual design of chromic acid and sodium dichromate analyser based on a titrimetric technique. A sample loop is flushed with fresh sample liquid, and transported to a titration vessel with water. The sample is titrated with sodium hydroxide to two equivalence-points and evaluated accordingly. The titration vessel is flushed and washed with clean potable water.

The following hardware equipment and software was purchased and configured according to the design.

- 1 x Personal computer with a Windows XP operating system, Microsoft Excel and National Instruments' LabVIEW Base Development System version 8.0, referenced as **(a)** on the diagram
- NI PCI-6221 M series data acquisition card, supplied by National Instruments, referenced as **(b)** on the diagram
- SC-2345 shielded carrier with SCC-PWR01 powered option, supplied by National Instruments, referenced as **(c)** on the diagram
- 4 x SCC-RLY01 relay modules, supplied by National Instruments , referenced as **(d)** on the diagram
- 2 x SCC-CO20 current output module, supplied by National Instruments, referenced as **(e)** on the diagram
- 1 x Auto-titrator, supplied by Metrohm, referenced as **(f)** on the diagram
- 1 x 2-way solenoid valve, supplied by Bürkert, referenced as **(g)** on the diagram
- 2 x 3-way solenoid valves, supplied by Bürkert, referenced as **(h)** and **(i)** on the diagram
- 1 x Pump 320 cm^3 min^{-1} flowrate, supplied by Metrohm, referenced as **(j)** on the diagram

The programme that controls the functioning of the on-line analyser was written in the LabVIEW platform. A graphical representation of this programme is detailed in Figure 4.27.

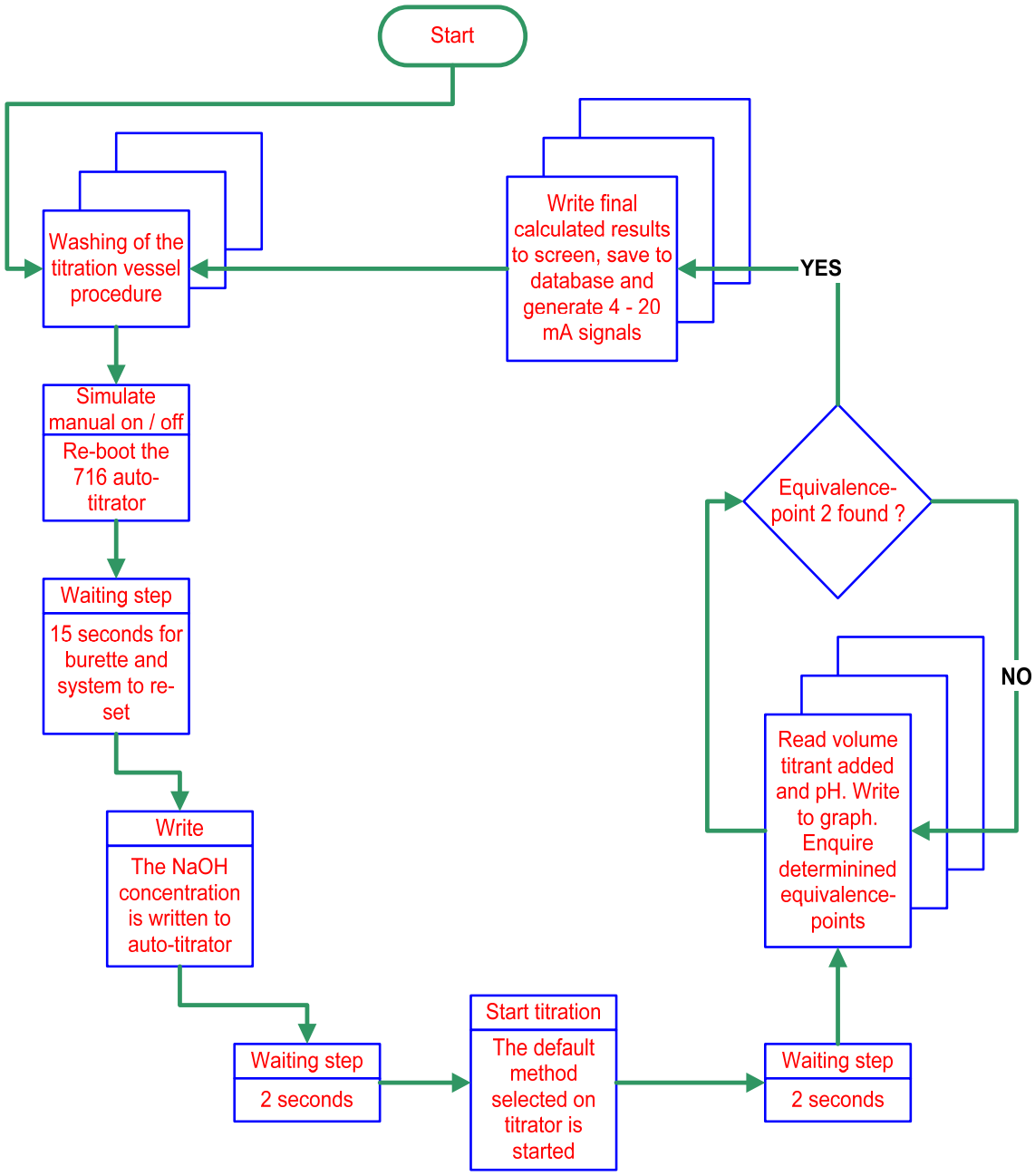

Figure 4.27. Graphical representation of the programme written to control the 716 auto-titrator, solenoid valves, peristaltic pump and signal inputs or outputs. National Instruments' LabVIEW software was used.

The individual files of the programme are available as *Ref. 18 - 25 on the attached CD*. The equivalence-point determination and calculations are performed directly on the 716 auto-titrator. The concentration of the titrant is recorded in the main screen of the programme window, and this is transferred via RS232 protocol to the auto-titrator at the start of the measuring cycle. Appendix 5 shows a screen shot of the front page of the programme that controls the functioning of the on-line analyser. The parameters required in the flushing, cleaning and sample taking steps, prior to the start of titrations are fully configurable. These four configurable steps are

1) Delay time (in seconds) for the addition of dilution water **(15 seconds)**
2) Delay time for the flushing of the sample loop **(10 - 60 seconds)**
3) Delay time for transporting the sample to the titration vessel by making use of water for flushing **(15 seconds)**
4) Delay time for draining of titration waste water and water used in the washing steps **(20 seconds)**

The suggested settings for the above mentioned parameters are indicated in bold above and used in the analysis further in this discussion. Potable water was used on the on-line analyser for the flushing and dilution steps.

The volume of sample taken by the on-line analyser (known as the “sample loop”) was 3.562 cm^3. The sample loop size was established by an acid base titration by flushing with c_{HCl} = 2.2340 (mol/dm^3) and titrating in the cell holder with c_{NaOH} = 1.0726 (mol/dm^3). The sample loop volume was calculated from the three known parameters of NaOH concentration, HCl concentration and equivalence-point volume according to the following equations.

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad (4.5)$$

$$\frac{Titer\ volume\ (cm^3)\ x\ c_{NaOH}\ (mol/dm^3)}{c_{HCl}\ (mol/dm^3)}$$

$$= Sample\ volume\ (cm^3)$$

Samples taken from the electrolytical production plant were analysed on the on-line analyser developed. They were titrated with freshly prepared sodium hydroxide solution according to the following parameters using a *monotonic* titration technique. Start volume 0 cm^3, start delay of 0 seconds, signal drift of 20 mV min^{-1}, waiting time 38 seconds, volume increment 0.1 cm^3 and a maximum dosing rate 50 cm^3 min^{-1}. The results were reported at a rate of 22 minutes per analysis cycle.

The following results were obtained for the determination of *chromic acid* using the on-line analyser developed on two real plant samples – anolyte product and mother liqour. The sample was compared against the standard laboratory method. In this method approximately 3 g of sample is weighed, and titrated to two equivalence points with 1 M sodium hydroxide titrant.

The sample's density is used to convert the measured data from a m/m basis expression to a m/v basis expression to compare with the on-line instruments data. The full data set may be seen as *Ref. 17 on the attached CD.*

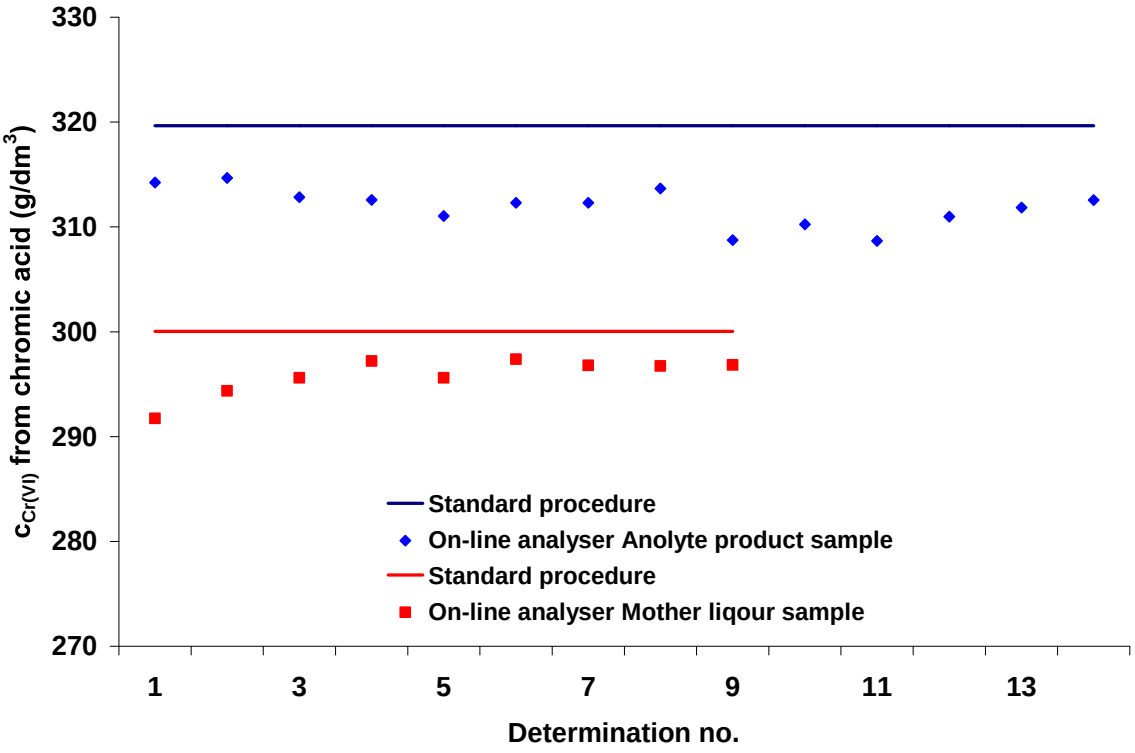

Figure 4.28. Results for the determination of chromic acid content in two samples. The standard laboratory method is compared to the on-line measurement developed.

A t-test was applied to measure the assumption that the standard laboratory result and measured quantities of chromic acid via the on-line analyser (14 determinations) were the same. t determined (2.230*) is less than t critical 2.447* (P = 0.05), and therefore it was found that the measured quantities of Cr(VI) from chromic acid via the on-line analyser in the anolyte product sample were not significantly different from the standard laboratory method. The measured average error of 2.42 % does not meet the requirements of less than 1 % as stipulated in section 4.1. The standard deviation of the on-line measurement was 1.82 g/dm^3 and that of the standard laboratory measurement was 9.09 g/dm^3.

Improvement was thus demonstrated as expected by the on-line measurement. The on-line measurement was negatively biased to that of the standard method, but the source of the systematic error was not investigated in this project.

Similarly the second sample (mother liquor) was evaluated. t determined (6.840*) is greater than t critical 2.262* (P = 0.05), and therefore it was found that the measured quantities of Cr(VI) from chromic acid via the on-line analyser (9 determinations) in the mother liquor sample were significantly different from the standard laboratory method.

The measured average error of 1.41 % does not meet the requirements of less than 1 % as stipulated in section 4.1. The standard deviation of the on-line measurement was 1.80 g/dm^3 and that of the standard laboratory measurement was 0.29 g/dm^3.

The on-line measurement was negatively biased to that of the standard method, but the source of the systematic error was not investigated in this project.

The following results were obtained for the determination of *sodium dichromate* using the on-line analyser developed on two real plant samples –
anolyte product and mother liqour.

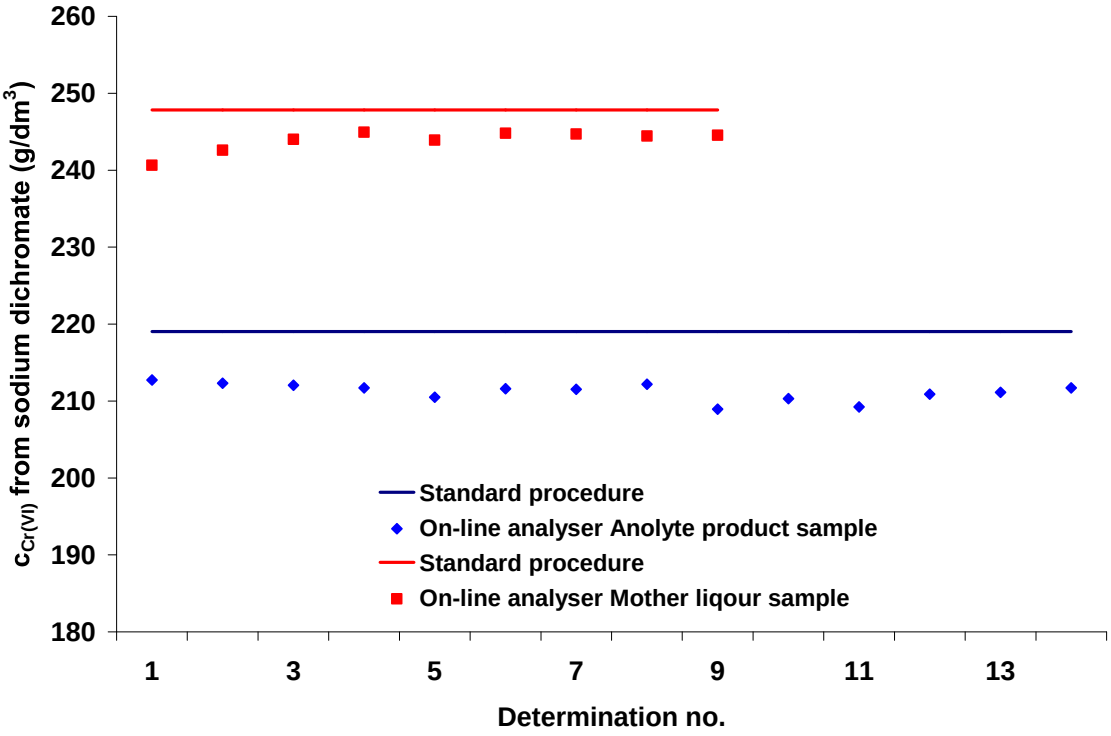

Figure 4.29. Results for the determination of sodium dichromate content in two samples. The standard laboratory method is compared to the on-line measurement developed.

A t-test was applied to measure the assumption that the standard laboratory result and measured quantities of sodium dichromate via the on-line analyser (14 determinations) were the same. t determined (3.725*) was greater than t critical 2.093* (P = 0.05), and therefore it was found that the measured quantities of Cr(VI) from sodium dichromate via the on-line analyser in the anolyte product sample were significantly different from the standard laboratory method.

The measured average error of 3.58 % does not meet the requirements of less than 1 % as stipulated in section 4.1. The standard deviation of the on-line measurement was 1.13 g/dm^3 and that of the standard laboratory measurement was 7.92 g/dm^3. Improvement was thus demonstrated as expected by the on-line measurement.

The on-line measurement was negatively biased to that of the standard method, but the source of the systematic error was not investigated in this project.

Similarly the second sample (mother liquor) was evaluated. t determined (2.402*) is greater than t critical 2.201* (P = 0.05), and therefore it was found that the measured quantities of Cr(VI) from sodium dichromate via the on-line analyser (9 determinations) in the mother liquor sample were significantly different from the standard laboratory method. The measured average error of 1.61 % does not meet the requirements of less than 1 % as stipulated in section 4.1. The standard deviation of the on-line measurement was 1.40 g/dm^3 and that of the standard laboratory measurement was 4.79 g/dm^3.

The on-line measurement was negatively biased to that of the standard method, but the source of the systematic error was not investigated in this project.

Careful consideration was paid to a using the guidelines of chapter 1, section 1.4 as detailed in Table 4.12.

Consideration requirements	Comment	Challenge or advantage
Selection of the process variable	Information gained could be used to operate the process more efficiently (chromic acid and sodium dichromate content)	None
Quantitative relation between the measured and controllable properties	Chromic aid and sodium dichromate content is measured directly. Mathematical manipulation of data to suit plant requirements	None
Places of sampling	Final stage of electrolysis production	None. Some initial costs for chromic acid resistant piping for sample take-off point.
Frequency of the measurements	Continuous analysis required as per sponsoring company's request. However the nature of electrolytical operations is that the norm is for a stable process. Slow changes are required. Therefore analysis cycle times are not instantaneous.	Guidelines of reporting of data between 10 to 30 minutes. Analysis cycle of 22 minutes was achieved.

Time duration of the measurements	Analysis cycle of 22 minutes was achieved.	Meets all requirements
Tolerance limits	Guideline of 1 % accuracy stipulated	Was met for Chromic acid based on laboratory accuracy tests. Was almost met for sodium dichromate based on laboratory accuracy tests. On-line measurements not as accurate as laboratory tests. However variance is less for the on-line measurements. Systematic error. Not investigated.
Selection of sensing or analysing instrument(s)	Automatic titrator with pH probe	Simple and relatively cheap.
Cost and maintenance of instruments	On-line titrator @ ca. R50 k. CPU and peripherals ca. R10 k. Two and three-way valves ca. R4500. Peristaltic pump R1500.	Moderate capital investment.
Calibration frequency of the instruments used	None required. Determinations are pH	Direct technique. Concentration of titrant

	sensitive. Method is robust in that it senses a pH change rather than an absolute pH.	needed as an input to the determination
Total cost of measurements	Relatively inexpensive. NaOH is inexpensive. Potable water is used for dilution and rinsing.	None.
Reliability, ease of operation and simplicity.	Simple. Reliability is proved in that the technique is well known.	Easily achievable in an environment where technical staff are responsible for analytical equipment.

Table 4.8. Summary of considerations for the development of a titrimetric technique for on-line application.

From the information and rationale derived from Table 4.12 it became clear that there where not too many challenges in the conceptual design of this on-line application. Costs were not excessive.

The on-line analyser developed in this project was suitable for the quantification of the chromic acid and sodium dichromate.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

This project addressed the design and development of an on-line monitoring system, for the liquid product (anolyte) in the electrolytical production of chromic acid.

The original scope of this project called for a spectrophotometric technique for the evaluation of the chromic acid and sodium dichromate content in the anolyte liquor. This was investigated by combining a UV-VIS technique with Artificial Neural Network technology and was found to be unsuccessful. The correlations between the actual and computed results were not satisfactory. Agreement was not found.

A second approach was investigated by combining a UV-VIS technique with Ion Selective Electrode measurements, as an indirect method for the quantification of chromic acid and sodium dichromate. By combining the data of the UV-VIS measurements and the Ion Selective Electrode measurements (UV-VIS / ISE) it was found that these measurements were *not* significantly different from the standard laboratory technique - an acid / base titration method. UV-VIS / ISE is a viable alternative method for these measurements, although not necessarily the best suited for an on-line application. The error measured for the sodium content was found to be 2.8 % and the error measured for the Cr(VI) was found to be 2.3 % using the UV-VIS / ISE methods.

The standard laboratory technique was considered as a development path and investigated for the construction of the on-line analyser.

A spike and recovery analysis of known quantities of chromic acid and sodium dichromate in mixtures of these two analytes, showed excellent results. An

average error of 0.6 % was measured for the chromic acid content and 0.7 % for the sodium dichromate content.

The arrangement of equipment according to Figure 4.27 was used to build an on-line analyser. The sample loop of this analyser was calibrated and found to be 3.562 cm^3. It is imperative that should adjustment be made to this loop for whatever reason, that it be recalibrated, and that the accompanying calculations and formulas on the auto-titrator are adjusted accordingly.

The required rate of reporting of the analysis by the sponsoring company of between 10 and 30 minutes was met. The actual reporting rate was found to be 22 minutes per result. This may be accelerated by making use of a dynamic titration mode (rather than a monotonic titration mode used in this work), but the impact of this on accuracy was not investigated in this dissertation.

Two sample streams (Anolyte product and Mother Liqour) analysed on the on-line instrument show average errors of 1.9 % for the chromic acid content and 2.6 % for the sodium dichromate content. The requirement of less than 1 % was not achieved. However, it is clear that the standard deviations measured on both analytes are better than that achieved in the laboratory methods. For example, the Mother liquor sample shows a decrease from 9.09 g/dm^3 to 1.82 g/dm^3 for the chromic acid content, and 7.92 g/dm^3 to 1.13 g/dm^3 for the sodium dichromate content.

The auto-titration apparatus (supplied by Metrohm) used for this project is a system making use of RS232 communication protocols. This protocol is outdated in the latest available equipment from the same supplier. The newest titration apparatus makes use of a USB communication port. The string functions used in the RS232 communication protocol are freely available and published in the operating manuals. The communication functions used for the USB protocol are however *neither freely available nor* published in the operating manuals. The

ideal scenario would have been to develop a modern analyser based on the newest available equipment.

There are alternative options in the market place for commercially available titrations systems. The most recent of these includes an at-line system called the *875 ProcessLab* supplied by Metrohm [54]. Applicon Analytical [55] also supply equally-capable modern titration systems.

Notwithstanding the restrictions of the older technology of the auto-titration device, the remaining equipment is modern, easy to use, easily replaceable and most of all simple in its design with the on-line analyser.

The main operating window of the programme controlling the on-line analyser, written in the LabVIEW platform, has adjustable options available. For example, the operator may choose to lengthen the washing cycle by the addition of more water for flushing. Another example may include the lengthening of the flushing time of the loop by the sample. If the analyser is installed far from the actual sampling point in the electrochemical process, this flushing time may be increased.

The existing design of the on-line analyser makes use of a personal computer and a carrier box (housing the electronic relays and current output modules). Ideally this is not the best suited equipment for an industrial environment. Fortunately *National Instruments* market the equivalent in industrially suited parts under the brand name LabVIEW Real-Time. A moderate investment of about R30 000 for hardware parts and about R25 000 for a software module is required. A conversion from a desktop-designed application to a standalone version in an industrial environment will be possible.

The on-line analyser developed is simple, robust, inexpensive to operate, moderately priced and suitable for the application of accurately measuring the

chromic acid and sodium dichromate content in liquors produced by the electrochemical production of chromic acid.

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APPENDIX 1

STANDARDISATION OF IRON(II) SULPHATE TITRANT

Hexavalent chromium (the analyte) is reduced to trivalent chromium by ferrous ions (the titrant). The potential of the solution being titrated is measured using an automatic titrator, fitted with a Titrode® electrode from Metrohm. The equivalence point in this determination is indicated by a rapid change in potential of the measuring solution.

The reactions taking place are as follows:

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^{-}$$

$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} \longrightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+}$$

Materials	*Supplied by*
• Deminerlised water	
• $K_2Cr_2O_7$	Merck 1.02403.0080 99.97 ± 0.05%
• $Fe_2SO_4.7H_20$	Saarchem AR > 98 %
• H_3PO_4	Saarchem, 4818040 LC, min. 85 %
• H_2SO_4	Saarchem, 5885060 LP, min. 95 %

Apparatus

- A-grade volumetric flasks and volumetric equipment
- Pipetting equipment or dosing equipment e.g. Metrohm auto-titrators and Dosimat
- 716 / 794 Metrohm auto-titrators and 814 USB Metrohm sample processor.
- Pt Titrode® Electrode from Metrohm
- Tiamo 1.1 Metrohm software

Procedure

- Remove potassium dichromate crystals (KDC) from oven and allow to cool to room temperature in a desiccator
- Weigh ca. 0.3 - 0.4 g KDC into a 150 cm^3 glass beaker. (4 samples). Record mass to 4 decimal places
- Place the samples in position on the 814 USB Metrohm sample processor and start the determination by selection of the appropriate method of analysis
- The sample's analyte concentration will be evaluated by the software as per calculation below

The automated method adds water and acid before the determination starts.

Calculation

$$\frac{Mass\ KDC\ (g)\ x\ 6\ x\ 1000}{M_{(KDC)}\ (g/mol)\ x\ Titer\ volume\ (cm^3)}$$

$$= c_{Fe(II)}\ (mol/dm^3)$$

APPENDIX 2

To get a smoother spectrum without losing information it is important to set in the software the correct smoothing parameter.

The optimal smoothing parameter depends on the distance between the pixels at the detector array and the light beam hat enters the spectrometer. For the AvaSpec-2048, the distance between the pixels on the CCD-array is 14 micron.

With a 200 micron optical fiber (no slit connected) the optical resolution is about 14.3 CCD-pixels. With a smoothing parameter set at 7, each pixel will be averaged with 7 left and 7 right neighbour pixels. Averaging over 15 pixels with a pitch distance between the CCD pixels of 14 micron will cover 15 x 14 = 210 micron at the CCD array. Using a fiber diameter of 200 micron, means that one will lose resolution when setting the smoothing parameter to 7. Theoretically the optimal smoothing parameter is therefore 6. If a 50 micron slit is installed in the spectrometer (as is the case in these experiments), the optical pixel resolution will therefore be 3.6 CCD-pixels, and the smoothing parameter should be set to 1.

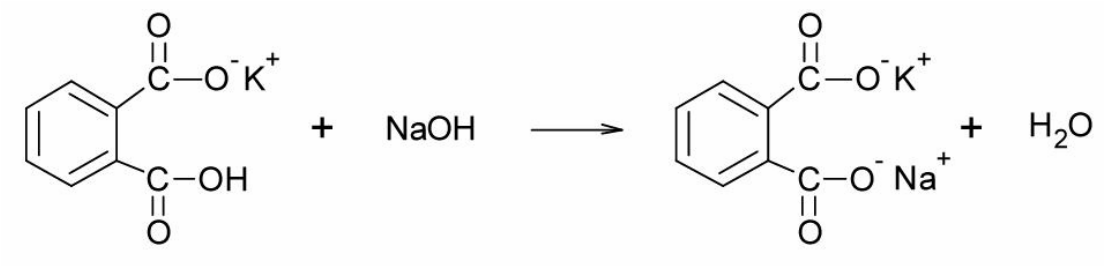
If resolution is not an important issue, a higher smoothing parameter can be set to decrease noise against the price of less resolution.

APPENDIX 3

STANDARDISATION OF SODIUM HYDROXIDE TITRANT

In an acid-base titration, a known mass of potassium hydrogen phthalate (KHP) crystals is titrated with sodium hydroxide solution. The equivalence-point in this determination is indicated by the neutralisation of the carboxylic acid group. The equivalence-point is detected by a rapid change in pH, and calculated using an automatic titrator and pH electrode.

The reaction taking place is as follows:



Materials	*Supplied by*
• Deminerlised water	
• $C_8H_5KO_4$	Merck 1.04874.0250 $\geq$99.95%
• NaOH	Saarchem SAAR5823200Fl > 98 %

Apparatus

- 50 cm^3 drying crucible
- Drying oven set at 105°C
- 150 cm^3 tall form beaker
- Spatula
- 4 decimal point analytical balance, Metler AG 204
- Stirrer plate
- 716 Metrohm auto-titrator fitted with 50cm^3 burette
- Tiamo 1.1 Metrohm software

- Desiccator

Procedure

- Remove KHP crystals from oven and allow cooling to room temperature in a desiccator
- Weigh ca. 6 g KHP crystals into a 150 cm^3 glass beaker. (4 samples). Record mass to four decimal places
- Place the samples in position on the 814 USB Metrohm sample processor and start the determination by selection of the appropriate method of analysis
- The sample's analyte concentration will be evaluated by the software as per calculation below

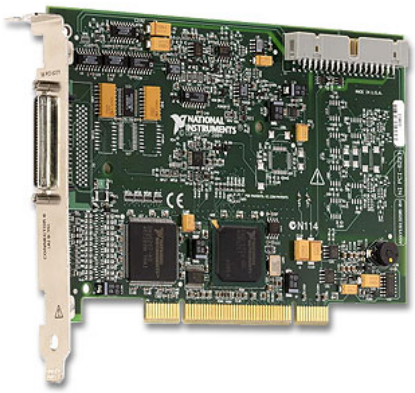
Calculation

$$\frac{Mass\ KHP\ (g)\ x\ 1000}{M_{(KHP)}\ (g/mol)\ x\ Titer\ volume\ (cm^3)}$$

$$= c_{NaOH}\ (mol/dm^3)$$

APPENDIX 4

Equipment that was used in the assembly of the on-line analyser is shown below.

NI PCI-6221 M series data acquisition card with NI-DAQ driver software. Labeled as **(a)** on Figure 4.26	16 Analog inputs, 24 Digital I/O, 2 analog outputs. Fitted with a SHC68-68-EPM shielded cable, supplied by National Instruments 
SC-2345 shielded carrier. Labeled as **(c)** on Figure 4.26	SCC-PWR01 5 V power option, supplied by National Instruments 

SCC-RLY01 relay modules. Labeled as **(d)** on Figure 4.26	Non-latching relay capable of switching 5 A at 30 VDC, supplied by National Instruments 
SCC-CO20 current output module. Labeled as **(e)** on Figure 4.26	0 – 20 mA output, supplied by National Instruments 
2-way and 3-way solenoid valve. Labeled as **(g, h and i)** on Figure 4.26	24 V DC PTFE body with Viton seals for wetted parts supplied by Bürkert 

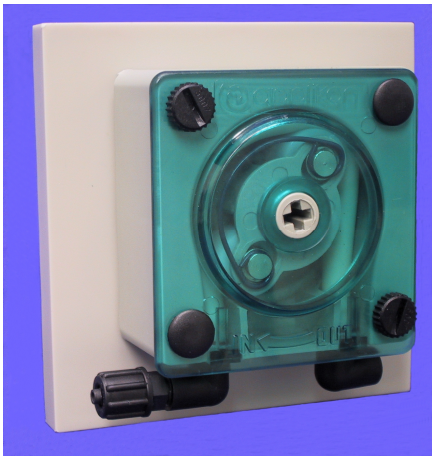
Auto-titrator. Labeled as **(f)** on Figure 4.26	A 716 DMS Titrino was used in this project similar to picture below, supplied by Metrohm 
Peristaltic pump. Labeled as **(g)** on Figure 4.26	320 cm^3 min^{-1}, supplied by Metrohm 

Table A4.1 Description and photographs of the individual components of the on-line titrator. Parts are labeled according to Figure 4.26.

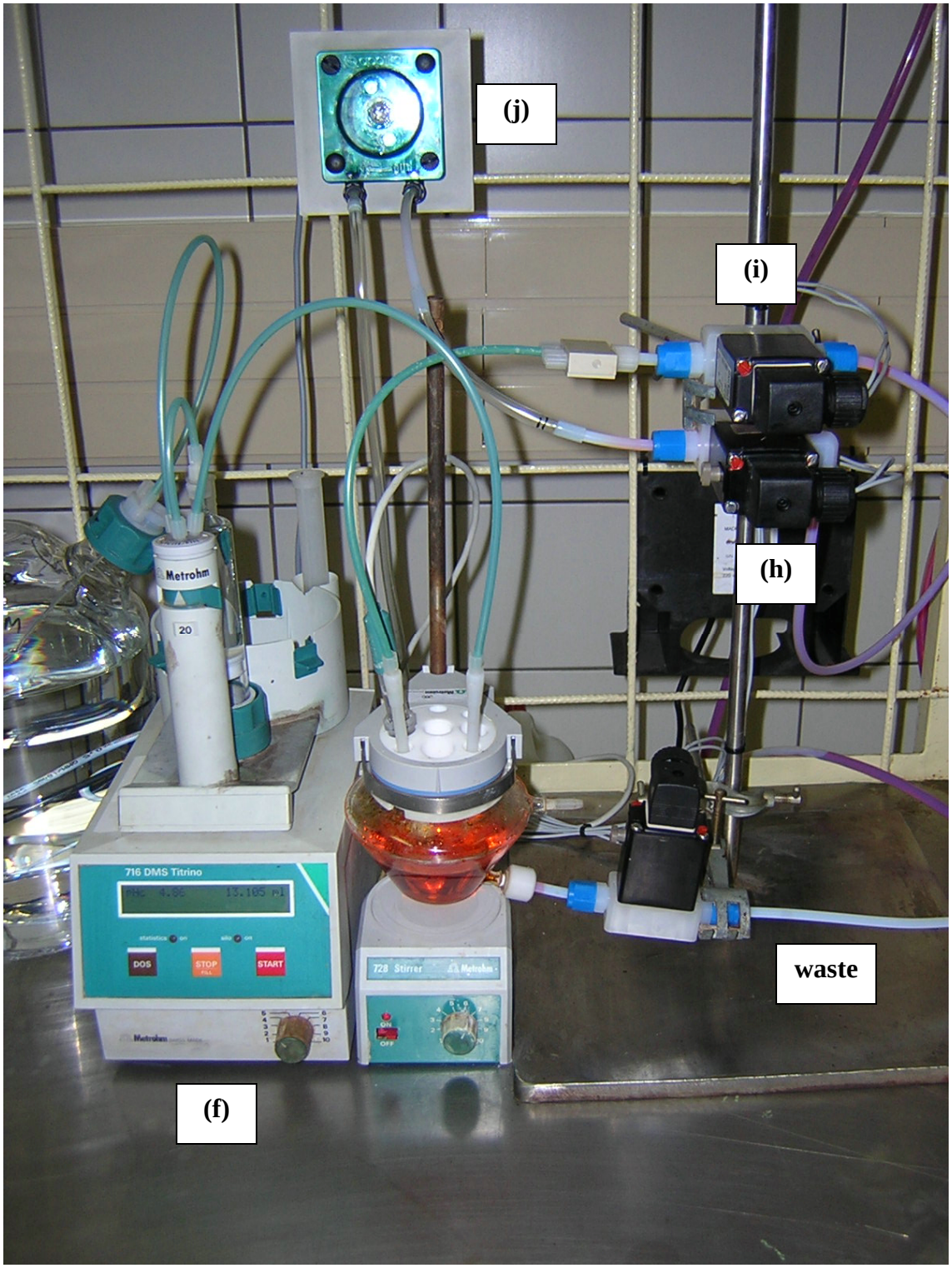


Figure A4.1 Photograph of the “wet” part of the on-line analyser. The computer and carrier box are not shown in the picture. Parts are labeled according to Figure 4.26.

APPENDIX 5

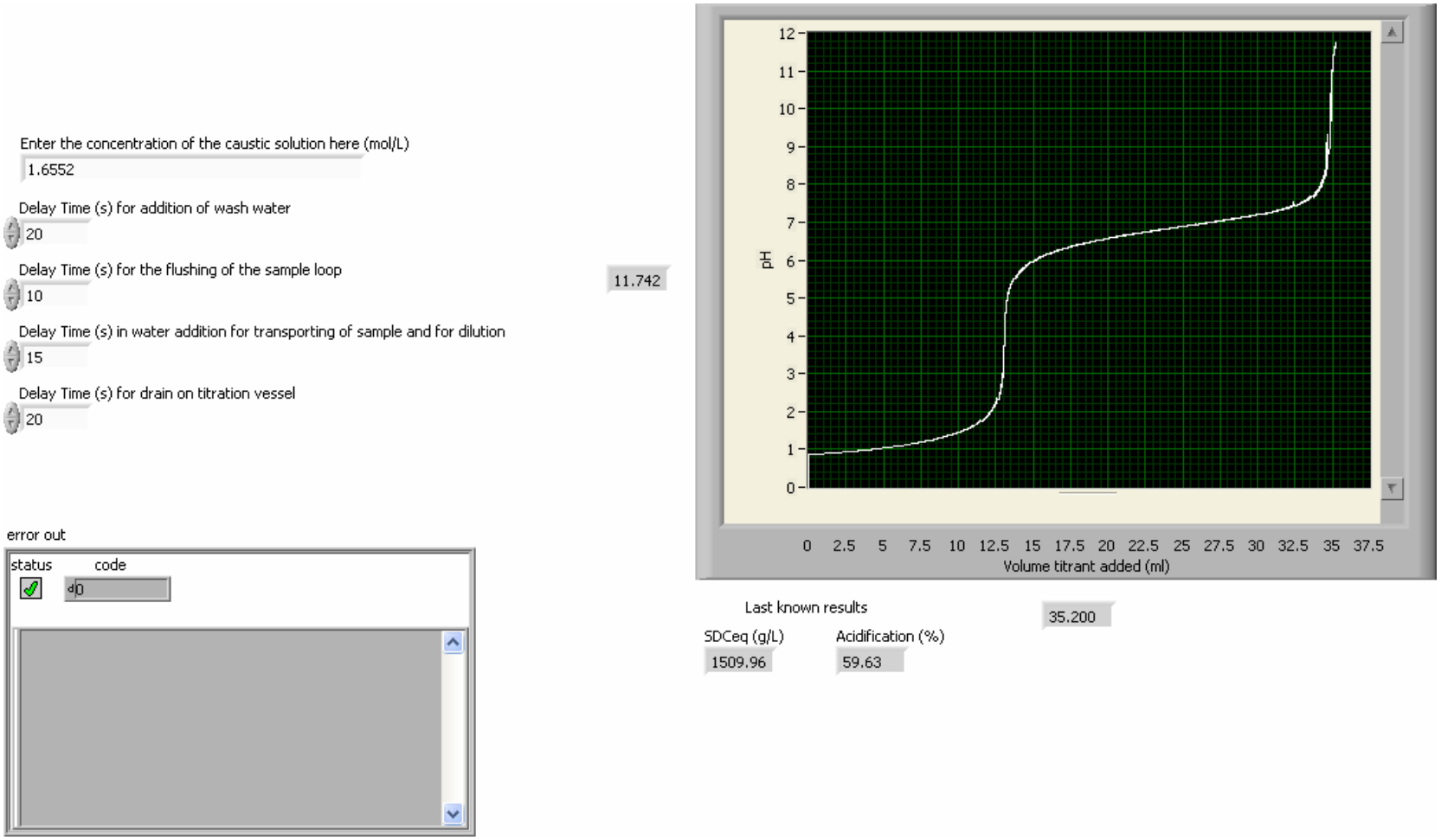


Figure A5.1 Shows a screen shot of the front page of the programme that controls the functioning of the on-line analyser.