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OPTIMISATION AND EVALUATION OF BORON ANALYSIS FOR PRESSURIZED WATER REACTOR PLANTS

by

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DECLARATION

I, Nomalanga Gloria Tasana, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed	**Date**

ABSTRACT

Boron concentration analysis is an important and critical analysis performed by the Analytical Chemistry Laboratory at Koeberg Nuclear Power Station (KNPS), because boron controls reactivity and the concentration determination is a Technical Specification Parameter (safety parameter). Hence accurate, precise results for boron concentration produced by laboratories and on-line analysers are important because of their operational implications associated with reactivity control and also for nuclear safety.

The project focused on comparing the quality of chemical analysis results of boron produced by analysis techniques/ methods used at Koeberg Nuclear Power Station namely; Potentiometric Titration, Atomic Absorption Spectrophotometry (Flame) and UV-VIS Azomethine-H method. The methods were described, optimised, evaluated and compared in terms of uncertainty of measurement, accuracy, precision, analysis range, limitations, appropriateness and applicability for boron analysis in 2500 mg B/kg concentration range. For Potentiometric Titration method, the measurement uncertainty = 2500 ±16 mg B/kg, accuracy= 0.2%, precision= 0.08% the range of analysis= 5-800 mg B/kg. For Atomic Absorption Spectrophotometry (Flame) the measurement uncertainty= 2500 ±51 mg B/kg, accuracy= 0.12%, precision= 0.44% the range of analysis= 0 -500 mg B/kg. For UV-VIS Azomethine-H the measurement uncertainty= 2500 ±72 mg B/kg, accuracy= 0.08%, precision= 0.44% the range of analysis= 0 -10 mg B/kg. The INPOs 95% accuracy and precision criteria for boron is ± 1%. So these techniques could be used for boron analysis in PWR. Based on the evaluation and assessments mentioned above; the Potentiometric Titration was found to be the most preferred method for boron analysis for Pressurised Water Reactors followed by Atomic Absorption Spectrophotometry (Flame) that can be of good use in determining boron especially in waste samples and samples with complex matrices. The UV-VIS Azomethine-H methods can only be used when it is really necessary to determine very low levels of boron between 0- 10mg B/kg of which it was never required before.

Since it is specifically the B-10 isotope that is responsible for the ability to control reactivity, the implementation of isotopic boron analysis (by Inductively Coupled Plasma – Mass Spectrometry) at KNPS is explained and the advantage of the programme is illustrated. Although the current state of instrumental capabilities is adequate for ^{10}B isotope determination, further work of optimising the methodology for even better results is recommended.

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DEDICATION

This work is dedicated to: My parents Mr MLuleki Alfred and Mrs Nogcinile Mavis Tasana.
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GLOSSARY

Acronyms/Abbreviations	Explanation
AA	Atomic Absorption
AES/AAS	Atomic Emission/ Absorption Spectrometry
AGR	Gas Cooled Reactors
ASTM	American Society for testing Material.
B	Boron
B10	Boron 10
BA	Boric acid
BWR	Boiling Water Reactor
CRM	Certified Reference Material
EBA	Enriched boric acid
EPR	Evolutionary Power Reactor
ERM	European Reference Material
ICP-MS	Inductively coupled Mass Spectra
ICP-OES	Inductively coupled Optical emission spectrometry
INPO	Institute of Nuclear Plant Operations
KER	Liquid Effluent Monitoring System
KNPS	Koeberg Nuclear Power Station
Li OH	Lithium hydroxide
Li	Lithium
LIMS	Laboratory Information Management System
NBA	Natural boric acid
OE	Operating Experience
PHP	Potassium Hydrogen Phthalate
PHVR	Pressurised Heavy Water Reactor
PT	Potentiometric Titration
PTR	Reactor and Spent Fuel System
PWR	Pressurised Water Reactor
PWSCC	Primary Water Stress Corrosion Cracking
QC	Quality Control
RBMK	Light Water Graphite Reactor
RCP	Reactor Coolant System
RCS	Reactor Coolant system
REA	Reactor Make-up System
RFE	Reactor Fuel Engineering
RIS	Reactor Safety Injection System
RRA	Residual Heat Removal
RSD	Relative Standard Deviation
SPC	Statistical Process Control
TEP	Boron Recovery System
TEU	Liquid Waste Treatment System
TRC	Technical Review committee
UV-VIS	Ultra Violet- Visible
Zn Ac	Zinc Acetate

Definition/Explanation

Analytes :	Are substances whose chemical constituents are being identified and measured, i.e. Boron: mg B / kg (water + chemical), Lithium: mg Li / kg (water + chemical), Zinc: µg Zn / kg (water + chemical) and Nickel: µg Ni / kg (water + chemical).
Accuracy:	Closeness of the agreement between a measurement result and a true value. As true value is not known, accuracy is a qualitative term only
Analyte concentration in [mg Analyte / kg]:	Mass of analyte in mg / Mass of solution in kg (total mass of water and the chemical in kg). Mass of boron in mg / Total mass of water and the boron, including boric acid impurities, in kg.
Analyte concentration in [µg Analyte / kg] :	Mass of analyte in µg / Mass of solution in kg (total mass of water mass and chemical in kg). -Mass of boron in µg/ Total mass of water containing the boron including boric acid impurities in kg.
Measurand:	Specific quantity subject to measurement.
Precision:	Precision describes the reproducibility of results, i.e. agreement between the numerical values of two or more measurements that have been made in the same way. Representing the scatter of results that one can expect from multiple analyses of the same sample.
Reproducibility Precision:	Describes the reproducibility of results i.e. agreement between numerical values of two or more measurements that have been made in exactly the same way by the single analyst over a large time scale. The RSD should be as low as possible.
Uncertainty:	a parameter, associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to measurement.

CHAPTER ONE: INTRODUCTION

1.1 Importance of analytical chemistry in industries

Analytical chemistry is the study of the separation, identification and quantification of chemical components of natural or artificial material [1]. Qualitative analysis gives an indication of identity of the chemical species in the sample and quantitative analysis determines the concentration of one or more the components [2]. Analytical methods can be separated into classical and instrumental methods. Classical methods (known as wet chemistry method) use separation such as precipitation, extraction, distillation and qualitative analysis by colour, odour or boiling melting point. Quantitative analysis is achieved by measurement of mass or volume of a specific chemical. Instrumental methods make use of apparatus to measure physical quantities of the chemical species such as light, absorption, fluorescence, pH or conductivity. The separation of materials can be accomplished by chromatography or electrophoresis methods. Analytical chemistry has numerous and varied applications worldwide; examples include forensics, bio-analysis, clinical analysis, environmental, petrochemical and material analysis.

For the analytical chemistry laboratory program to function it requires a well-equipped laboratory with material to be used, analytical procedures, guides and standards that describe the methods to be employed. The laboratory must also be able to verify the validity of the data produced. Each method should be validated and documented as evidence regarding the applicability and the method limitations, the level of accuracy precision, repeatability, reproducibility and uncertainty of measurement.

Chemical analyses in all industries and countries

Chemical analyses in all industries and countries play a critical role of providing the analytical measurements results used in decision making. If we take forensic science for the process of law as an example, wrong results reported could lead to wrongful conviction or the guilty go unpunished. The function of an analytical laboratory facility is to provide accurate and precise analytical data to its customers. To ensure accuracy, with minimum or no errors to be committed and to ensure precision, uncertainties in sampling and analyses methods need to be minimised. There is however, uncertainty in all analytical measurement. It is therefore the duty of the laboratory management to continuously ensure that uncertainty of measurement is kept to a minimum. To keep uncertainty of measurement to a minimum, homogenous samples, well characterised reference materials, maximum replicates of analysis of sample, maximum replicate of analysis of reference materials, high calibration sensitivity and reliable instrumentation is required. Moreover, the use of independent forms of analysis of samples and statistical comparison of results is good analytical practice that gives confidence in the analytical data produced by the laboratory. The use of competent analysts with the necessary skills, passion for excellence and responsibility is also a key requirement for the reliability of analytical data. With the plethora of analytical techniques and instrument suppliers available to the laboratory it is important that the procurement of instrumentation adequately covers the specifications, service availability, and availability of spare parts. The use of competent materials such as correct grade, certified purity and the effective storage of such materials are tantamount to the laboratory achieving reliable analytical data. The use of competent methods that have been proven to be fit for purpose through method validation are a cornerstone of good analytical practice. Methods should be evaluated for uncertainty, accuracy, precision, working range and sensitivity.

In the nuclear power plant

Analytical chemistry laboratory plays a major role in monitoring the chemistry of the plant. Boron concentration analysis is one of the most important and critical analysis performed by the analytical chemistry laboratory at Koeberg Nuclear Power Station. This is due to the fact that it is used during the fission process in the reactor for reactivity control and the concentration determination is a safety parameter – Operating Technical Specification. The control of the fission process in the reactor core of a pressurised water reactor (PWR) is achieved through the absorption of the fast or energetic neutrons by a burnable poison, namely boron. This is primarily because boron has a high neutron absorption coefficient, widely used by commercial PWRs to limit or control reactivity. Boron has two naturally occurring isotopes, Boron-10 (^{10}B = 19.9%) and Boron-11 (^{11}B = 80.1%) introduced into the reactor coolant as boric acid which is supplemented with solid boron in the form of borosilicate glass rods. B-10 isotope is responsible for the ability to control reactivity. When B-10 is consumed through neutron absorption, this alters the natural relative abundances of the two isotopes in the reactor coolant water. The variation in boron concentration allows control rod usage to be minimised, which results in a flatter flux profile over the core that can be produced by control rod manipulation. By varying the concentration of boric acid (and hence also the ^{10}B concentration) in the coolant, through a process referred to as borating (adding concentrated boric acid solution) or diluting (adding demineralised water), the reactivity of the core can be easily managed. An increase in boron concentration (borating) creates negative reactivity and if the boron concentration is reduced (diluting), positive reactivity is added. The changing of boron concentration in a PWR is used primarily to compensate for fuel burn-up or poison build-up. In a normal fuel cycle, as the nuclear fuel is being consumed, the reactor coolant boric acid (^{10}B) concentration is reduced by dilution with purified water to maintain the reactor at constant power. Besides in the reactor coolant water, boric acid concentration is also important in the chemical and volume control system and reactor make-up system for operation. For nuclear safety, boric acid concentrations are technical specification parameters, maintained and monitored in the spent fuel system and safety injection systems. Boron concentration determination is also required for boron recovery and liquid waste treatment.

Some of the reasons why boron concentration is so important in these systems are: There could either be an inadvertent boron dilution of the safety related system, in which case the system in question will not have sufficient boron concentration required in a case of accident. The other is that if too high boron concentration is maintained in the system, it can lead to molar solubility being exceeded with the result that crystallisation would occur; the consequence being that the pumping of boric acid solution to the required destination won't be possible. Both these scenarios would pose a nuclear safety incident which is not desirable. The boron concentration on all the systems must conform to the limits as set in the Operating Technical Specification which is a Nuclear Licence Binding document for the safe operation of Koeberg. Failure to meet the requirements as per this document can result in the shutdown of Koeberg Units by the National Nuclear Regulator (NNR).

When Koebeg is shut down, there will be insufficient electricity supplied to the grid in the Western Cape and in South Africa and thus will affect the South African Economy as a whole. Accurate, precise concentration of boron results produced by laboratory is important because of its operational implications associated with reactivity control and also for nuclear safety. Koeberg Nuclear Power Station Analytical Laboratory is playing a major role in electricity generation and it contributes to the South African economy.

Some Operating Experiences at Koeberg Nuclear Power Station involving boron determination has been shared, one involving a safety injection tank that went out of specification on boron concentration and another where an erroneous quality control check caused an apparent boron dilution concern. An operating experience at KNPS involving boron isotopic ratio B-10: B-11 determination is presented, where incorrect (lower than expected) boron 10 results were reported due to instrument drift.

Laboratories use ISO 17025:2005 to implement a quality system aimed at improving their ability to consistently produce valid results. It is also the basis for recognition from an Accreditation Body. The ISO 17025:2005 standard is about competence. Accreditation is simply formal recognition of a demonstration of that competence. To make analytical data to be technically sound and defensible, it is important to consider the limitations to be assigned to the data presented. The first to consider is the accuracy the second is precision of the data and the third one measurement of uncertainty.

In this project three methods used for boron analysis at Koeberg Nuclear Power Station, will be optimised and evaluated to assess the reliability of results through determination of uncertainty measurement, accuracy, precision, applicability and appropriateness. It has been said that, measurement/ validity of measurement of a parameter is meaningless unless the range which the value reported is defined or uncertainty of the test is known. The uncertainty estimation will be carried using the modelling approach according to Gum and the EURACHEM guides.

1.2 Boron / boric acid background and information

1.2.1 Boron properties

Boron is a chemical element with atomic number 5 with a molecular weight of 10.811. The melting point of boron is 2075 ℃, it's boiling/sublimation point is at 4000 ℃, the specific gravity of crystalline boron is 2.34, the specific gravity of the amorphous form is 2.37, and its valence is 3 [20].

Boron has interesting optical properties. The boron mineral ulexite exhibits natural fibrotic properties. Elemental boron transmits portions of infrared light. At room temperature, it is a poor electrical conductor, but it is a good conductor at high temperatures. Boron is capable of forming stable covalently bonded molecular networks. Boron filaments have high strength, yet are lightweight. The energy band gap of elemental boron is 1.50 to 1.56 eV, which is higher than that of silicon or germanium. Although elemental boron is not considered to be a poison, assimilation of boron compounds has a cumulative toxic effect [20, 29].

Elemental boron is one of the high thermal neutron absorption cross section of 755 barns. Elemental boron has two natural occurring isotopes, Boron-10 (^{10}B) and Boron-11 (^{11}B). The ^{10}B isotope is good at capturing thermal neutrons. In the nuclear reactors ^{10}B isotope is used for reactivity control. Boron exists naturally as 19.9% ^{10}B isotope and 80.1% ^{11}B isotope [28].
Elemental boron is a trivalent non-metallic element which occurs abundantly in the evaporate ores borax and ulexite. Boron has the following electronic configuration, $1s^2$, $2s^2$, $2p^1$, which indicates that it has three valence electrons to work with [36]. This makes the ion polarisable and consequently does not hydrate. For this reason, boron is not eager to donate electrons in an electrovalent bond and can also not accept them easily. Therefore, most of its bonds are covalent. Boron is never found as a free element in nature. High-purity crystalline boron may be prepared by the vapour phase reduction of boron dichloride or tribromide. The impure or amorphous, boron, a brownish-black powder, can be obtained by heating the trioxide with magnesium powder. Boron of 99.9999% purity has been produced and is available commercially. Elemental boron has an energy band gap of 1.50 to 1.56 eV, which is higher than that of either silicon or germanium [36][20]. Amorphous boron is used in pyrotechnic flares to provide a distinctive green colour and it is also used in rockets as an ignite [38]. Chemically boron is electron deficient, possessing a vacant p-orbital. It is an electrophile. Compounds of boron often behave as Lewis acids readily bonding with electron–rich substances to compensate for boron's electron deficiency. The reactions of boron are dominated by such requirement for electrons. Boron is the least electronegative

non-metal meaning that it is usually oxidised. Boron is similar to carbon and it has capability to form stable covalently bonded molecular networks. The carboranes, the metalloboranes, the phosphocarboranes, and the other families comprise thousands of compounds. By far the most commercially important boron compound in terms of USD sales is $Na_2B_4O_7 \cdot 5H_2O$. This pentahydrated borate is used in very large quantities in the manufacture of insulation fiberglass and sodium perborate bleach. Boric acid is also an important boron compound with major markets in textile fiberglass and in cellulose insulation as a flame retardant. Next in order of importance is borax ($Na_2B_4O_7.10H_2O$) which is used principally in laundry products. Use of borax as a mild antiseptic is minor in terms of dollars and tons. Boron compounds are also extensively used in the manufacture of borosilicate glasses. Boron nitride has remarkable properties and can be used to make a material as hard as diamond. The nitride also behaves like an electrical insulator but conducts heat like a metal. It also has lubricating properties similar to graphite. The hydrides are easily oxidised with considerable energy liberation, and have been studied for use as rocket fuels. Demand is increasing for boron filaments, a high strength, lightweight material chiefly employed for advanced aerospace structures. The isotope of boron (^{10}B) is used as a control for nuclear reactors, as a shield for nuclear radiation and in instruments used in detecting neutrons. Elemental boron and the borates are not considered to be toxic, and they do not require special care in handling. However, some of the more exotic boron hydrogen compounds are definitely toxic and do require care [20].

1.2.2 Boron health effects

Humans can be exposed to boron through fruit and vegetables, water, air and consumer products. We have a regular daily intake of about 2 mg and about 18 mg in our bodies in total. When humans consume large amounts of boron-containing food, the boron concentrations in their bodies may rise to levels that can cause health problems. Boron can infect the stomach, liver, kidneys and brain and can eventually lead to death. When exposure to small amounts of boron takes place irritation of the nose, throat or eyes may occur. It takes 5 g of boric acid to make a person ill and 20 grams or more to put the person’s life in danger. Eating fish or meat will not increase the boron concentrations in our bodies, as boron does not accumulate within the tissues of fish and animals [29].

1.2.3 Boron (Environmental effects)

Boron occurs in the environment through natural causes such as air release, soil and water through weathering. It may also occur in groundwater in very small amounts. Humans add boron by manufacturing glass, combusting coal, melting copper and through the addition of agricultural fertilisers. The concentrations of boron that are added by humans are smaller than the naturally added concentrations through natural weathering. Boron exposure through air and drinking water is not very likely to occur, but the risk of exposure to borate dust in the workplace does exist. Boron exposure may also occur from consumer products such as cosmetics and laundry products. Plants absorb boron from the ground and through plant-consuming animals it can end up in food chains. Boron has been found in animal tissue, but it is not likely to accumulate to higher levels. When animals absorb large amounts of boron over a relatively long period of time through food or drinking water the male reproductive organs will be affected. When animals are exposed to boron during pregnancy their offspring may suffer from birth defects or delayed development. Furthermore, animals are likely to suffer from nose irritation when they breathe in boron [29].

1.2.4 Boric Acid

Boric acid commonly known as orthoboric acid H_3BO_3, its formula can also be written as $B(OH)_3$, boron hydroxide. If boron were a normal metal, the hydroxide ions would separate in water, creating the trivalent boron ions B^{3+}. This however does not happen even to the smallest degree and does not form ionic bonds. Boric acid is not gelatinous, like aluminium hydroxide, but crystallises well. In aqueous solution boric acid is a very weak acid, weaker even than carbonic acid; its first ionization product is 6.4×10^{-10} [44]. Boron in $B\ (OH)_3$ would rather lose hydrogen than the oxygen, it can form chains like –B-O-B-O-B where each intermediate boron has a free valence electron to work with. This is seen in tetraboric acid, O=B-O-B(OH)-O-B(OH)-O-B=O or $H_2B_4O_7$, which can be derived from $B(OH)_3$ by dehydration:

$H_3B(O)_3 \rightarrow H_2B_4O_7 + 3H_2O$ ………………………..…………………………………………...1

Dehydration of boric acid also gives boron trioxide:

$2B(OH)_3 \rightarrow B_2O_3 + 3H_2O$ ..……………..……………………………………………..2

Boric acid crystals are white, odourless, and nearly tasteless. It looks like fine table salt in the granular form or like baby powder in the powdered form.

Boric acid is one of the most commonly produced borates and is widely used throughout the world in many industries such as pharmaceutical and cosmetic industries, as a nutritional supplement, flame retardant, in the manufacture of glass and fiberglass, and in the production of wood preservatives to control pests and fungus [45].

Boric acid is chemically the most stable neutron poison over the operating temperature range. Boric acid plays a very important role in the generation of electricity by fission process in nuclear power plants because it helps the operators in controlling the reaction that can be out of control [44].

In the fission generation of energy, the uranium atom is split apart by the neutrons. The splitting of atoms creates heat (the process: $_0n^1$ to 3 $_0n^1$ is the essence of the chain reaction, if the reaction is uncontrolled the total released energy causes an explosion, (this is the basis of the atomic bomb). This is extremely important as this chain reaction must be controlled for safety reasons.

$_0n^1 + {}_{92}U^{235} \rightarrow {}_{36}Kr^{89} + {}_{56}Ba^{144} + 3{}_0n^1 + 210\ \text{Mev}$……………………………..……………………3

In pressurised water reactors by varying the concentration of boric acid in water, a chemical shim for supplementary control of the reactor is obtained which has proved to be effective.
The ^{10}B isotope acts as a chemical shim in the cooling circuit and is used for controlling the rate of the nuclear reaction. Chemical shims provide long term gradual control of the reactor while the control rods provide the short term control during start-up and shut-down or under unusual conditions. Although the control rods are also used for reactor control, the boric acid makes reactor control more flexible. It also has economic advantages of reducing the number of control rods required in the core as well as keeping the power across the core constant [44].

1.2.5 Advantages of using boric acid for reactivity control

As boric acid is soluble in water, no extra space is needed for boric acid to absorb neutrons. It simplifies the reactor core's configuration and the top structure of reactor pressure vessel (RPV). Boric acid is evenly soluble in the moderator (water) and avoids the unevenness of neutron-flux density in the reactor core due to the use of control rods. The use of boric acid allows drawing out all control rods when reactor operates so that reactor core power can be evenly distributed. Boric acid in pressurised water reactor can be used as natural boric acid (NBA) or enriched boric acid (EBA). Natural boric acid contains 19.9% ^{10}B and 80.1% ^{11}B isotope .Enriched boric acid contains ^{10}B higher than 20% and ^{11}B lower than 80% depending on the required amounts [40].

1.2.6 Disadvantages of using boric acid to control reactivity

Normally, it takes several minutes to regulate the concentration of boric acid via pouring concentrated boric acid or pure water into the primary loop. So this method is slow in controlling reactivity.

Boric acid is highly corrosive to carbon steel and it is much less corrosive to stainless steel. There was an operating experience that was shared amongst the Nuclear Power Plants that, the boric acid leaked and caused corrosion due to the leaking coolant that evaporated leading to a strong boric acid solution. This boric acid was not removed immediately because it was not viewed as a safety concern and there was inadequate boric acid corrosion control [42].

1.2.7 Enriched boric acid and its application

Natural boric acid contains the two isotopes of 19.9% ^{10}B and 80.1%^{11}B, with respect to enrichment. The ^{10}B isotope is good for capturing thermal neutrons and its absorption of neutrons is much larger than that of ^{11}B. The cross section of ^{10}B for thermal neutron absorption is 3837 barns while the cross section of ^{11}B is only 0.005 barns [40][46] . Since ^{11}B makes up the bulk of the total boron present in natural boric acid, it is necessary to reduce or eliminate ^{11}B from total boric acid inventory to produce boric acid enriched with ^{10}B isotope. Hence, the enriched boric acid with higher ^{10}B will be more popular for neutron absorption.

Compared with natural boric acid, enriched boric acid can control the reactor better because it increases the concentration of ^{10}B in the reactor coolant system, but decreases the amount of boric acid utilised. On one hand, higher concentration of ^{10}B allows stronger reactivity control and higher enrichment of uranium-235. In this case the burning of Mixed-Oxide Fuel (MOX) fuel will increase and the fuel's cycle will be extended. On the other hand, the decrease of boric acid will lower the sedimentation and crystallisation, increase heat exchange, controls the pH value more effectively, relieve corrosion, reduce radiation exposures to employees, improve the safety of Nuclear Power Plants (NPP) and optimise NPP's operational cycle. Even though enriched boric acid has distinctive advantages, its high costs hinder its application in nuclear power plants. The reason why enriched boric acid is so expensive rests with the costly concentration process of ^{10}B. The operation of a nuclear reactor with an EBA solution in the reactor coolant system allows for maintaining a milder chemistry within the reactor coolant system. The prior method of reactor operation with a NBA solution required a higher boric acid concentration and therefore a higher concentration of lithium hydroxide for pH balancing purposes. The use of EBA allows for the same effective ^{10}B concentration in the reactor coolant with its accompanying control capacity, while decreasing the total boric acid concentration required supplying that level of the ^{10}B isotope. Due to the higher expense of an EBA solution as opposed to an NBA solution, there's an invention that provides procedures which minimise the mixing between the EBA solution in the primary reactor coolant system and the NBA solution in the other boric acid systems. This allows for the operation of the nuclear reactor plant using the EBA solution and therefore taking advantage of the associated benefits while minimising the added incremental costs of such an operation.

Currently, enriched boric acid replacing natural boric acid has been applied to EPR reactors and has been used in many French, Finnish and Chinese EPR plants [40].

1.3 Overview of power generation

The discovery of the phenomenon of electromagnetism in the 18th century by Michael Faraday made possible a whole range of applications using this phenomenon, the notable one which has had a significant impact in the bettering of human life being the generation of electricity [41].

Within the South African context, Eskom is one large company that produces electricity and accounts for 95% of the country's generated electricity capacity. Eskom has a number of power stations, most of which are coal fired, and only one nuclear power station, located in the Western Cape. There are significant differences between coal and nuclear power stations but the principle involved in the generation of electricity are exactly the same. With a coal power station, energy is extracted from the chemical bonds of the hydrocarbons constituting the coal (by burning the coal). This bond energy is released as heat energy used to heat up the water in the boilers to generate steam, which is then used to turn the turbines which turn the rotor inside the stator to generate electricity. On the other hand, a nuclear power plant extracts energy from nuclear atomic forces holding the nucleus together [48]. The nuclear power plant uses a reactor. A nuclear reactor is a device designed to maintain a chain reaction producing a steady flow of neutrons generated by the fission of heavy nuclei. They are, however, differentiated either by their purpose or by their design features. In terms of purpose, they are either research reactors or power reactors.

1.3.1 The Nuclear Power Plants

On 26 June 1954 at Obninsk, Russia, the nuclear power plant APS-1 with a net electrical output of 5 MW was connected to the power grid, the world's first nuclear power plant that generated electricity for commercial use. On August 27, 1956 the second commercial nuclear power plant, Calder Hall 1, England, with a net electrical output of 50 MW was connected to the national grid. Since 18 January 2013 437 nuclear power plant units are in operation in 31 countries with an installed electric net capacity of about 372 GW. In 15 countries 68 plants are under construction with an installed capacity of 65 GW. At the end of 2011 the total electricity production since 1951 amounts to 69,760 billion kWh. The cumulative operating experience amounted to 15,080 reported at the end of 2012. All nuclear reactors are devices designed to maintain a chain reaction producing a steady flow of neutrons generated by the fission of heavy nuclei. They are, however, differentiated either by their purpose or by their design features. In terms of purpose, they are either research reactors or power reactors [39 and 49].

In South Africa it was decided in the mid-1970s to build a nuclear reactor of some 1800 MW of nuclear capacity. Construction of the Nuclear Power Plant in South Africa commenced in Cape Town. Koeberg Nuclear Power station construction began in 1976 and Unit 1 was synchronised to the grid on 4 April 1984, with Unit 2 following suit on 25 July 1985 [48].

1.3.2 Research reactors

Research reactors are operated at universities and research centres in many countries, including some where no nuclear power plant stations are operated. These reactors generate neutrons for multiple purposes, including producing radiopharmaceuticals for medical diagnosis and therapy, testing materials and conducting basic research.

1.3.3 Power reactors

Power reactors are usually found in nuclear power plants. Dedicated to generate heat mainly for electricity production, they are operated in more than 30 countries (see Nuclear Power Reactors). Their lesser uses are drinking water or desalination water production. In the form of smaller units, they also power ships. There are many different types of power reactors. What is common to them all is that they produce thermal energy that can be used for its own sake or converted into mechanical energy and ultimately, in the vast majority of cases, into electrical energy. In these reactors, the fission of heavy atomic nuclei, the most common of which is uranium-235, produces heat that is transferred to a fluid which acts as a coolant. During the fission process, bond energy is released and this first becomes noticeable as the kinetic energy of the fission products generated and that of the neutrons being released. Since these particles undergo intense deceleration in the solid nuclear fuel, the kinetic energy turns into heat energy.

In the case of reactors designed to generate electricity, to which the explanations below will now be restricted, the heated fluid can be gas, water or a liquid metal. The heat stored by the fluid is then used either directly (in the case of gas) or indirectly (in the case of water and liquid metals) to generate steam. The heated gas or the steam is then fed into a turbine driving an alternator. Since, according to the laws of nature, heat cannot fully be converted into another form of energy, some of the heat is residual and is released into the environment. Releasing is either direct – e.g. into a river – or indirect, into the atmosphere via cooling towers. This practice is common to all thermal plants and is by no means limited to nuclear reactors which are only one type of thermal plant.

1.4 Power reactors classification

Nuclear power reactors can be classified according to the type of fuel they use to generate heat.

1.4.1 Uranium –fuelled reactors [39]

The only natural element currently used for nuclear fission in reactors is uranium. Naturally occurring uranium comprises, of three isotopes: U-234 (0.0054%), U-235 (0.71%) and U-238 (99.3%). U-238 and U-234 are not fissionable. The principal nuclide utilised in the fission process is U-235 which is present in the amount of 0.71%. Increasing the U 235 isotope above its natural concentration of 0.71% is called uranium enrichment. Research reactors usually require uranium enrichment ranging from natural to greater than 90% ^{235}U. Light water reactors nuclear power plants (e.g. PWRs and BWRs) require fuel to be enriched to 2-5% ^{235}U. ^{235}U can be fission by thermal (i.e. slow) neutrons. As the neutrons emitted in a fission reaction are fast, reactors using U-235 as fuel must have a means of slowing down these neutrons before they escape from the fuel. This function is performed by what is called a moderator, which, in the case of certain reactors (see table of Reactor Types below) simultaneously acts as a coolant. It is common practice to classify power reactors according to the nature of the coolant and the moderator plus, as the need may arise, other design characteristics.

Reactor Type	Coolant	Moderator	Fuel	Comment
Pressurised water reactors (PWR, VVER)	Light water	Light water	Enriched uranium	Steam generated in secondary loop
Boiling water reactors (BWR)	Light water	Light water	Enriched uranium	Steam from boiling water fed to turbine
Pressurised heavy water reactor (PHWR)	Heavy water	Heavy water	Natural uranium	
Gas-cooled reactors (Magnox, AGR, UNGG)	CO_2	Graphite	Natural or enriched uranium	
Light water graphite reactors (RBMK)	Pressurised boiling water	Graphite	Enriched uranium	Soviet design

Table1.4.1 Table of reactor types [39]

Pressurised Water Reactors and Boiling Water Reactors are the most commonly operated reactors in Organisation for Economic Cooperation and Development (OECD) countries. VVERs, designed in the former Soviet Union, are based on the same principles as PWRs. They use “light water”, i.e. regular water (H_2O) as opposed to “heavy water” (deuterium oxide D_2O). Moderation provided by light water is not sufficiently effective to permit the use of natural uranium. The fuel must be slightly enriched in U-235 to make up for the losses of neutrons occurring during the chain reaction. On the other hand, heavy water is such an effective moderator that the chain reaction can be sustained without having to enrich the uranium. This combination of natural uranium and heavy water is used in PHWRs, which are found in a number of countries, including Canada, Korea, Romania and India.

Graphite-moderated, gas-cooled reactors, formerly operated in France and still operated in Great Britain, are not built anymore in spite of some advantages.

RBMK-reactors (pressure-tube boiling-water reactors), which are cooled with light water and moderated with graphite, are now less commonly operated in some former Soviet Union bloc countries. Following the Chernobyl accident (26 April 1986) the construction of this reactor type ceased. The operating period of those units still in operation will be shortened.

1.4.2 Plutonium–fuelled reactors [39]

Plutonium (Pu) is an artificial element produced in uranium-fuelled reactors as a by-product of the chain reaction. It is one hundred times more energetic than natural uranium; one gram of Pu can generate as much energy as one tonne of oil. As it needs fast neutrons in order to fission, moderating materials must be avoided to sustain the chain reaction in the best conditions. The current Plutonium-fuelled reactors, also called “fast” reactors, use liquid sodium which displays excellent thermal properties without adversely affecting the chain reaction. These types of reactors are in operation in France, Japan and the Commonwealth of Independent States (CIS).

1.4.3 Light Water Reactors [39]

The Light Water Reactors category comprises pressurised water reactors (PWR, VVER) and boiling water reactors (BWR). Both of these use light water and hence enriched uranium. The light water they use combines the functions of moderator and coolant. This water flows through the reactor core, a zone containing a large array of fuel rods where it picks up the heat generated by the fission of the U-235 present in the fuel rods. After the coolant has transferred the heat it has collected to a steam turbine, it is sent back to the reactor core, thus flowing in a loop, also called a primary circuit.

In order to transfer high-quality thermal energy to the turbine, it is necessary to reach temperatures of about 300 °C. It is the pressure at which the coolant flows through the reactor core that makes the distinction between PWRs and BWRs.
In PWRs, the pressure imparted to the coolant is sufficiently high to prevent it from boiling. The heat drawn from the fuel is transferred to the water of a secondary circuit through heat exchangers. The water of the secondary circuit is transformed into steam, which is fed into a turbine.

In BWRs, the pressure imparted to the coolant is sufficiently lower than in a PWR to allow it to boil. It is the steam resulting from this process that is fed into the turbine.
This basic difference between pressurised and boiling water dictates many of the design characteristics of the two types of light water reactors, as will be explained below. Despite their differing designs, it must be noted that the two reactor types provide an equivalent level of safety [39]

1.4.3.1 Boiling Water Reactors [39]

In a Boiling Water Reactor (BWR), ordinary light water is used as both a moderator and coolant, like the PWR. However unlike the PWR, in a Boiling Water Reactor there is no separate secondary steam cycle. The water from the reactor is converted into steam and used to directly drive the generator turbine. These are the second most commonly used types of reactors.

Having delivered a large amount of its energy to the turbine, it is then fed back into the primary cooling circuit where it absorbs new heat in the fission zone. Since the steam produced in the fission zone is slightly radioactive, mainly due to short-lived activation products, the turbine is housed in the same reinforced building as the reactor [39]

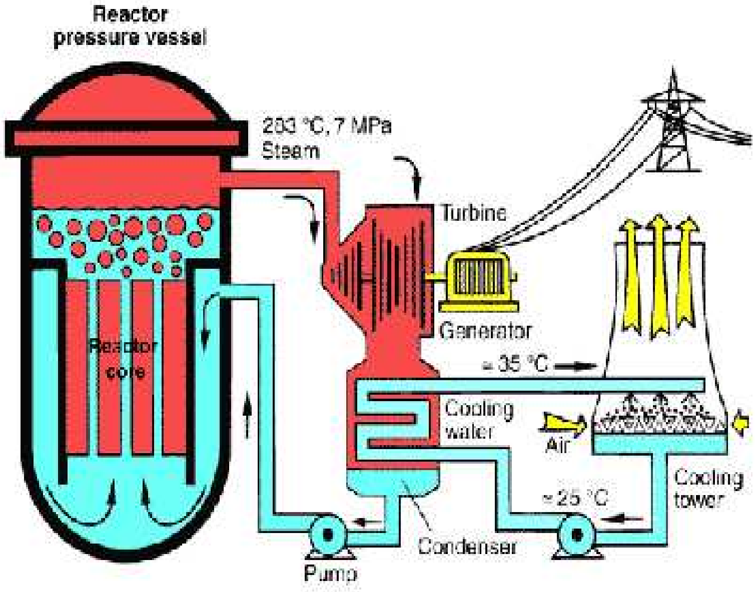

Figure 1.4.3.1 Principle of a nuclear power plant with boiling water reactor [39]

1.4.3.2 Pressurised Water Reactors [39]

Pressurised Water Reactors (PWR's) are by far the most common type of nuclear reactor deployed to date. Ordinary water is used as both neutron moderators and coolant. In a PWR the water used as moderator and primary coolant is separate to the water used to generate steam and to drive a turbine. In order to efficiently convert the heat produced by the nuclear reaction into electricity, the water that moderates the neutron and cools the fuel elements is contained at pressures 150 times greater than atmospheric pressure. Koeberg Nuclear Power Station consist of two PWRs units.

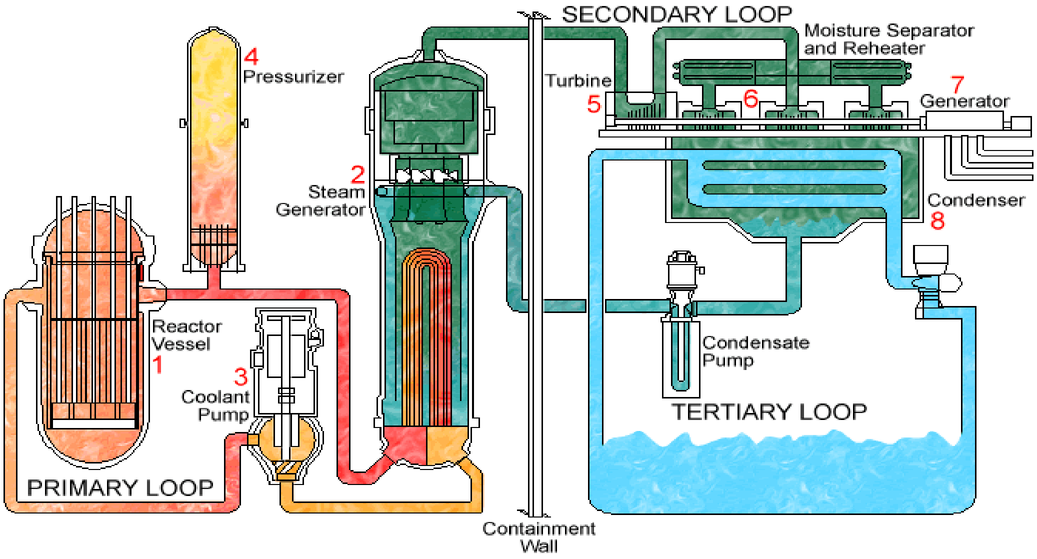

Figure 1.4.3.2 Principle of a nuclear power plant with pressurised water reactor [48]

1.5 The energy cycle used at KNPS's Pressurised Water reactor [48]

1.5.1 The primary loop

In the primary loop, the reactor vessel is filled with water known as the coolant; this coolant carries the heat energy produced as a result of the fission process and transports it to the three steam generators. In the steam generators, feed water is pumped into a preheat section where it is heated to saturation temperature before the boiler section. The resultant water / steam mixture flows upward through the tube bundle and into the steam drum section. A set of centrifugal moisture separators, located above the tube bundles, removes most of the entrained water from the steam. The steam quality is then increased to a minimum of 99.75% dry steam by use of steam driers.

1.5.2 The secondary loop

At the secondary loop the steam is then used to drive a set of turbines, one high pressure and three low pressure turbines. The turbines are connected to a generator which produces the desired electricity and is capable of producing 920 MW of electricity. The total combined output of Koeberg's two units is 1800 MW, which is enough to supply the whole of Western Cape with electricity in summer. This accounts for approximately 6% of South Africa's electricity needs.

1.5.3 The Tertiary loop

The tertiary loop is used in the condensers. The cooling water system for the condensers uses seawater at the rate of 80 tons per second to cool the steam in the condensers. Once it has cooled the steam the seawater is returned to the sea.

1.6 The reactor core is composed of four main elements

1.6.1 The fuel

Uranium is the fuel used in PWRs as a source of energy which is mined as uranium oxide and contains about 0.71% percentage of the desired U-235 atoms. Uranium oxide is enriched with U-235 atoms to about 5.0 %. Nuclear fuel consists of pellets of enriched uranium dioxide encased in long pencil-thick metal tubes, called fuel rods.

The fuel rods are bundled together into fuel assemblies. The completed assemblies are then ready to be installed into reactor vessel. The fuel assembly of nuclear fuel usually consists of uranium or uranium / plutonium mixtures. The fuel assembly is usually a rectangular block of gridded fuel rods.

1.6.2 The Control Rods

The control rods contain (boron carbide $^{10}B_4C$ or B_4C) stainless steel material that regulates the rate of the chain reaction. If they are pulled out of the core, the reaction starts and if they are inserted the reaction stops. A boron solution is added to the coolant to slow down the reaction and boron is taken out of the system to speed up the reaction.

1.6.3 The Moderator

A moderator, i.e. water, slows down the speed at which neutrons travel. This reduction in speed actually increases the opportunity to split the U-235 atoms, which release heat and radiation energy.

1.6.4 The Coolant

A coolant, also water, is pumped through the reactor to carry away the heat produced by the fission of the fuel. This is comparable to the water in the cooling system of a car, which carries away the heat built up in the engine. Boron is added to the reactor coolant in the form of boric acid for neutron poisoning.

1.7 Reactor Coolant System Chemistry and the effects

1.7.1 The effect of boron in the reactor vessel

In a nuclear fission reaction, a uranium atom is bombarded with neutrons producing two or three neutrons and other fission products. These neutrons, which are in abundance, results in a neutron flux in the reactor core. Boron is added as boric acid to control the neutron flux and therefore the number of fission reactions. This is extremely important as this is a chain reaction and must be controlled for safety reasons apart from other reasons. The concentration of boric acid before the start of a fuel cycle is high enough, about 2000 mg B/kg to keep the reactor sub-critical. It is then reduced by dilution to allow the reactor to go critical and as the fuel is burned up. Boric acid is a weak acid and dissociates to give hydronium ions in water as follows:

$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^{-2} + H^+$ ……………………..……………………………………….4

The Ka_1 value for boric acid is about 6.4×10^{-10}. An approximate 2100 mg/kg boric acid solution has a pH of approximately 4.6 at 25^0C and 5.08 at 300^0C which is typical reactor coolant temperature.

Although control rods are also used for reactor control, the addition of boric acid makes the reactor more flexible (finer control). It also has economic advantages of reducing the number of control rods required in the core as well as keeping the power across the core constant. Boric acid creates an acidic medium in the reactor coolant, since this acidic medium is not preferred in the vessel, lithium hydroxide is added to neutralise the acidic medium to a more preferable pH of 7[44].

Boric acid added into the reactor core has two natural occurring isotopes namely ^{10}B and ^{11}B. Boric acid comes as either Natural Boric Acid (NBA) or Enriched Boric Acid (EBA) with respect to enrichment. Natural boric acid contains 19.9% ^{10}B and 80.1%, ^{11}B with respect to enrichment. EBA contains ^{10}B greater than 20% and ^{11}B less than 80.0%, with respect to enrichment.

Two major neutron absorption reactions are observed with

$^{10}_{5}B + ^{1}_{0}n$ (Thermal) $\rightarrow\ ^{7}_{3}Li + ^{4}_{2}He$ …..5

$^{10}_{5}B + ^{1}_{0}n$ (Fast) $\rightarrow\ ^{3}_{3}H + 2[^{4}_{2}He]$ ……...……………………………………………………….6

The reactivity control mechanism of soluble boron is primarily due to the large thermal neutron absorption cross-section of ^{10}B. After absorbing a neutron, the excited nucleus decays by alpha emission and is transformed into a lithium nucleus as shown in reaction number 5.

Throughout the fuel cycle ^{10}B is continuously being depleted. As ^{10}B depletion progresses, the poison (total B) value of analysed soluble boron concentration is decreased because there are fewer ^{10}B atoms available. Since it is specifically the ^{10}B isotope that is responsible for the ability to control reactivity, it is important to determine not only total boron concentration but also to have specific knowledge of the boron isotopic ratio, ^{10}B: ^{11}B.

The availability ^{10}B analysis data provides Reactor Fuel Engineering (RFE) accurate weight percentages of ^{10}B as it depletes while a cycle is in progresses. Having this information allows RFE to make the necessary adjustments to the calculated boron concentrations to taking ^{10}B depletion into account. This increases the reliability of flux calculations and improves the accuracy of estimated critical boron calculations and safety margins.

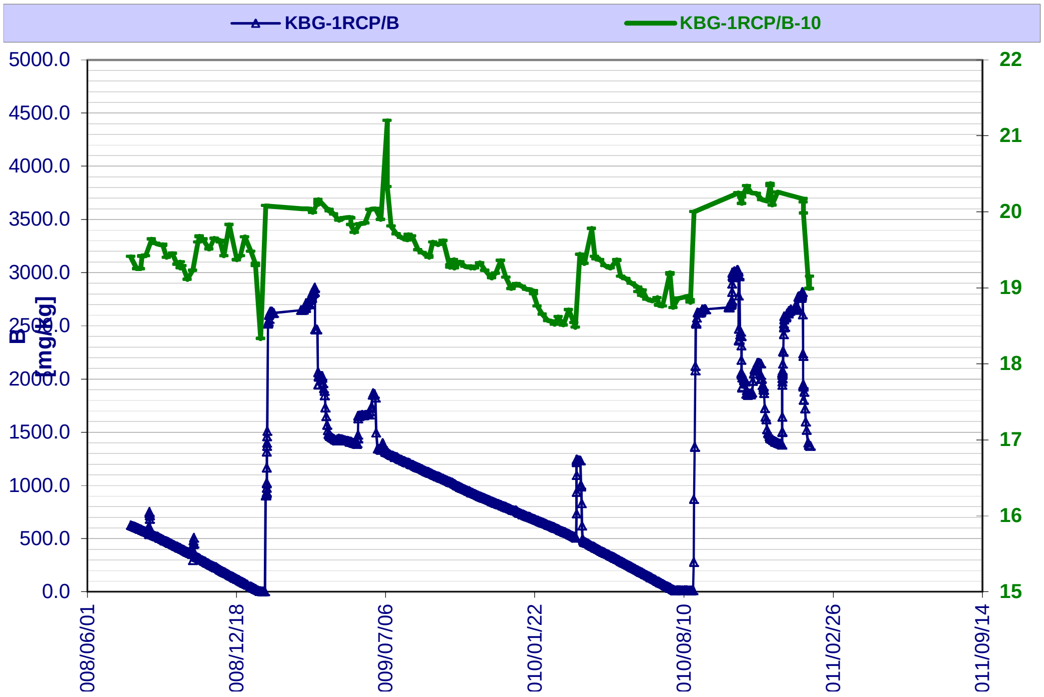

Figure 1.7.1 Unit 2 Reactor coolant system data for boron concentration and %B10

The best known method to perform isotopic determination in a practical routine manner is by Inductively Coupled Plasma – Mass Spectrometry. In 2006 Agilent 7500 ce ICP-MS was commissioned at KNPS. ^{10}B is determined on the reactor coolant on a monthly frequency and during the fuel physics tests (flux map). ^{10}B measurements are also routinely performed on the spent fuel pool system, boron make-up tanks and the safety injection tanks. Further isotopic boron analysis issues will be discussed and dealt with individually on chapter 3.

1.7.2 The effect of lithium hydroxide in the reactor vessel

The addition of boric acid creates an acidic environment in the reactor coolant. A 1500 mg B per kg boric acid solution has a pH of 4.78 at 25 ^{0}C and 5.41 at 300 ^{0}C. To ensure low general corrosion and the minimum crud transportation, a strong alkali (base) lithium hydroxide must be added to the reactor coolant to achieve the desired pH at a certain temperature. At the beginning of the fuel cycle, for pH 6.9 at 300 ℃, the typical lithium concentration is in the range of 1.8 to 4 mg Li/kg for corresponding boron level in the range of 1000 to 2000 mg B/kg, and then it is reduced as the boron concentration reduces. A minimum pH value of 6.9 is required to avoid heavy crud deposits on fuel rods, which can cause accelerated corrosion of fuel rod cladding and increased radiation fields. However, as the pH of the coolant drops, corrosion increases which can lead to loss in power generation and high repair and maintenance costs. Therefore, it is important to maintain the appropriate pH and to determine lithium concentration.

To keep the constant pH_T (of 6.9 to 7.4) at average, it becomes important for the reactor operators to coordinate the Lithium Boron Chemistry in the reactor core. With this principle, the lithium concentration must be reduced as the boron concentration is reduced due to dilution. It becomes obvious that the concentration of boron and lithium must be monitored closely throughout the fuel cycle as indicated on the graph below [44].

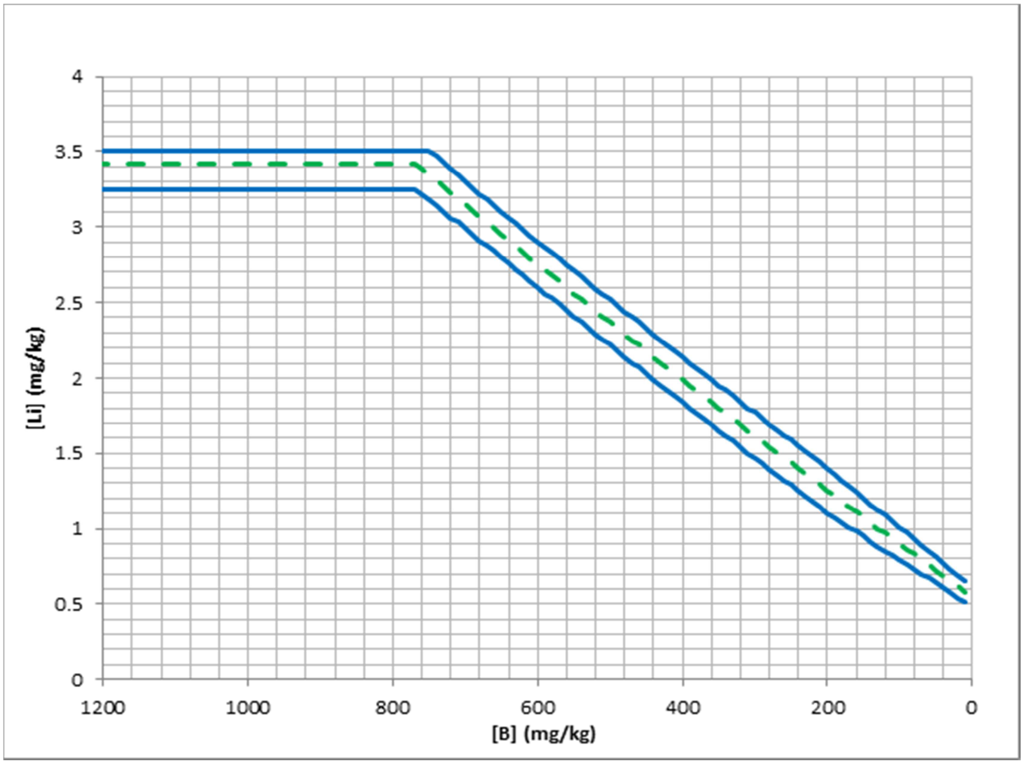

Figure 1.7.1 Boron – Lithium Plot for pH = 7. 25 at 296ºC [17]

1.7.3 The effect of zinc (as zinc acetate) addition in the reactor vessel

The number of pressurised water reactors (PWR) injecting zinc into the primary system has increased. Koeberg Nuclear Power Plant is injecting zinc on both units. Plants inject zinc for two primary reasons: dose rate reduction and primary water stress cracking corrosion (PWSCC) initiation mitigation [53]. Additional goals for zinc injection programmes are to mitigate corrosion product generation and crud deposition on fuel surfaces.

Approximately 85% of the plants injecting zinc report dose rate reduction as the primary goal, with the remainder identifying PWSCC mitigation and crud mitigation as the primary drivers. Typical zinc injection strategies employ reactor coolant system (RCS) zinc concentrations of 5-20 µg/L. In the presence of a neutron flux, Zn-64 can absorb a neutron to become Zn-65, which is radioactive (1.1 MeV gamma) with a 243.8 day half-life. Therefore, plants adding natural zinc, experience a smaller radiation dose benefit because of the production of Zn-65. Zinc injection achieves the noted benefits via mechanisms at the molecular level. As zinc is incorporated into the oxide films of wetted surfaces in an operating PWR, it changes the morphology and composition of oxide films, thereby changing their corrosion characteristics. In addition, it is believed that zinc displaces nickel and cobalt from the crystalline lattice sites in the inner layer of system surfaces. With time, this process makes the oxide layers thinner, more stable and more protective. In laboratory data, zinc uptake into fresh surface oxide formation has also shown to reduce the corrosion rate and release rate of stainless steel. Steam generators used in PWRs consist of Ni-base alloys that can be oxidised by the primary water. During this oxidation process, nickel can be released in the primary coolant, which increases contamination and leads to stress corrosion cracking [54].

Additionally, it was hypothesised that zinc atoms would displace other divalent cations, for example radio-cobalt and nickel from the RCS surface oxide as zinc ions were more thermodynamically favoured in the inverse spinel structure. Therefore the determination of nickel concentration is critical as they provide data to prevent or minimise stress corrosion cracking in nuclear power plants. Other trace cations are present in the reactor vessel and their analysis is critical and they are monitored as required. Zinc is added into a reactor coolant system as zinc acetate salt. The area of concern related to zinc addition was in the laboratory. The authorities wanted to know what impact the presence of zinc acetate will have on boron analyses methods. The effect of zinc acetate addition was investigated in the laboratory on all the methods. The report of titrimetric determination of boron in the presence of zinc acetate is attached as in Appendix B

1.8 Other systems with boron

With our main focus on reactor vessel, it is worth mentioning that there are a number of systems which are also monitored for boron concentration; some of these are referred to as safety related systems. The systems in which boron is sampled and analysed, their respective definitions and boron concentration specifications are: RCP (Reactor Coolant System) with specifications of (5-2500 mg B/kg) depending on the status of the plant at neutral pH ;PTR (Reactor and Spent Fuel System) specification of 2500-2700 mg B/kg, REA (Reactor Make-up System) specification of 7300-7700 mg B/kg, RIS (Reactor Safety Injection System) with specification of 2500-2700 mg B/kg, RRA (Residual Heat Removal System) with specification of 5-2500 mg B/kg, TEP (Boron Recovery System) with specification of 20 -1700mgB/kg KER (Liquid effluent Monitoring System) with specification 20-1700mgB/kg , and TEU (Liquid Waste Treatment System) with boron specification 20-5000mgB/kg.

For different plant systems with different specifications of boron concentrations mentioned above it is required that the laboratory be able to determine boron concentration of boron all systems irrespective of the nature of the samples and range. For waste samples, the currently used method (AA flame) which measures the boron samples of up to 20-500mgB/kg. Samples with higher concentration will need to be diluted to get results within the calibration range. Challenges when reporting boron results of more than 500 mg B/kg has been experienced. For neutral pH samples, the currently used method (Titration by Potentiometers) for boron determination measures boron from 5-8000 mg B/kg. It was observed that for samples and standards of ±1000 mg B/ kg and less, the accuracy and precision is satisfactory. It was also observed that with samples of 2500mgB/kg and more, it becomes more challenging to get accurate and reproducible results. The 2500 mg B/kg boron standard will be used in this project for investigation because it has almost the same chemical constituents as PWR samples. The 2500 mg B/kg is prepared from pure boric acid salt and the demineralised water.

Boron concentration must conform to the limits as set out in the Operating Technical Specification; which is a licence binding document for the safe operation of Koeberg. Failure to meet the requirements as per this document can results in the shutdown of the units.

Some of the reasons why boron concentrations are so important in these systems are that there could either be an inadvertent dilution of the safety related system in which case the system in question will not have sufficient boron concentration required in the case of an accident. The other one is that if too much boron concentration is maintained in the system, it can lead to its molar solubility being exceeded with the results that crystallisation would occur, the consequence being that the pumping of boric acid solution to the required destination won’t be possible. Both of these scenarios would pose a nuclear safety issue, which is undesirable. So being able to detect very small changes of boron in the plant systems is very important to implement corrective actions on time.

1.9 The problem

Boron plays an essential role in nuclear safety and reactivity management in pressurised water reactors. Worldwide there have been several chemistry events relating to boron concentration reported by INPO [13, 14, and 15].
At KNPS there were three notable operating experiences related to boron measurement. The first was in November 2005, where a safety injection tank went out of specification because of an unknown dilution. In this event the analysis showed the downward trend, but a contributing factor that led to it not being noticed initially was attributed to the variation in boron analysis results from one month to another. The second event was in discovered during April 2009, where a check that was performed subsequent to calibration actually caused an apparent downward trend in all the borated systems.

The third incident occurred in 2011 whereby lower than expected boron-10 (B-10) concentration results were reported due to instrument drift.

1.9.1 Dilution of a safety injection tank

At 20:46 on 23 November 2005 KNPS Unit 2 was forced to be shut down when the monthly routine sample of the Reactor Safety Injection System Tank 2 (2 RIS 002 BA) indicated that the boron concentration was below the required minimum safely limit of 2500 mg B/kg [16]. Plant Operating Technical Specifications compels the shutdown of the reactor within 24 hours when this limit is transgressed.

The investigation into the event determined the root cause as the failure to identify the decreasing boron trend in 2 RIS 002 BA. The direct cause was passing valves that connected systems with lower boric acid concentration to the piping used to top up 2 RIS 002 BA.

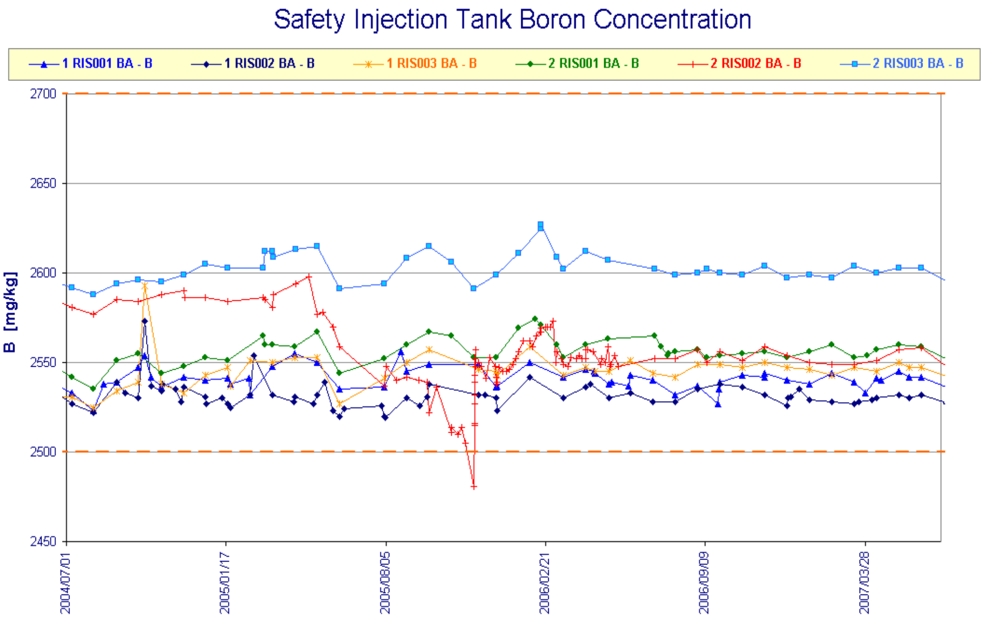

Figure 1.9.1.1 RIS tank B results, indicating the decreasing trend in 2 RIS 002 BA

The Chemistry Group at the plant was severely criticised because the station was not alerted to the initial downward trend which may have averted the unit shutdown, as a plant intervention could have prevented further dilution of 2 RIS 002 BA before the limit was eventually transgressed. Both units at KNPS have three identical safety injection tanks (RIS 001 BA, RIS 002 BA and RIS 003 BA), one on each of the three primary loops (Figure 1). These vessels contain boric acid solution with boron limit values 2500 mg B/kg (minimum) and 2700 mg B/kg (maximum). A sample of each tank is taken on a monthly surveillance frequency to verify that the tanks are within specification [17]. Because the RIS tanks are designed to be static during normal operation, the boric acid concentration is expected to remain constant during this period.

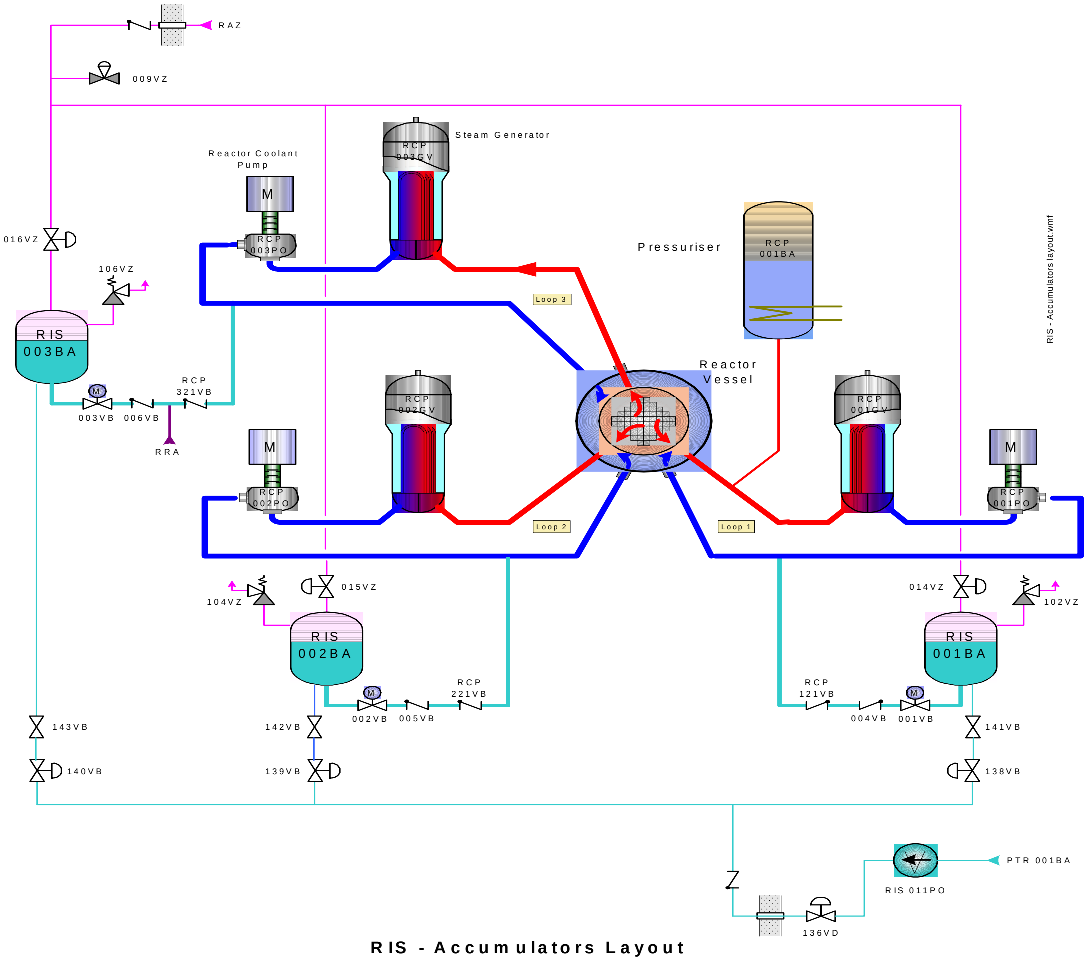

Figure 1.9.1.2 the safety injection tanks (RIS accumulators) on the primary loops [62]

The monthly boron concentration is determined by the alkalimetric titration described under evaluation methods. Although the RIS tanks boron concentrations are expected to remain constant, the analysis results do show some variation from month to month due to natural sampling and analytical phenomena including the uncertainty of measurement. During the investigation it was suggested that it may be because of the monthly variation of boron analysis, that the downward trend was not attributed to a dilution, but to the ‘inaccuracy’ of the analysis. When studying all the laboratory data obtained for both units, it was clear that the 2 RIS 002 BA dilution event was obvious and that the natural variation in the monthly analytical results should not have caused the misinterpretation of the downward trend (see the redline in Graph in figure1.9.1.1).

However, questioning of the variations in the monthly RIS results raised the important point that the normal variation and uncertainty of measurement must be quantified.

The corrective action for the Chemistry Group was to improve monitoring and trending of data. This was achieved by the acquisition of a more appropriate trending tool, a modern Laboratory Information Management System (LIMS), and focussing attention of the staff on the trending of the data. Trends of all control and diagnostic chemistry parameters are now displayed (graphically by LIMS) and discussed as appropriate by the staff attending the daily Chemistry Production Meeting. A target value of 2600 mg B/kg was added to the specification document to allow a sufficient warning parameter prior to approaching the lower limit value.

1.9.2 A quality control problem

Subsequent to the year 2005 RIS dilution event discussed in 3.1, the new LIMS was implemented at KNPS and the Chemistry monitoring and trending improved significantly. Viewing graphical trends directly from the LIMS data base, projected onto a screen at the production meeting greatly enhanced the capability of recognising adverse chemical parameter trends.

Viewing the boron analysis results for 2008 it was noticed that the results showed a decreasing trend over several months (see Figure1.9.2). The decreasing trend was slight, and nowhere close to approaching specification limits values. The suspicion was that the decreasing trend phenomena was observed on both units, all the safety injection tanks (RIS) and on the spent fuel tank (PTR) samples. The target value of 2600 mg B/kg was reached and this was observed at the daily Chemistry Production Meeting where the system trends are displayed.

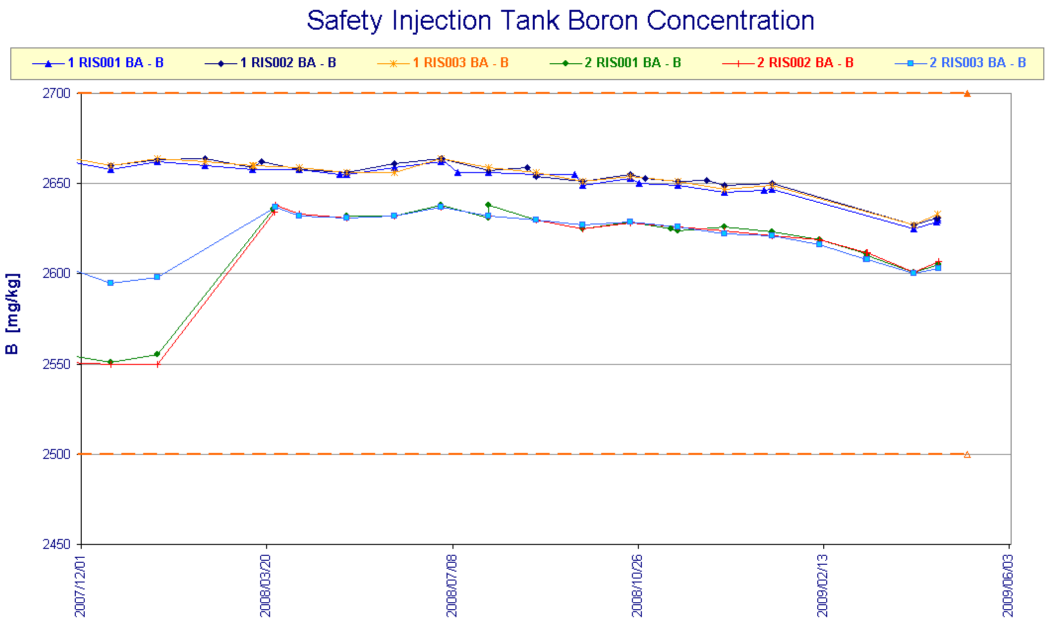

Figure1.9.2 LIMS data showing B trend on RIS and PTR of both units

It was acknowledged by the Chemistry Group that it was highly improbable that all these boron tanks, across both units, could be undergoing a similar dilution. The observation was reported to the station management and problem notification was raised for the concern to be investigated [18].

The investigation considered laboratory quality control and the calibration of the autotitration method for the determination of boron [10]. It was not possible to detect a similar trend on the quality control charts as that observed on the sample analyses results. The control charts appeared to be stable even over the longer term, indicating good quality control.

Quality control (QC) samples were run daily and a full calibration (pH electrode calibration with certified buffers and standardisation of the sodium hydroxide solution with a primary standard of PHP as explained in chapter 2) was performed monthly, or when the QC sample falls outside the control limits. The investigation found that when the monthly calibration was performed and the procedural calibration criteria met, a sample that was analysed prior to the calibration was reanalysed under the new calibration conditions. The result of the reanalysed sample was then reported to the laboratory supervisor. The laboratory supervisor then made a decision whether to accept or reject the new calibration, and based this decision on the difference between the results obtained from the same sample analysed before and after the calibration. This practice is fundamentally flawed, and was found to be the cause of the apparent dilution observed in the samples over several months.

In principle, the understanding was that if the reanalysed sample did not differ greatly from the result before the calibration, the new calibration was accepted. If the difference was too large, a recalibration was requested. The calibration was accepted when the new conditions gave a result that was close to the 'before calibration result'.

The rationale for the practice was to prevent a 'step change' in boron results from one day to the next after the monthly calibration. When this had occurred in the past, the plant staff challenged the result as it was not explained why the results differed from the previous day. For example, the reactor coolant boron concentration is expected to decrease daily by approximately 3 mg B/kg due to primary system dilution. If after calibration, this normal decrease was not observed, or perhaps even a slight increase in boron concentration was reported, the laboratory was challenged. To prevent the 'step change' in results and the subsequent questioning after calibration, the supervisor only accepted new calibration conditions when the resulting change would not be significant. This practice had the desired effect, but is flawed in that the effect of the calibration is essentially negated, and over the longer term caused a downward shift in the calibration which led to all the results responding in a similar manner. It caused bias by not allowing natural variation to occur.

To correct the problem, the autotitrator was recalibrated according to procedure accepting that this calibration will result in a small step change. The laboratory and the plant staff underwent continuing training to provide better understanding of natural variation of results, instrument calibration drift, the purpose and the expected effect of calibration.

Further corrective actions included; no longer using the flawed acceptance for the calibration (accepting that a calibration may result in a small step change), the calibration frequency was increased, the use of a certified reference boron standard and the use of bulk controls so that QC can be evaluated over longer periods.

The overall downward trend that had occurred over the year was only slight and did not challenge flag or action levels. It was observed because of the improved trending tools provided by the new LIMS and the focussed attention of the Chemistry Staff on monitoring and trending.

1.9.3 Lower than expected boron-10 percentage results were reported due to instrument drift

On 26 July 2011 after a fuel physics test that was conducted, Chemistry sampled and analysed Unit 2 RCP LP2 for B-10. The B-10 results produced by Chemistry were unexpectedly low (19. 16% and19. 18%) and Reactor Fuel Engineer requested re-analysis of samples. Re-analysed sample results were 19.42% and 19. 44%. The normal quality control check for B-10 has been within the acceptable limits of 22% ± 0.3% with acceptance change Δ of 0.6%.

On investigation, it was found that there was an analytical error. The analytical error was observed when the same 2RCP sample sampled on 26 July 2011 was analysed at different times and gave inconsistent results of 19.16% and 19.44%.

Furthermore, two Unit 2 RCP LP2 samples were taken on different dates 01-08-2011 (Sample 1) and 08-08-2011(Sample 2) for investigation purpose. The two samples were analysed concurrently at different time intervals. The set of results produced at different times were as follows:

Sampled Date	08/08/2011 @14:00	08/08/2011 @14:50	10/08/2011 @08:45	10/08/2011 @09:00	10/08/2011 @11:00
Sample1	19.75%	19.70%	19.51%	19.84%	19.85%
Sample 2	19.72%	19.65%	19.51%	19.77%	19.64%

The change in B-10 results for each sample analysed from time to time is tabulated below:

Sampled Date	Δ for 08/08/11 14:00& 14:50	Δ for 08/08/11 14:50 & 10/08/11 08:45	Δ for 10/08/11 08:45 & 09:00	Δ for 10/08/11 09:00 & 11:00
Sample 1	Δ =0.05%	Δ =0.2%	Δ =0.33%	Δ =0.01%
Sample 2	Δ =0.07%	Δ =0.14%	Δ =0.26%	Δ =0.13%

Table 1.9.3 for B10 results interpretations

The change in B-10 results illustrated above shows that there is an instrument drift and the drift has no specific direction:

As shown on the table, Sample 1 results changes from time to time by 0.05%; 0.2%; 0.33% and 0.01%. Sample 2 results changes from time to time by 0.07%; 014%; 0.26% and 0.13%. After observing these fluctuations, the instrument installation specification check was performed and was found to be within acceptable limits. The 20 minutes' stability test was also performed and all parameters passed the test. Although these tests are acceptable from the supplier's specifications, the tests revealed that the instrument stability has reduced as compared to original settings when the instrument was new.

Interventions to rectify the problem included the changing of the sample introduction technique and instrument component change (e.g. nebuliser). After these interventions were made, an increase in B-10 results of 0.45% was observed. There was an improved reproducibility of boron -10 results for the flux map conducted on the 23 August 2011(19.88% and 19.89%) also the consistency and expected trend increase has improved the degree of confidence in result.

The instrument drift is expected in any analytical technique and chemistry had to ascertain the acceptable drift for boron-10 analysis.
After this incident, some corrective action had to be implemented

The corrective actions implemented were to:

- Develop a technique to remove the effect of instrument drift and determine what can be done to make the results more accurate and reproducible. To liaise with the supplier to ascertain whether there is any operating experience they can share to minimise the drift in results.
- Update the relevant procedure to reflect the implemented changes.
- Train all relevant staff on the new implemented changes.

1.10 Literature review for methods used for Boron Analysis

Boron can be measured by several different analytical techniques. Sah and Brown from the University of California reviewed boron analysis methods in 1997 [5]. They reported that common methods for the determination of boron concentration are spectrophotometric and plasma-source spectrometric methods. Spectrophotometric methods involve colourimetric reactions of boron with azomethine-H, curcumin, or carmine. Other colourimetric and fluorometric methods have also been used to some extent. These methods, in general, suffer from numerous interferences and have low sensitivity and precision. The azomethine-H method is the most commonly used spectrophotometric method and is the ASTM method for the determination of boron in PWR coolant water. This method is fast, simple, and sensitive and does not require concentrated acids, which make it desirable for automation [6]. Application of nuclear reaction and atomic emission/absorption spectrometric (AES/AAS) methods has remained limited because these methods have poor sensitivity and suffer from serious memory effects and interferences because the very high emission intensity of the resonance lines hinder the absorption measurements. Among published nuclear reaction methods prompt-γ spectrometry has been of practical use for measuring the B-10 isotope [7]. Inductively coupled plasma optical emission spectrometry (ICP-OES) created a new dimension in boron determination because of its simplicity, sensitivity, and multi element capability. ICP-OES however also suffers spectral interferences and is not adequately sensitive. All methods involving the measurement of boron isotopic composition require a mass spectrometer [5]. Development of inductively coupled plasma mass spectrometry (ICP-MS) has overcome most of the drawbacks of earlier methods and measuring boron isotopes is possible, therefore plasma source MS appears to be the method of choice among present-day technologies. The determination of the boron isotopic ratio is carried by a variety of methods, including atomic absorption spectrometry, chemical ionisation, and electron impact mass spectrometry. Because of their high precision, thermal ionisation mass spectrometric methods [58, 59] have been favoured for many applications. A precision of $s(R)$ between 0.2 % and 0.3 % is typically reported. An important disadvantage of these methods is the time required for the sample preparation and for the isotopic ratio determination.

One of advantages of the inductively coupled plasma mass spectrometry (ICP-MS) [60] over other techniques is a speed of the analysis and a relative short time to prepare the sample. This method consists in the ionisation of boron in state of plasma. The boron isotopic ratio is determined with a precision of about 0.7 %.

Neutron absorption analysers are used for the on-line determination of the boron concentration of the primary coolant in most PWRs. The most commonly used laboratory method for the determination of total boron in primary coolant water at nuclear power stations is the alkalimetric titration of boric acid with a standard solution of sodium hydroxide [8]. This method is also used to determine total boron concentration in chemical and volume control system, reactor make-up tanks, spent fuel system and safety injection system at KNPS.

PWR primary coolant is a solution of boric acid in purified water. The beginning of a fuel cycle requires a relatively high concentration (approximately 2000 mg B/kg of boron to control reactivity but as the fuel is depleted by fission; the boron concentration is reduced accordingly to maintain a constant reactor power. The primary coolant is diluted with purified water from the reactor make-up system. The end of cycle boron concentration may be as low as less than 5 mg B/kg. The concentration of the reactor boric acid make-up tanks is approximately 7500 mg B/kg. At KNPS, the alkalimetric technique is used to determine concentration range (8000 to 5 mg B/kg) .The AA is used to determine boron concentrations on the samples containing more species that could interfere with the neutralisation titration method/ technique.

1.11The basis of the Project

Boron concentration analysis is one of the most important and critical analysis that is performed by the analytical laboratory at KNPS. This is due to the fact that it is used in most of the primary plant system components for primarily safety and other reasons.

In the past there have been several anomalies around reporting boron concentration results, for example inconsistent or out of trend boron concentrations being reported. Reporting incorrect boron results can have a negative impact in the safe operation of the plant and could lead to disaster. Reporting incorrect results can have a negative impact in electricity generation thus affecting the amount of electricity supplied to the Western Cape region, the South African market and therefore the greater South African economy. For this reason it was decided by the Chemistry Technical Review Committee (TRC) to take some steps in validating the boron concentration results. One of the requests made was to develop the acceptance criteria that can be used by the analyst when reporting these boron results and to give direction on what to do when unexpected results are produced. The guideline developed and drawn can be seen in Appendix A. It was developed for reporting the results produced by titration method. This guideline was developed specifically for reporting boron results in 2000-3000 mg B /kg.

To develop this acceptance criterion and the guideline for the reporting of these boron results the following differences in analysis were to be taken into account:

- The sampling technique
- Instrument calibration and stability i.e.
- Reagent Purity
- Skills and experience of personnel.
- Use of historical data and statistical process control (SPC).
- Calibration of equipment i.e. general laboratory glassware
- The matrix effect or chemical species present in samples analysed i.e. lithium hydroxide, zinc acetate and other chemical species that are not mentioned.

Evaluation and Optimisation of boron analysis for Pressurised Water Reactor**,** is about evaluating the quality of analytical results produced using different methods or techniques used at KNPS for boron concentration determination. The analytical methods or techniques used include Potentiometric Titration, UV-VIS (Azomethine H) method and AA flame method. Optimisation includes the adjustment of mechanical or physical components of the instruments, correct methods of reagents preparation and of the working procedures when needed. The differences in analyses mentioned on the previous paragraph with bulleted points had to also be taken into account. After that the accuracy, precision and uncertainties on each method will be determined and be evaluated. The techniques will be compared and this comparison will be done to check which technique or method is the best in producing the best results at the wide range of analysis. The time it takes to produce the results the practicality, the safely precision accuracy of the final result from these techniques will also be evaluated.

In determining the analytical methods to be employed, consideration will be given to the expected concentration of the chemistry parameter of interest. The method chosen must provide sufficient sensitivity to ensure meaningful information can be obtained at concentrations typically found in plant systems. Interferences, which may influence the accuracy of boron results will be considered and identified for each method/technique. Consideration will be given to ensuring that standard solutions contain approximately the same level of chemical interference as the samples (sample matrix effects) for each analytical method or verifying that the sample matrix does not have interference. Calibrations will be performed with standards that are matrix matched to the sample unless it is known that matrix effects will not interfere with the accuracy of the analysis.

Choosing an appropriate analytical technique is dependent on the concentration of the parameter of interest in the samples to be analyzed. Methods used for boron analysis should be capable of providing results within required ranges. Accuracy for the methods chosen should meet established industry standards and the desired detection capability of the particular application. The limit of quantification described for each technique or method indicates the minimum concentration needed to quantify boron concentration.

The three techniques Potentiometric Titration, AA-Spectrophotometry, UV-Spectrophotometry azomethine-H method and ICP-MS) have been evaluated for determination of boron concentration in nuclear reactor coolant water. The ICP-MS has been evaluated for determination of isotopic boron.

The chapters in this thesis are divided into four sections, those pertaining to Potentiometric Titration to AA-spectrophotometry, UV-spectrophotometry and ICP-MS. Each section is developed independently with an introduction, theoretical, experimental, and discussion section. A general conclusion covering the four techniques experiments as they apply to the monitoring of boron in nuclear reactor coolant water is included in the final section of this thesis.

CHAPTER TWO: ANALYTICAL METHODS USED FOR DETERMINATION OF BORON

2.1 Neutralisation titration methods.

Neutralisation titration is the process whereby the base/alkali of a known concentration is added into an acid solution of unknown concentration until the resulting solution is completely neutralised. With known volume of known concentration of a base and the known volume of acid used, it becomes possible then to calculate the concentration of an unknown acid solution. Such determination is also known as volumetric determination as volumes of acid and the alkali or base must be known for concentration determination. Neutralisation titration can be performed manually and/or automatically. At Koeberg Analytical Laboratory, a manual titration method and automatic titration by means of METTLER model DL50 and T50 (auto titrators) are used.

Manual titration

Manual titration method uses general laboratory glassware, i.e. glass graduated burets, pipettes, Erlenmeyer flasks and chemical indicators. In manual titration, an indicator (organic chemical) is used to determine the exact point of neutralisation which is known as end point. The endpoint is determined by a certain colour change of indicator. When performing a manual titration extra care must be taken. The manual titration used at Koeberg is not automated in any way in that it uses the general laboratory glassware, salts and reagents. The manual titration method is always available when needed. It is used in case of emergency (i.e. when instruments are not available), when there is no power available and it is useful for the research and troubleshooting purposes. This method is used as a backup of all the boron analysis methods. Manual titration requires a well-trained skill full analyst to produce the more reproducible and accurate results.

Potentiometric Titration

Potentiometric Titration for boron determination uses automated instruments, e.g. METTLER DL50 and T50 Models. Automatic titrators use potentiometers for end point determination and there is no need for use of chemical/ organic indicators. The use of automatic titrators is easy, quick, reproducible and more accurate than manual titration. Further discussion on boron analysis by neutralisation titration will be discussed in Chapter 3.

2.1.1 Method for determination of boron by Manual Titration

Experimental details are in Appendix D

2.1.2 Method for determination of boron by Automatic Titration

Experimental details are in Appendix F

2.2 Spectrophotometric methods

The Hach DR 5000 and 6000 models are examples of spectrophotometer used at Koeberg. At Koeberg, determination of boron by UV - Visible spectrophotometric method is available. This technique is not used as it quantifies boron concentrations of less than 10mg B/kg. This method was revisited to be checked if it can be used for high concentration boron. Another method was adopted from the book of standard methods and it was tested if it will be suitable for PWR analysis.

Method for determination of boron by Carminic acid was evaluated and discontinued due to the hazards associated with the use of concentrated acid. Of the two UV methods, azomethine H method was used for evaluation and optimisation process.

2.2.1 Method for determination of boron by Carminic acid

Experimental details are in Appendix G

2.2.2 Method for determination of boron by Azomethine H

Experimental details are in Appendix G

2.3 Atomic Absorption Spectrophotometry method

The Perkin Elmer Analyst 700 and AA 200 models are examples of Atomic Absorption spectrophotometers used at Koeberg. This technique is used to determine boron concentration range from 20 - 1200 mg B/kg for waste treatment tanks and any water samples with complex matrices. The Perkin Elmer Analyst 700 was used for experiments purposes in this project.

2.3.1 Method for determination of boron AA flame

Experimental details are in Appendix D

2.4 Determination of Isotopic boron analysis using ICP- MS

At Koeberg the ICP-MS used is the Agilent Inductively coupled plasma-mass spectrometer 7500ce. ICP-MS is an elemental analysis technique. It can detect and quantify the elemental composition of an introduced sample. ICP-MS essentially consists of two parts combined together to form the technique.

The ICP-MS is a combination of the following techniques:

The Inductively Coupled Plasma (ICP):

Is a high temperature ion source. Its purpose is to break down the introduced sample from a molecular (or solvated molecular) species through to a collection of elemental ions. These are then passed through a series of ion lenses to the second part of the technique, the mass selective detector.

The Mass Spectrometer (MS):

Is the detection device for ions generated by the ICP. There are a number of different types of mass spectrometers offering different types of mass filters, such as quadrupole, magnetic sector, or time of flight. The most common mass filter is a quadrupole scanning spectrometer.

The 7500 series quadrupole has a mass range from 2 to 260 amu. This allows full coverage of all elements and their isotopes (Li to U). The quadrupole is a very fast scanning mass filter that allows all elements to be mass separated during a single analysis of a sample. Once the elements have been separated, they are detected using a dual mode detector that allows linear detection limits from ppm to sub ppt (9 orders of magnitude).

2.4.1 Method for determination isotopic boron by ICPMS

Experimental details are in Appendix J

The currently used method for isotopic boron involves the use of tuning solution, the rinsing solution (nitric acid), the blank (MILLIQ water), the 20 % ^{10}B calibration standard and 22 % ^{10}B that is used as Quality Control standard.

The reactor coolant samples have natural boric acid which contains about 20% ^{10}B. During power generation, the 20% ^{10}B decreases gradually to about 18%^{10}B. For this reason, it becomes necessary for the lab to be able to obtain the calibration standards and the quality control standards in the range of samples analysed. Suppliers of isotopic boron standards will be contacted to purchase the standards that are lower than 20% ^{10}B.

2.5 Reporting of analytical results and data limitations

One of the prime objectives of quality assurance is to evaluate measurement uncertainty. The analytical uncertainty must always be known when using data to make a decision. When this is ascertained, the tolerance at which the reported results can be known and one can decide whether this is large enough to influence adversely the decision making process. Clearly tolerances must be known before any use of the data for a specified purpose. It's always assumed that the measurements were made by an unbiased measurement process. Biased processes would under-estimate or over-estimate the concentration by a constant amount depending upon the sign and magnitude of the bias in addition to any random error of measurement.

2.5.1 Summary of the steps in estimating uncertainty

The steps in estimating uncertainty were adopted from different sources [11, 12 and 57].

1. Identify and list all factors contributing to uncertainty of measurement. This will be totally dependent on the method used.

The use of cause and effect diagram is convenient way of listing the uncertainty sources showing how they relate to each other and indicating their influence on the uncertainty of the result. It also helps with double counting. This also helps with categorising the types of uncertainties i.e. Type A and Type B.

Type A evaluation of uncertainty is by a statistical calculation from a series of repeated observations. The statistically estimated standard deviation of those observations is called a Type A standard uncertainty. Note that it is sometimes appropriate to weight the estimated standard deviation by a sensitivity coefficient.

Type B evaluation of uncertainty is by means other than that used for Type A. For example, information about the sources of uncertainty may come from data in calibration certificates, from previous measurement data, from experience with the behaviour of the instruments, from manufacturers' specifications and from all other relevant information. Type B components are also characterised by estimated standard deviations which, when weighted by sensitivity coefficients, become Type B standard uncertainties.

Examples of factors contributing to uncertainty:

- **Purity uncertainty (P**): This is available from the chemical suppliers either in the form of a certificate, or listed on the chemical itself e.g. 99.9 % pure. Hence, it is important that reputable suppliers are used at all times.
- **Mass uncertainty (m):** When balances are calibrated ensure that this uncertainty figure is included on the calibration certificate.
- **Volume uncertainty (v):** This can be obtained in two ways. The first one is to obtain a calibration certificate from the glassware supplier. The second one is that the laboratory must carry out its own glassware validation.
- **Regression uncertainty (Szo)**
- **Repeatability uncertainty (SIP)**

Convert the standard uncertainties by applying sensitivity coefficients (conversion factors that allow one to convert the units of an input quantity) where necessary and quantify these factors in terms of standard deviation.

3. Combine arithmetically all the individual factors.

4. Calculate the square root of sum of their squares to produce a combined standard uncertainty.

5. Extend the uncertainty by multiplying the combined standard uncertainty by coverage factor K, selected on the basis of confidence level required to produce an expanded uncertainty. In the absence of a particular confidence level being specified by in the standard or by the client, the coverage factor should normally be k =2 giving a confidence level of approximately 95%.

6. This result is then multiplied by X (concentration of QC or sample) to give the total uncertainty. See calculations on chapter 3 for actual examples.

CHAPTER THREE: ANALYTICAL METHODS USED AT KOEBERG

3.1 Neutralisation titration technique

3.1.1 Neutralisation titration technique principle

The study of acid-base titrations involves consideration of the reactions which occur between acids and bases. For this purpose, it is convenient to distinguish between strong and weak acids and bases. The term "strong" usually refers to a substance which is completely dissociated into its ions in solution, while "weak" generally refers to a substance which is partially dissociated. Of course, various degrees of "strong" and "weak" exist. The reaction of a strong base and a strong acid involves the combination of $H^+$and OH^- to form H_2O and it is governed by the ion product of water. The reaction $H^+ + OH^- = H_2O$ and the pH is dictated by the concentration of excess acid or base reactants. Thus the equivalence point of such a titration is pH = 7, 0. In the titration of a weak acid, HA, with a strong base, two sources of protons must be considered in order to compute the pH of the system. First, there are protons originating from the dissociation of the acid [62].

$$HA = H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

and secondly there are protons from the dissociation of water

$$H_2O = H^+ + OH^- \qquad K_w = [H^+][OH^-] \ldots\ldots\ldots\ldots\ldots\ldots 3$$

The second reaction can be neglected for values of pH outside the range 6 to 8. The titration of HA with strong base, OH-, can be represented.

$$HA + OH^- = H_2O + A^- \ldots\ldots\ldots\ldots\ldots\ldots 4$$

The pH of the system can be calculated from stoichiometric and equilibrium relationships:
***Initial pH**.* If the total concentration of HA added is C_{HA} we can write

$K_a = [H^+][A^-]/[HA] = [H^+]^2/(C_{HA} - [H^+])$, since the stoichiometry shows $[H^+] = [A^-]$ as long as the contribution of H^+ from H_2O is negligible. Solving for $[H^+]$, we obtain

$$[H^+] = \sqrt{K_a(C_{HA} \;\; [H^+])} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5$$

$$\text{If } C_{HA} >> [H^+] \text{ then } \quad [H^+] = \sqrt{K_a C_{HA}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 6$$

***Prior to the equivalence point*.** The base reacts stoichiometrically with HA to yield A-. Also by stoichiometry $[HA] = C_{HA} - [A^-]$. The sample is a buffer, a mixture of HA and A^-. Its pH is computed from the Henderson - Hassel Bach equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \tag{7}$$

At the equivalence point. At this point, the moles of OH^- added exactly equals the moles of the weak acid used to prepare the sample. This solution is one of the conjugate weak base A^-. Its pH is computed from its hydrolysis reaction

$$A^- + H_2O = HA + OH^- \quad K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} \tag{8}$$

$$[OH^-] = \sqrt{K_b(C_A - [OH^-])} = \sqrt{\frac{K_w}{K_a}(C_A - [OH^-])} \tag{9}$$

this is derived in an analogous fashion to that for the weak acid. Note that the pH is not 7 and that it is concentration dependent.

Past the equivalence point. The OH^- added will stoichiometrically react with HA. The pH can be computed from the OH^- in excess of HA.

To determine the equivalence point of an acid-base titration, either a pH meter or an acid-base indicator can be used.

The definition of pH is:

$$pH = -\log a_{H^+} \tag{11}$$

A pH electrode is an electrochemical cell responding (ideally) only to the H^+ concentration. Nernst law then gives:

$$E = E^\circ + \frac{RT}{nF}\ln a_{H^+} \tag{12}$$

Introducing the definition of pH, setting n=1 gives:

$$E = E^\circ - \frac{R'T}{F}pH \tag{13}$$

E° is a constant, but it is temperature dependent. Replacing E° with E'T makes the calibration simpler. Real electrodes do not always follow the Nernst slope. The sensitivity, s, is therefore introduced. The working equation then becomes:

$$E = E'T - s\frac{R'T}{F}pH \tag{14}$$

E' and s can be found by measuring the EMF in two solutions with known pH values. S is the slope of E versus pH while E' is found from the intersection of the y-axis.

An example of electrode test/calibration is shown below. The EMF was measured in 4 different buffers with pH from 1.68 to 10. The line was found by linear regression. The calibration parameters are given in the figure. When E' and s is known, the above equation can be rearranged and pH can be calculated from:

$$pH = \frac{E'T - E}{s\frac{R'T}{F}} \quad \text{...15}$$

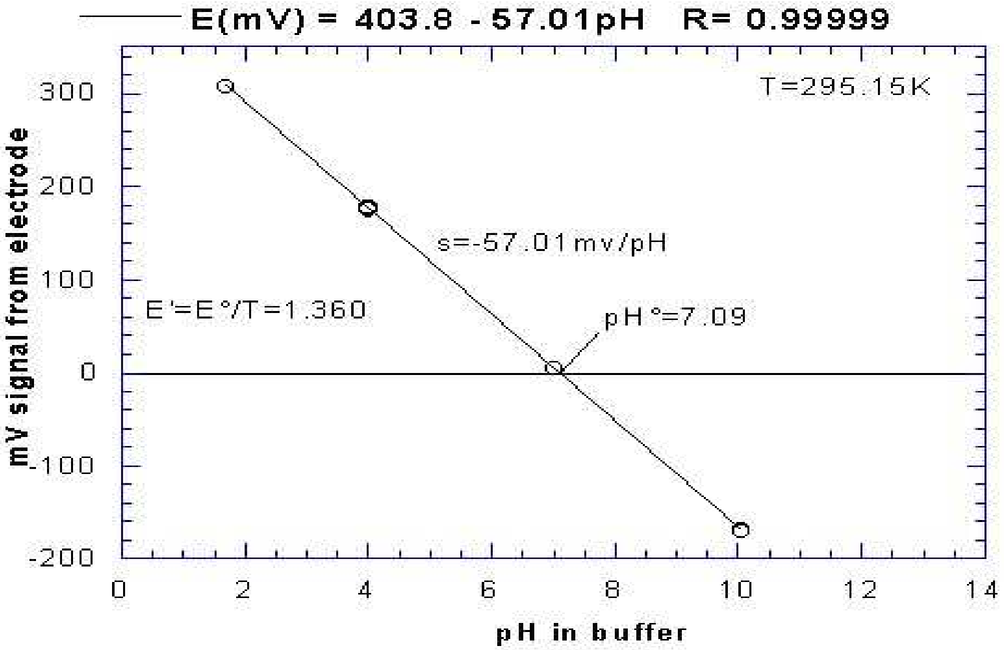

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Figure 3.1.1 Representation the pH probe calibration curve.

Determination of boric acid by titration methods

Boric acid, is a weak monoprotic acid, and therefore cannot be titrated accurately with a standard alkali. However, by the addition of certain organic polyhydroxy compounds, such as mannitol, glucose, sorbitol or glycerol, it forms a complex which behaves as a much stronger acid.

Boric acid concentration can be determined using a manual titration or Potentiometric Titration after the reaction of the boron with a polyhydroxyl compound (usually d-mannitol, $C_6H_{14}O_6$) to create a complex that behaves as a medium strength monovalent acid and is titrated to an endpoint with sodium hydroxide solution [9].

This phenomenon allows convenient determination of boron concentration by direct titration with a strong base of known normality, such as sodium hydroxide.
H [Boric acid complex] + NaOH → Na [Boric acid complex] + H_2O

1 *mL* of 1.0 M NaOH = 0.06184 *g* H_3BO_3

$\therefore$ 1 mL of 1.0 M NaOH = 0.01081 g B

This last equation is used to quantitatively determine the boron concentration.

The end point for the manual titration is indicated by the colour change from colourless to a pale pink colour. For Potentiometric Titration with a pH electrode, the end point is set at pH 8.5 (found to be the equivalence point on the titration curve).

The sodium hydroxide solution used in the titration must be standardised. This is achieved by using the primary standard, potassium hydrogen phthalate (PHP). Although this method is very practical and is extensively employed to analyse boron in PWR plants it must be understood by the users that it is an indirect determination of boron concentration. It is assumed that the sample being analysed is a pure solution of boric acid which is an acceptable assumption for ideal conditions.

3.1.2 The neutralisation titration technique Interferences

Chemical species that interfere with an acid/base titration between pH 3.0 and 8.0 will interfere with this analysis. This means that when conditions are not ideal (e.g. CRUD burst, impurity ingress), the measured boron result may be incorrect. Because of the function of boron, the consequences of misinterpretation of an analysis result could be serious from an operation and safety perspective.

With this in mind, the direct techniques (spectrophotometric, e.g. azomethine-H or carminic acid methods) or Atomic Absorption will provide more reliable results.

3.1.2.1 Lithium hydroxide interference

Lithium hydroxide is added into the Reactor Coolant System (RCS) which contains boric acid for pH adjustment. When determining the boron concentration on the RCS water by titration method, lithium hydroxide interferes with the method. The effect of lithium hydroxide on alkali metric determination of boron was investigated and evaluated. This was done by preparing different concentrations of boron standards in lithium hydroxide matrix by diluting 7000mg B/kg, 100mgLi/kg concentration to make a cocktail of lithium and boron concentrations. The resultant concentrations were 10, 100, 500, 2000 mg B / kg and 4, 3, 2, 1, 0.5 mg Li / kg. Since these solutions contain different concentration of lithium hydroxide and boric acid, the pH of them differed accordingly. These cocktails were analysed for boron concentration. It was noted that the boron results differ from what was expected. This was due to the concentration of lithium hydroxide added into to the boric acid solution.

In an attempt to get the correct boron results in the presence of lithium hydroxide the two methods were applied.

An excess acid method

In an attempt to neutralise the pH physically, the pH of cocktail solutions were adjusted by adding excess hydrochloric acid to the cocktail to adjust the pH to be the same as in pure boric acid. This was done to compensate for this lithium hydroxide interference on this method, before adding the mannitol, the pH of the boric acid solution was adjusted to the value corresponding boric acid solution of the same concentration using a dilute hydrochloric acid solution. The boron lithium cocktail standards prepared in different concentrations of lithium and boron concentration were analysed using METTLER T50 automatic titration method as mentioned on the methods above after being neutralised with hydrochloric acid. The results found did not differ much from the expected results but the process takes longer when the pH has to be adjusted on the reactor coolant samples as they are radioactive. Practically this pH adjustment practice is not the preferred method of analysis as the analyst has to be in contact with the radioactive sample trying to adjust the pH thus spending more time preparing the sample conditions before the actual sample analysis. This is not preferred because of the implications of personal safety and on dose reduction.

Calculated results:

When using Potentiometric Titration, since the samples contained lithium hydroxide, variation in results will occur depending on the mannitol technique employed. According to ASTM 19.11[55], hydroxide ion can be accounted for in the boron calculation by determining the lithium level and applying an appropriate factor.

If the Lithium concentration in the sample for boron determination is known the correction factor can be applied:

Boron corrected= Boron measured + (CF x Li measured)
CF= mw B / mw Li
=10.811 g/mol / 6.941 g/mol
=1.56

Failure to compensate for the presence of lithium hydroxide could bias the boron results if the method does not automatically compensate for hydroxide presence.

3.1.2.2 Zinc acetate interference

Prior to Koeberg Nuclear Power station‘s zinc acetate injection process on both units for dose reduction purposes, the Analytical Laboratory needed to establish before commencing with this project that the methods for boron analysis used are not affected or the extent to which they are affected is known in advance. An investigation on the boron analysis method (on Potentiometric titration method), after addition of different concentrations of zinc acetate was carried out and the report with experimental work was written as shown on Appendix B.

From the report attached, it is evident that the addition of zinc acetate into the RCS will not have an effect on boron results produced by titrimetric method.

3.1.3 Optimisation of boron analysis when using Auto Titrator

3.1.3.1 Basic parts and operation of Autotitrator

The details are given in Appendix E

3.1.3.2 Optimisation of boron analysis process for automatic titration technique

After the incidents specified in chapter one, the boron analysis method using the METTLER autotitrator(s) was evaluated and optimised.
The optimisation of methods involved mechanical adjustments on the instrument, sample handling i.e. volume/ mass measurement, titrant reservoir volume, titrant burette volume.
The sample results before the incident and after the incident were analysed to check if the optimisation performed had an impact on the results.

Optimisation of Instruments:

Sodium Hydroxide reservoir optimisation

The METTLER model T50 and DL50 are supplied with 1 L container:

The 1 L container is used to store the 1 L sodium hydroxide. It was noticed that the 1 L sodium hydroxide runs out quickly. When it is finished it requires preparation and standardisation more frequently. The calibration of the instrument frequency and the standardisation frequency for sodium hydroxide is monthly. So it was decided that the 1 L container be replaced with a 5 L container. Then the calibration and QC checks can be done weekly.

Burette optimisation

The METTLER model T50 and DL50 are supplied with a standard 10 mL burette.

The 10 mL standard burette is used in the titration process to deliver the required volume to react with a titrant or sample to reach the specific endpoint. The problem with the 10mL burette is that it is not big enough to deliver the required volume when the end point is above 10 mL volume. When the endpoint is at more than 10 mL volume, it necessitates the empting and filling that causes bubbles to be formed. To overcome the problem of bubble formation while the titration is in progress, the 10mL burette was replaced with the 20 mL burette.

Optimisation of volume/mass of samples to be analysed

In this method, a wide range of samples with different concentration ranges are analysed on the same calibration. A calculation was developed to estimate how much sample must be used when analysing different concentration ranges of boron.

The suitable mass for the expected concentration was calculated by using the following equation. This mass is used to analyse boron samples that will produce the results of boron concentration at approximately10mL sodium hydroxide.

$$\text{Mass to be measured} = \frac{10000}{Expected\ \ boron\ concentration}$$

$$= \quad xg$$

The details are as per Appendix F

Evaluation and Optimisation of quality of reagents used

Salts and water used for boron concentration determination needs to be of high quality
The most important salt that must be of high quality is Potassium Hydrogen Phthalate.

Quality of reagents:

Potassium Hydrogen Phthalate (PHP)

PHP is used as a primary standard and that means it must be stable, have high molecular weight and must react readily with other reagents when it is in the solution form. As the primary standard (PHP) when preparing concentrations of PHP it is assumed to be 100% (PHP).

The purity of the PHP has its own safety significance. The safety significance is that the PHP standard is used for standardisation of sodium hydroxide which is in turn used to determine the boron concentration in the primary coolant system. Use of sodium hydroxide standardized with a lower-than-expected PHP concentration would overestimate the boron concentration in the primary coolant system.

Overestimation of the primary system boron concentration could reduce the capability to shut down the reactor and to maintain the plant in a safe condition.
For this reason the analytical laboratory is supplied by accredited suppliers of reagents i.e. MERCK and if the product is not satisfactory it can be traced and returned back to the supplier.

Preparation of 1% PHP

1% PHP is prepared by weighing 5.0000 g of a dried PHP using a weighing boat, transferring it quantitatively using a funnel into a 500 mL volumetric flask dissolved and diluted to the mark with demineralised water.
1% PHP or 0.051 M PHP.

Sodium Hydroxide (NaOH)

Sodium hydroxide is used in the direct determination of boric acid. Sodium Hydroxide solution is not as stable as PHP solution so it needs to be standardised frequently to check

the exact concentration before it can be used for boron concentration determination. When determining the concentration of sodium hydroxide (NaOH), PHP is used as a primary standard. The following information needs to be considered when calculating the concentration of PHP to be used for standardisation of Sodium Hydroxide:
The purity of the PHP, mass of the PHP used (taking into account the calibration of balances),

Volume of the PHP used (taking into account the pipette calibration supplier specification) and operating temperatures.
All these factors are shown on the cause and effect diagram for NaOH Standardisation below: These factors contribute to the uncertainty of analysing the boron concentration correctly.

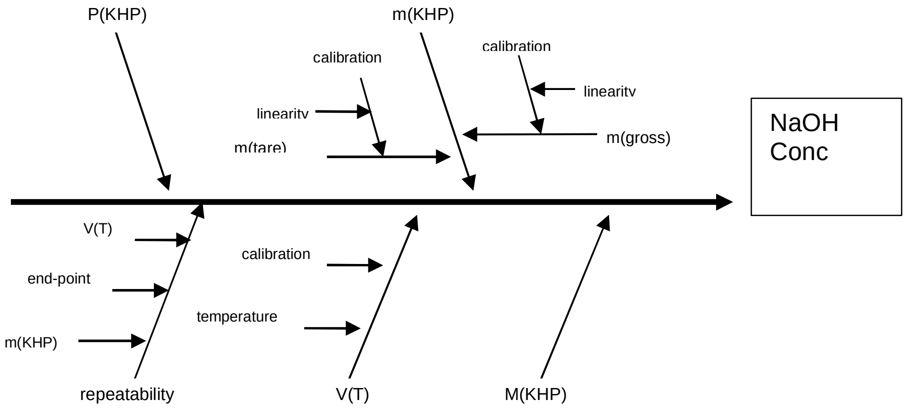


Figure 3.1.3.2 the cause and effect diagram [11]

Preparation of 0.1 M NaOH

Sodium Hydroxide is prepared by weighing 20.0000 g sodium hydroxide pellets using a weighing boat, transferred quantitatively into a 5000 mL volumetric flask, dissolved and diluted to the mark.

Other factors that influence boron concentration

- The repeatability of the instrument.
- The weight of the boron sample weighed for boron determination.

All the uncertainty factors are combined and calculated as to total uncertainty under results calculation section.

Evaluation of the titration method using statistical analyses

For statistical purposes, the data of boron concentration results were extracted from the laboratory management (LIMS) system. These were the results of the six tanks sampled from Unit 1 RIS 001BA, 1 RIS 002BA and 1 RIS 003 BA and Unit2 RIS 001BA, 2 RIS 002BA and 2 RIS 003 BA. These tanks have the boron concentration of about 2500 mg/kg.

The boron concentration results on six tanks are analysed monthly by different people on different shifts.

As mentioned before everybody who is performing boron concentration analysis is properly trained and the standard procedures for sampling and analysis are used for consistency purposes, for trending to be able to see if there were any dilutions or boration on these tanks.

From the data extracted, the mean, standard deviation, the minimum and a maximum boron concentration was calculated using Microsoft excel spread sheet.
The mean the minimum and the maximum boron concentration results were different from each tank. The standard deviation on all these tanks was about 6 mg/kg.

Unit1 RIS Accumulators data.

Date Sampled	1RIS 001BA	Date Sampled	1RIS 002BA	Date Sampled	1RIS 003BA
19-Jan-05	2541	12-Jan-05	2530	19-Jan-05	2547
22-Jan-05	2538	19-Jan-05	2527	22-Jan-05	2537
14-Feb-05	2541	22-Jan-05	2525	16-Feb-05	2551
16-Feb-05	2532	16-Feb-05	2532	16-Mar-05	2550
16-Mar-05	2548	16-Mar-05	2532	13-Apr-05	2553
13-Apr-05	2555	11-Apr-05	2528	11-May-05	2553
11-May-05	2550	13-Apr-05	2531	03-Aug-05	2541
08-Jun-05	2535	06-May-05	2527	31-Aug-05	2550
03-Aug-05	2536	11-May-05	2532	28-Sep-05	2557
31-Aug-05	2545	20-May-05	2539	29-Nov-05	2546
28-Sep-05	2549	30-May-05	2523	21-Dec-05	2545
29-Nov-05	2549	08-Jun-05	2520	22-Dec-05	2543
21-Dec-05	2536	13-Jun-05	2524	01-Feb-06	2559
22-Dec-05	2537	31-Jul-05	2526	15-Mar-06	2543
01-Feb-06	2550	03-Aug-05	2520	12-Apr-06	2547
15-Mar-06	2542	04-Aug-05	2519	23-Apr-06	2545
12-Apr-06	2546	31-Aug-05	2530	11-May-06	2545
22-Apr-06	2545	16-Sep-05	2526	07-Jun-06	2551
23-Apr-06	2544	26-Sep-05	2531	05-Jul-06	2544
11-May-06	2538	28-Sep-05	2538	02-Aug-06	2542
15-May-06	2539	29-Nov-05	2532	30-Aug-06	2549
04-Jun-06	2537	07-Dec-05	2532	27-Sep-06	2549
07-Jun-06	2543	21-Dec-05	2530	**X-bar=**	**2547.590909**
05-Jul-06	2540	22-Dec-05	2523	**Std Dev**	**5.6**
02-Aug-06	2532	01-Feb-06	2542	**Min=**	**2537**
30-Aug-06	2537	15-Mar-06	2530	**Max=**	**2559**
26-Sep-06	2535	12-Apr-06	2536		
27-Sep-06	2539	18-Apr-06	2538		
Xbar=	**2541.392857**	11-May-06	2530		
Std Dev=	**5.964954973**	07-Jun-06	2533		
Min=	**2532**	05-Jul-06	2528		
Max=	**2555**	02-Aug-06	2528		
		30-Aug-06	2535		
		27-Aug-06	2539		
		X-bar=	**2529.882353**		
		Std Dev=	**5.687651195**		
		Min=	**2519**		
		Max=	**2542**		

Date Sampled	2RIS 001BA	Date Sampled	2RIS 002BA	Date Sampled	2RIS 003 BA
19-Jan-05	2551	19-Jan-05	2584	19-Jan-05	2603
04-Mar-05	2565	04-Mar-05	2586	04-Mar-05	2603
06-Mar-05	2560	06-Mar-05	2585	06-Mar-05	2612
16-Mar-05	2560	16-Mar-05	2581	16-Mar-05	2609
13-Apr-05	2559	16-Mar-05	2588	16-Mar-05	2612
11-May-05	2567	13-Apr-05	2594	13-Apr-05	2613
03-Aug-05	2552	01-May-05	2598	11-May-05	2615
31-Aug-05	2560	11-May-05	2577	03-Aug-05	2594
28-Sep-05	2567	18-May-05	2578	31-Aug-05	2608
26-Oct-05	2565	30-May-05	2570	28-Sep-05	2615
23-Nov-05	2553	08-Jun-05	2559	26-Oct-05	2606
21-Dec-05	2553	03-Aug-05	2537	21-Dec-05	2599
18-Jan-06	2569	05-Aug-05	2548	18-Jan-06	2611
15-Feb-06	2571	18-Aug-05	2540	07-Mar-06	2609
07-Mar-06	2560	31-Aug-05	2542	15-Mar-06	2602
15-Mar-06	2553	15-Sep-05	2540	12-Apr-06	2612
12-Apr-06	2560	26-Sep-05	2539	10-May-06	2607
10-May-06	2563	28-Sep-05	2522	07-Jul-06	2602
07-Jul-06	2565	07-Oct-05	2536	02-Aug-06	2599
16-Jul-06	2559	26-Oct-05	2511	30-Aug-06	2600
23-Jul-06	2554	26-Oct-05	2514	10-Sep-06	2602
25-Jul-06	2555	03-Nov-05	2510	27-Sep-06	2600
02-Aug-06	2556	08-Nov-05	2514	**Mean=**	**2606.045455**
30-Aug-06	2557	12-Nov-05	2505	**Std dev=**	**5.963997323**
10-Sep-06	2553	23-Nov-05	2481	**Min=**	**2594**
27-Sep-06	2554	24-Nov-05	2515	**Max=**	**2615**
Mean=	**2559.269231**	24-Nov-05	2516		
Std dev=	**5.779672602**	24-Nov-05	2527		
Min=	**2551**	24-Nov-05	2532		
Max=	**2571**	24-Nov-05	2539		
		24-Nov-05	2543		
		24-Nov-05	2552		
		24-Nov-05	2557		
		25-Nov-05	2548		
		28-Nov-05	2550		
		02-Dec-05	2548		
		07-Dec-05	2541		
		12-Dec-05	2553		
		19-Dec-05	2548		
		21-Dec-05	2538		
		21-Dec-05	2542		
		22-Dec-05	2539		
		24-Dec-05	2547		
		28-Dec-05	2545		
		02-Jan-06	2545		
		07-Jan-06	2546		
		11-Jan-06	2549		
		14-Jan-06	2552		
		18-Jan-06	2556		
		24-Jan-06	2562		
		01-Feb-06	2562		
		04-Feb-06	2559		

		09-Feb-06	2565		
		13-Feb-06	2567		
		15-Feb-06	2567		
		15-Feb-06	2569		
		21-Feb-06	2570		
		23-Feb-06	2570		
		26-Feb-06	2570		
		02-Mar-06	2573		
		05-Mar-06	2550		
		06-Mar-06	2556		
		12-Mar-06	2552		
		15-Mar-06	2549		
		21-Mar-06	2548		
		24-Mar-06	2553		
		31-Mar-06	2552		
		03-Apr-06	2554		
		07-Apr-06	2552		
		12-Apr-06	2552		
		12-Apr-06	2557		
		15-Apr-06	2557		
		21-Apr-06	2556		
		01-May-06	2549		
		02-May-06	2552		
		06-May-06	2550		
		10-May-06	2559		
		12-May-06	2548		
		14-May-06	2549		
		18-May-06	2554		
		22-May-06	2548		
		07-Jul-06	2552		
		02-Aug-06	2552		
		30-Aug-06	2557		
		10-Sep-06	2550		
		27-Sep-06	2556		
		Mean=	**2550,755814**		
		Std dev=	**19,99702098**		
		Min=	**2481**		
		Max=	**2598**		

Table 3.1.3.2 Historical Sample results for Unit1 and Unit 2 Accumulators

On the results obtained on the six tanks, the decision was taken to eliminate the results of Unit 2 RIS 002 BA. This is due to the fact that this tank has experienced a lot of interventions like diluting and borating the tank and there is a high variance between the results. This includes the incident presented earlier.

The remaining five tanks results were used to determine the experimental deviation The experimental deviation was found to be 6 mg/kg. The boron concentration results reported are analysed monthly, so we can conclude and say that the month to month deviation of boron results in 2500mg/kg range is 6 mg/kg.

The request was made to determine the total uncertainty of the reagents the instrument and the equipment used in the laboratory without taking into account the changes happening in the plant.

Total uncertainty is defined as “A parameter associated with the result of a measurement that characterises the dispersion of the values that could be reasonably be attributed the measured.” To calculate the total uncertainty calculation requires the following information:
Identification of the source of uncertainties
The following sources of uncertainties were identified: purity of commercial salt PHP for standardisation of Sodium Hydroxide which is the secondary standard. Uncertainty of the weighing balance, uncertainty of volumetric glassware, uncertainty of repeatability, uncertainty of dilution and regression uncertainty.

3.1.4 Uncertainty calculations for automatic titration [12][56][57]

Purity uncertainty, (u P)

% Purity for (PHP)
The supplier quotes that the PHP = 99. 5% pure.
100% - 99. 5% = 0.5%
Here we assume $\sqrt{\mathbf{3}}$ = coverage factor because the probability of obtaining any value within the limits has equal chance.

$\frac{\mathbf{0.5\%}}{\sqrt{\mathbf{3}}}$ = 0. 29 %

Mass uncertainty: (Um)

Mass pieces of 1.000g and 5.000 g that are used for a balance check were weighed on the balance. Duplicate readings from the four corners of the balance and at the centre were taken and the mean result was found to be 0.0002 g.

Then we assume triangular distribution for normal distribution factor.
Um $=\frac{0.0002\text{g}}{\sqrt{6}} \text{X } 1.96$
= 0. 16 mg

Therefore, the uncertainty in weighing the mass of PHP (5000 mg) = 0. 16 mg

The uncertainty in weighing the mass of Sample (4000 mg) = 0. 16 mg

Volume uncertainty for a 500mL volumetric flask

Mass of PHP is made up to the mark using 500 mL volumetric flask
Manufacturer states that 500 ± 0.20 mL at 20 ^{0}C, we assume triangular distribution

Volume uncertainty of filling a 10 mL pipette.

Twenty weights measurement of 10 mL water were weighed to determine the deviation that is found in volume delivery when pipetting the solution using a 10 mL pipette.

V_1 = Uncertainty of filling the pipette to the mark:

A series of 10 fill and weigh experiments gave a mean of 9.939 and deviation standard deviation SD = 0.0062 for a 10mL pipette
See appendix 1B for volume checks results.
SD = 0.0062 mL
$\bar{x}$ = 9.9394 mL

Manufacturer specification:
Internal volume uncertainty:
Manufacturer specified that the error for the grade A pipette at 20 ^{0}C = 0. 02 mL
Here we assume triangular distribution because the 100% containment limits are known and values are more likely to be near the mean than at the extremes.

V_2 = Manufactured $\frac{\mathbf{0.02}\text{mL.}}{\sqrt{\mathbf{6}}}$
= 0.00816 mL for a 10 mL

Laboratory conditions that affects the volume:
Laboratory effects on the volume
Temperature uncertainty Uv_3
Laboratory temperature = 20.0^{0}C ± 2^{0}C
Coefficient of volume expansion for water = $2.1 \text{ x } 10^{-4}$ and we assume a rectangular distribution.

$$\mathbf{V_3} = \frac{2\text{x}2.1\text{x}10^{-4}}{\sqrt{\mathbf{3}}}\ \text{x}\ 10\ \text{mL}$$

$$= 0.0024\ \text{mL}$$

Total uncertainty of filling the pipette:

$$\text{UV}_\text{T} = \sqrt{(0.0062)^2 + (0.00816)^2(0.0024)^2}$$

$$= \sqrt{0.000110785}$$

$$= 0.011\ \text{mL}$$

Repeatability uncertainty

For repeatability determination, a boron quality control standard solution of 2500 mg/kg was analysed using METTLER Autotitrator.

Twenty readings were taken. See appendix 1 for repeatability testing results.

See appendix 1a for repeatability testing results.

Standard deviation $= 1.35$ mg B/kg

$\bar{x} = 2502$ mg B/kg

Total uncertainty (TU) calculation

$$\text{TU} = \sqrt{\left(\frac{1.35\ mg/kg}{2500\ mg/kg}\right)^2 + \left(\frac{0.29\ ml}{100\ ml}\right)^2 + \left(\frac{0.011\ ml}{10\ ml}\right)^2 + \left(\frac{0.16\ mg}{5000\ mg}\right)^2 + \left(\frac{0.16\ mg}{4000\ mg}\right)^2}$$

$$= \sqrt{2.91\text{x}10^{-7} + 8.41\text{x}10^{-6} + 1.21\text{x}10^{-6} + 1\text{x}10^{-9} + 2\ \text{x}10^{-9}}$$

$$= 0.0031$$

Total uncertainty is 0. 0031 x 2500 mg B/kg

= 7. 75 mg B/kg

≈ 8

The total uncertainty of boron analysis using the Potentiometric Titration method was found to be 8 mg B/kg.

Using the analytical Methodology developed and employing ISO guidelines combined relative uncertainty and expanded relative uncertainty (with coverage factor k =2) of measurement were calculated to be 16 mg B / kg.

Therefore when reporting the results in 2500 mg B/kg using Potentiometric Titration method.

We accept 2500 ± 16 mg B/kg

2500± 0.6%

3.1.5 Accuracy calculations for automatic titration

Calculation for determination of accuracy of the method using a prepared 2500 mg B/kg standard

$$\text{Accuracy} = \frac{2500 mg/Bkg - 2502 mgB/kg}{2500}\ X\ 100$$

$$= \frac{2\ mgB/kg}{2500} X\ 100$$

$$= 0.0008 X\ 100$$

$$= 0.08\%$$

3.1.6 Precision calculations for automatic titration

$$\%\ \text{Precision} = \frac{11.60\ mg\ B/kg}{2502\ mgB/kg} x\ 100$$

$$= 0.0046 x\ 100$$

$$= 0.46\%$$

3.1.7 Advantages of using titrimetric method for boron determination

Potentiometric Titration method for boron analysis is simple to set-up, the method is appropriate for the plant boron concentrations and can be applied over the wide range of concentrations of 5 - 8000 mg B /kg.

The instrument for this method can be set up in any laboratory where there is a supply of demineralised water and the waste container. There is no excessive ventilation needed or extraction needed for setup.

This method can provide rapid and reliable results. The accuracy, precision reproducibility and speed of analysis are acceptable to the Pressurised Water Reactor Plant.

Potentiometric titration method is required to be calibrated once a month. On this method, the QC standard is required to be analysed and is expected to be within the acceptable level before a sample is analysed, the sample can be analysed as soon as possible and produce the results within 3 minutes.

Overall it is very practical, but it is important to be aware of the limitations discussed earlier.

3.1.8 Disadvantages of using titrimetric method for boron determination

Titrimetric method for boron determination is affected by the sample matrix i.e. Lithium hydroxide (LiOH), a strong base that is added to the reactor coolant system (RCP) to provide the optimum pH.

Waste treatment samples like KER and TEU cannot be analysed using the titration method because they contain large amount of other species like sodium, acid and or bases which can affect the boron results produced due to pH difference.

This technique / method is known to be used on analysis of boron samples containing pure boric acid.

This method has low sample throughout compared to AA and ICP-MS

3.2 Spectrophotometric Analysis

3.2.1Spectrophotometric Analysis principle

Spectrophotometric methods are based upon the measurement of decrease in radiant power of a beam of light as it passes through an absorbing medium of known dimension. When light of a small wavelength range passes through a sample containing an absorbing species, the radiant power of the beam is progressively decreased as more of the energy is absorbed by molecules in solution. The decrease in radiant power depends upon the concentration of the absorber and the length of the path traversed by the beam. The transmittance, T, of a solution is defined as the ratio of the intensity of light transmitted through the sample solution to the intensity of light transmitted through a blank solution which does not absorb light. The experimental absorbance is defined as log T, and has been given the symbol abs. The Beer Lambert law relates the absorbance to the concentration C of the absorbing species and the optical path length b as follows:

$$\text{Abs} = \epsilon bC \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

In this equation, ϵ is the molar absorptivity, which is dependent on wavelength. In spectrophotometric determinations a calibration curve of Abs versus C is prepared from measurements of absorbance standards. This curve is then used to determine C in a sample from the measured absorbance for the sample. The total absorbance of a solution at a given wavelength is equal to the sum of the absorbance of the individual species present. Thus, for a multicomponent system:

$$\text{Abs}_{\text{total}} = \epsilon bC = \epsilon_i bC_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

Where the subscript i refers to all absorbing substances.

To obtain accurate results with spectrophotometry it is desirable for the absorbance measured to be due predominately to the analyte. Absorption due to other species should be compensated by a blank measurement. The absorbance signal should generally be in the range of 0.01 to 2.0 absorbance units (A.U.) for highest accuracy. Below 0.01 A.U. or above 2.0 A.U. the precision decreases. Although many substances absorb strongly in the visible and near UV wavelength regions, many others do not. Boric acid is one of those substances which does not absorb. To determine the concentration of the non-absorbing boron, $B(OH)_3$ is reacted with a reagent to form an absorbing reaction product. It is important that the reagent be selective for the species to be determined, in order to prevent interference from other species in solution. The reagent azomethine-H has been selected for use in this study because of the rapid analysis time and the simplicity of its procedure. Azomethine-H is readily available as the condensation product of H acid, 8 amino-1-naphtho -3,6- disulphuric acid and salic aldehyde. (Since only the H acid derivative was used in this study, azomethine-H will be referred to as azomethine). In aqueous solution azomethine, Figure 3.2.1 is orange, whereas H acid and Salic aldehydes are practically colourless. Boron is complexed by the oxygen of the hydroxyl groups of the azomethine molecule SO_3H.

Azomethine-H structure

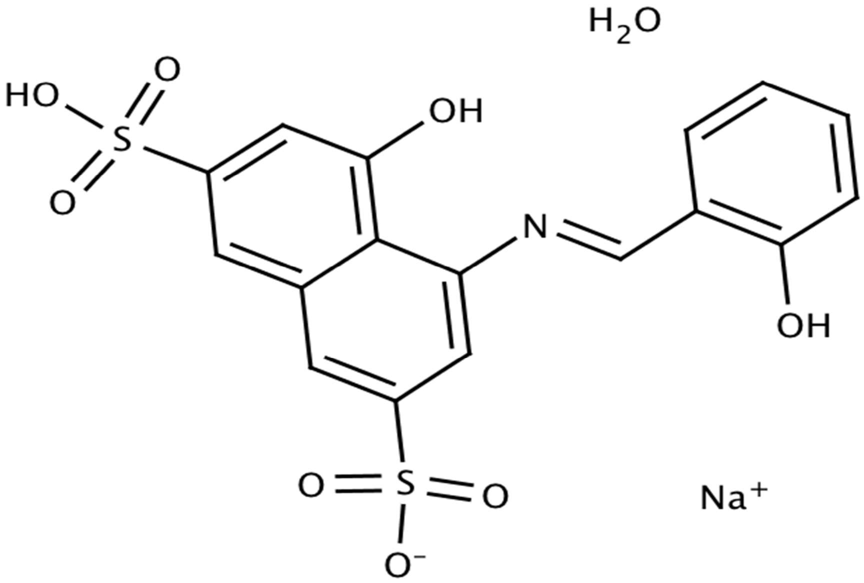


Figure 3.2.1 Structure of Azomethine-H [34]

3.2.2 Interferences when using the UV technique

In literature, the UV azomethine H method for the determination of boron is relatively free of interference from a many elements [65] [66]. A buffer solution is added in the process of analyses as this method is affected by pH changes.

3.2.3 Optimisation of the UV technique for boron analysis

Optimisation of the instrument

The method for boron analysis using the UV technique requires that the instrument be calibrated once a year. The calibration range is as (0.00; 1.00; 2.00; 3.00; 4.00; and 5.00 mg B/kg.

The reference filter is checked on a monthly basis to check if there are any changes. This method is robust and does not become influenced easily by small changes. There is no variety of results caused by the instrument calibration.

Optimisation of reagents and standards used:

All Standards and reagents used in the laboratory are of good quality. Reagents and standards selected and prepared in accordance with KWC-003 (preparation of analytical Chemistry reagents), all the analysts use the same procedure to prepare boron reagents. There have been no significant changes in the results. CRMs are also available to be checked against the in-house prepared standards.

Optimisation of samples to be analysed:

For this method, a calibration range is 0.00 -5.00 mg B/kg. Samples with higher concentration must be diluted to read within the calibration range. For 2500 and 1000 mg B/kg sample, large dilutions have to be made for samples to be within the calibration range.

This large dilution required for boron concentration greater than 5 mg B/kg creates too much experimental error. Although the dilutions are high, the dilutions were standardised for all analysts to perform dilution in the same way. Example: when the sample is expected to be within 2500 mg B/kg, a 500 times dilution is required and for a 1000 mg B /kg a 200 times is required and must be performed in the same way to have stability and consistency in results.

The volumetric flask used and aliquots of samples use for dilution must be the same for all analysts.

3.2.4 Uncertainty calculation for UV technique.

Uncertainty sources for UV-VIS and AAs are similar, and below is the cause and effect diagram that shows what sources contribute to the method's uncertainty:

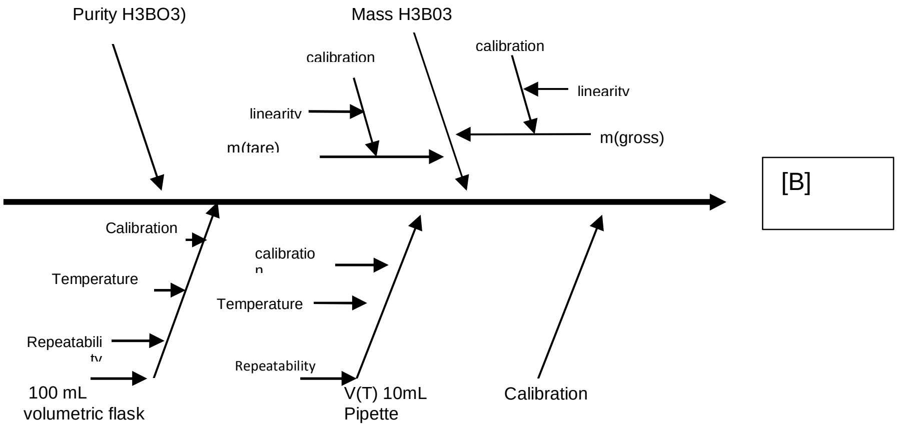


Figure 3.2.4 the cause and effect diagram for UV-VIS and AAS.

Purity of the salt boric acid used to prepare boron calibration standards (uP)

Certificate of analysis states that Purity = 100 ± 0.2%

No purity distribution is given

We assume a rectangle distribution with coverage factor = $\sqrt{3}$

U (P) = $\frac{0.2}{\sqrt{3}}$ = 0.115

Mass uncertainty (um)

Assume mass weighed to prepare a 1000 mg/kg boron standard = 5. 7193 g.

Balance calibrator certificate:

Balance linearity = 1. 5x10^{-4}

We assume a rectangle distribution with coverage factor = $\sqrt{3}$

U (m) = $\frac{1.5\text{x}10-4}{\sqrt{3}}$g = 8. 7x10^{-5} g

Volume uncertainty :(Uv1)

The weights of the 10 mL water were weighed to determine the deviation that is found in volume delivery when pipetting the solution using a 10 mL pipette.

$V_{1=}$ Uncertainty pipette:

Std dev. = 0.0062

$\bar{x}$ = 9.9384

Manufacturer specification:

$V_{2=}$Manufactured $\frac{\mathbf{0.02}}{\sqrt{\mathbf{6}}}$ = 0. 00816 mL

Laboratory conditions that affects the volume:

V_3= $\frac{2\text{x}2\text{x}10^{-9}}{\sqrt{\mathbf{3}}}$ x 10 mL

$= 0.0024\ \text{mL}$

Total volume uncertainty of a 10 mL pipette.

UV_{10mL}= $\sqrt{(0.0062)^2 + (0.00816)^2(0.0024)^2}$

=$\sqrt{0.000110785}$

= 0.011 mL

Volume Uncertainty of the 100 mL volumetric flask uv$_2$)

Manufacturer: States that 100.0 ± 0. 2 mL at 20^{0}C

Three volumetric flasks were topped up to the mark with water and gave the following volumes (assumed 1 g =1 mL).

$V_{1\,=}$ 0. 0408 mL
$V_{2\,=}$ 0.020 mL
$V_{3=}$ 0.050 mL

U (V) $_{\mathbf{100\ mL}}$ = $\sqrt{(0.0408)^2 + (0.020)^2(0.05)^2}$
= $\sqrt{(0.0408)^2 + (0.020)^2(0.05)^2}$
= $\sqrt{0.00456464}$

= 0.068 mL for 100 mL

Uncertainty due to imported CRM (U_{crm})

The label on imported CRM states that 1000 ± 3 mg B/kg.

Certificate coverage factor =2.57

∴Uncertainty will be $\frac{3}{2.57}$ = 1.16mgB/kg

Calibration uncertainty/ regression uncertainty S_{X0}

The following table represents the standards used for calibration and the absorbance response of each standard.

Cncentration (x)	Absorbance (y)
0	0.00
1	0.057
2	0.119
3	0.206
4	0.256
5	0.312

Sum of x_i =$\sum(x_1 \ + x_2 \ \ + x_3 \ \ldots x_n \,)$

Average of $\overline{\mathrm{x}}$ $= \frac{\sum(x_1 + x_2 \ + x_3 \ldots x_{n)}}{n}$

Standard deviation of x_i/Degree of spread= $s_x^2 = \sqrt{\frac{\sum(x_i - \overline{x})^2}{n-1}}$

x_i	y_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$	$(y_i - \bar{y})$	$(y_i - \bar{y})^2$	$(x_i - \bar{x})(y_i - \bar{y})$
0	0	-2.5	6.25	-0.15833	0.0250694	0.3958333
1	0.057	-1.5	2.25	-0.10133	0.0102684	0.152
2	0.119	-0.5	0.25	-0.03933	0.0015471	0.0196666667
3	0.206	0.5	0.25	0.047667	0.0022721	0.0238333333
4	0.256	1.5	2.25	0.097667	0.0095388	0.1465
5	0.312	2.5	6.25	0.153667	0.0236134	0.384166667
$\sum$ =15	0.95	0	17.5	0	0.0723093	1.122
Ave= 2.5	0.15833					

Regression Uncertainty in Sample analysis: s_{x0}

Evaluation of the calibration curve

Is the calibration plot linear? We assume that the plot is a straight line and takes the algebraic form of: Y=bx + a

In order to estimate how well the calibration standard fit the straight line, we calculated the correlation coefficient, r.

The value of r is given by:

$$r = \frac{(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{(x_i - \bar{x})^2 \, (y_i - \bar{y})^2}}$$

$$= \frac{1.122}{\sqrt{(17.5)(0.0723093)}}$$

$$= \frac{1.122}{1.124905663}$$

= 0.0997

If r= 0.0997 then r^2 = 0.9948

The slope b is given by:

$$b = \frac{\sum(x_i - \overline{x})(y_i - \overline{y})}{\sum(x_i - \overline{x})^2}$$

$$= \frac{1.122}{17.5}$$

$$= 0.06411$$

For the equation $y = bx + a$ we need to know the value of a .

At the centroid we can calculate the intercept

$$\overline{y} = b\bar{x} + a$$

$$\therefore 0.15833 = (0.06411)2.5 + a$$

$$\therefore 0.15833 = 0.16028 + a$$

$$\therefore a = 0.1583 - 0.16028$$

$$\therefore a = -0.00195$$

From what we have got we can write the expression of our calibration line

$y = bx + a$ as:

$y = 0.0641\,x - 0.00195$

Since we have got the values of the slope (b) and the intercept (a) the ŷ residuals may be calculated by substituting from the equation; y=bx +c

y_i an observed result and $\widehat{y_i}$ is a predicted value. The difference between the observed and predicted values is called residuals and is presented as follows: Y residuals = $y_i - \widehat{y_i}$

x_i	${x_i}^2$	y_i	$\hat{y}_i$	$(\lvert y_i - \hat{y}_i \rvert)$	$(y_i - \hat{y}_i)^2$
0	0	0	-0.00195	0.00195	3.803E-06
1	1	0.057	0.06216	-0.00516	2.663E-05
2	4	0.119	0.12627	-0.00727	5.285E-05
3	9	0.206	0.19038	0.01562	0.000244
4	16	0.256	0.25449	0.00151	2.28E-06
5	25	0.312	0.3186	-0.0066	4.356E-05
$\sum$ =15	55	0.95	0.94995	8.33E-06	0.0003731

We can calculate the errors in the intercept and of the regression line, $y = 0{,}0641\, x - 0{,}00195$ by using the following formulae:

Standard error of regression/ random calibration uncertainty = $s_{y/x}$

$$s_{y/x} = \sqrt{\frac{\sum(y_i - \hat{y}_i)^2}{n-2}}$$

$$= \sqrt{\frac{0.0003731}{6-2}}$$

$$= \sqrt{\frac{0.0003731}{4}}$$

$$=0.009658$$

Uncertainty in the slope

$$s_b = \frac{\mathrm{s_{y/x}}}{\sqrt{\sum_{\mathrm{i}}^{\mathrm{n}} \left(\mathrm{x_i} - \bar{\mathrm{x}}\right)^2}}$$

$$= \frac{0.009658}{\sqrt{17.5}}$$

$$= \frac{0.009658}{4.1833}$$

$$=0.002309$$

Uncertainty in the intercept

$$s_a = s_{y/x}\sqrt{\frac{\sum x_i{}^2}{n\sum(x_i-\bar{x})^2}}$$

$$s_a = 0.002309\sqrt{\frac{55}{6(17.5)}}$$

$$= 0.002309\sqrt{0.52381}$$

$$= 0.002309\ (0.72375)$$

$$= 0.001671$$

Regression Uncertainty in Sample analysis: s_{x0}

Unknown sample was analysed three times under the same calibration condition and the absorbance were as follows: 0.309; 0.308 and 0.310 resulted in the average of 0.309 for the sample mean response.

The response of 0.309 absorbance unit is equivalent to 4.83 on the calibration curve.

$$s_{x0} = \frac{s_{y/x}}{b}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum (x_i - \bar{x})^2}}$$

$$= \frac{0.009658}{0.06411}\sqrt{\frac{1}{3} + \frac{1}{6} + \frac{(0.3090 - 0.1583)^2}{(0.06411)^2\,(17.5)}}$$

$$= 0.15064\sqrt{0.5 + \frac{0.0227}{0.0720}}$$

$$= 0.15064\sqrt{0.5 + 0.3153}$$

$$= 0.15064\sqrt{0.8153}$$

$$= 0.15064\ (0.903)$$

$$= 0.1360$$

Repeatability uncertainty/ Uncertainty due to reproducibility (SIP)

2500 mg B/kg CRM was diluted to make about 5.0mg B/kg that means a 500 times dilution was made to prepare the 5.0mg B/kg sample. The diluted CRM was run on UV-VIS on different dates and were as follows:

Reading No	Date ran	Results	Results multiplied by 500 dilution factor
1	2012/03/16	5.03	2515
2	2012/03/12	4.98	2490
3	2012/01/13	5.00	2500
4	2012/03/16	5.01	2505
5	2012/03/03	5.03	2515
6	2012/03/10	4.97	2485
7	2012/03/13	5.02	2510
8	2012/03/15	4.99	2495
9	2012/03/16	5.03	2515
10	2012/03/20	4.98	2490
Average=		5.004	2502
Std dev=		0.023	11.60

Repeatability of the results when dilution factor has been applied was found to be 11.60mg/kg for a 2500 mg B/kg sample.

Total Uncertainty Calculation at 95% confidence level.

$$\frac{\mathrm{U(t)}}{XO}=\sqrt{\left(\frac{u(P)}{P}\right)^2+\left(\frac{U(m)}{m}\right)^2+\left(\frac{U(v1)}{v1}\right)^2+\left(\frac{U(v2)}{v2}\right)^2+\left(\frac{U(Crm)}{Crm}\right)^2+\left(\frac{S(x0)}{xo}\right)^2+\left(\frac{SIP}{S}\right)^2}$$

$$\frac{\mathrm{U(t)}}{XO}=\sqrt{\left(\frac{0.115\%}{100\%}\right)^2+\left(\frac{8.7x10-5g}{5.7193g}\right)^2+\left(\frac{0.011ml}{10\,ml}\right)^2+\left(\frac{0.068\,ml}{100ml}\right)^2+\left(\frac{1.16}{1000}\right)^2+\left(\frac{0.1360}{4.83}\right)^2+\left(\frac{11.60}{2500}\right)^2}$$

$$\frac{\mathrm{U(t)}}{XO}=0.0286$$

$$\therefore \mathrm{U(t)}=0.0286X\ 25OO\ mgB/kg$$

$$=71.5\ mgB/kg$$

$$=72\ mgB/kg$$

The total uncertainty for Boron analysis using the UV spectrophotometer for a 2500 mg B /kg was found to be 72mg B /kg.

Using the analytical Methodology developed and employing ISO guidelines combined relative uncertainty and expanded relative uncertainty (with coverage factor k =2) of measurement were calculated to be 143 mg B /kg.

Therefore when reporting the results in 2500 mg B range using Azomethine H UV method.
We accept 2500mgB/kg ± 143mg B/kg
2500± 5.72

3.2.5 Accuracy calculation for UV technique

Calculation for determination of accuracy of the method using a prepared 2500 mgB/kg standard:

$$\%\ \mathrm{Accuracy}=\frac{2500mg/Bkg-2502mgB/kg}{2500}\ X\ 100$$

$$=\frac{2\ mgB/kg}{2500}X\ 100$$

$$=0.0008X\ 100$$

$$=0.08\%$$

3.2.6 Precision calculation for UV technique

$$\% \text{ Precision} = \frac{11.60\ mg\ B/kg}{2502\ mgB/kg} x\ 100$$

$$= 0.0046 x\ 100$$

$$= 0.46\%$$

3.2.7 Advantages of UV technique for boron analysis

This method provides linearity up to 5mg B kg within 95% confidence level. This analytical method is suitable for quantification of trace amount of boron in water. The proposed analytical method demonstrates good sensitivity, accuracy and highly selective for determination of boron in aqueous solution in the low levels.

Due to the buffer solution that is added in the analyses process, interferences are minimised.

3.2.8 Disadvantages of UV technique

The UV method for analysis of boron is not suitable for use when determining high boron concentration range of Pressurised Water Reactor. In the PWR, laboratories are interested in analysing samples with boron that are within the 5-8000 mg B/kg. This method requires dilution of samples and large dilution will create too much experimental error. The time it takes to analyse samples is approximately fifty minutes, this is not acceptable as at times the lab requires sample results within five minutes when there is dilution to criticality.

3.3 Atomic Absorption Spectrometry

3.3.1 Atomic Absorption Spectrometry (flame) principle

The instrument employs a double beam technique where the emitted radiation from the light source of hollow cathode lamps of elements of interest is split into two beams, a reference beam and a sample beam. Sample beam travels through the flame while reference beam travels around the flame.

The liquid sample is reduced to a vapour mist of atomic population by a nebuliser with support gas. Mixed with proper fuel, it is sprayed over the flame. The reference beam going around the flame is not affected because the energy of sample beam going through the flame is absorbed by the sample element present in the liquid sample and amount of absorption being proportional to the element concentration. Both these beams are combined together before entering the monochromatic region which selects the appropriate resonance line and direct it to the wide range photo multiplier tube. The electronics there after separates reference and sample signal in time reference single is used to compensate for drift in lamp intensities and sample signal is processed for photometric computation of the result [33].

When a liquid sample containing a chemical constituent element of interest is reduced to a spray mist of atomic vapour, mixed with proper fuel and burned over a burner head and if light radiation of the same element from an emitting source is passed through the flame, as atoms of the element in the sample vapour are present in ground state of unexcited condition they absorb an amount of corresponding radiation passing through the flame. The amounts of absorption by the analyte depend on its concentration in the sample and are directly proportional to each other. Hence measurement of absorption value forms the base for calculation of its concentration in the sample [31].

Every time when an element is estimated, the system is calibrated by aspirating a set of different strength standard solution of known concentration of the element and graphical representation of absorbance verses concentration is made to get a calibration curve for the standard solution. When a unknown sample is aspirated in the same condition, with reference to its measured absorbance and the standard curve concentration of the element in the test sample is displayed in part per million (mg/kg).

3.3.2 Atomic Absorption Spectrometry Flame interferences

Non-spectral interferences

Matrix interference

Most waste system samples containing boron become viscous and have more surface tension than the standards and those results in differences in sample uptake rate due to changes in nebulization. This is called matrix effect. The matirix effect is minimized by matching as closely as possible the matrix composition of standard and sample.

Chemical interference

Some boron containing samples contain species which forms a thermally stable compound with the analyte that is not completely decomposed by the energy available in the flame then chemical interference exists. Refractory elements such as Ti, W, Zr, Mo and Al in the sample may combine with oxygen to form thermally stable oxides. Analysis of such elements can be carried out at higher flame temperatures using nitrous oxide – acetylene flame instead of air-acetylene to provide higher dissociation energy.

Ionisation interference

Ionisation interference is more common in hot flames. The dissociation process does not stop at formation of ground state atoms. Excess energy of the flame can lead to excitation of ground state atoms to ionic state by loss of electrons thereby resulting in depletion of ground state atoms. In cooler flames such interference is encountered with easily ionized elements such as alkali metals and alkaline earths. Ionisation interference is eliminated by adding an excess of an element which is easily ionised thereby creating a large number of free electrons in the flame and suppressing ionisation of the analyte. Salts of such elements as K, Rb and Cs are commonly used as ionization suppressants.

Spectral Interferences

Spectral interferences are caused by the presence of another atomic absorption line or a molecular absorbance band close to the spectral line of the element of interest. Most common spectral interferences are due to molecular emissions from oxides of other elements in the sample. The main cause of background absorption is presence of undissociated molecules of matrix that have broad band absorption spectra and tiny solid particles, unvaporized solvent droplets or molecular species in the flame which may scatter light over a wide wavelength region. When this type of non-specific adsorption overlaps the atomic absorption of the analyte, background absorption occurs. The problem is overcome by measuring and subtracting the background absorption from the total measured absorption to determine the true atomic absorption.

3.3.3 Optimisation of Atomic Absorption Spectrometry flame method

Instrument optimisation

Boron analysis by AA involves a lot of the components that need to be optimised.

The lamp, Burner head and the Nebuliser. The lamp requires pre warm up for 15 minutes before commencing with the analysis.

Burner height requires adjustment to the certain length to get the optimum results.

Nebuliser spray requires adjustment in order to produce the required amount of a sample that is needed for analysis. All analysts who work on the AA were trained and competent to perform the adjustments.

Reagents Optimisation

All Standards and reagents used in the laboratory are of good quality. Reagents and standards selected and prepared in accordance with KWC-003 (preparation of analytical Chemistry reagents). All the analysts use the same procedure to prepare boron reagents. There have been no significant changes in the results. CRMs are also available to be checked against the in-house prepared standards.

3.3.4 Uncertainty calculations for AA flame technique

Uncertainty measurements when using AA may be affected by the following qualitative factors:

- Knowledge of the Operator
- Experience of the Operator
- Training of the Operator
- Skill of the Operator

If the operator lacks any of the above mentioned attributes when performing AA work this may affect the results. The chemical analysts who are employed at Koeberg, they all have the minimum requirements on the attributes stated above.

Uncertainty measurements when using AA may be affected by the following quantitative factors:

- Purity of the salt used for preparation of standards
- The mass weighed when preparing the stock
- Volume made Uncertainty dilution of the samples
- Certified Reference Material (CRM)
- Regression uncertainty s_{x0}:
- Repeatability (real sample analysed 3 x)

Total Uncertainty

Purity of the salt boric acid used to prepare boron calibration standards

Certificate of analysis states that Purity = 100 ± 0.2%

No purity distribution is given

We assume a rectangle distribution with coverage factor = $\sqrt{3}$

U (P) = $\frac{0.2}{\sqrt{3}}$ = 0.115

Mass uncertainty

Assume mass weighed;

Balance calibration certificate:

Balance linearity = $1.5\text{x}10^{-4}$

We assume a rectangle distribution with coverage factor = $\sqrt{3}$

U (m) = $\frac{1.5\text{x}10{-4}}{\sqrt{3}}$g = $8.7\text{x}10^{-5}$ g

Volume uncertainty:

The masses of the 10 mL water were weighed to determine the deviation that is found in volume delivery when pipetting the solution using a 10 mL pipette.

See appendix 2 for volume checks results.

V_1 = Uncertainty pipette:

Std dev. = 0. 0062

$\bar{x}$ = 9.9384

See appendix 1B for volume checks results.

Manufacturer specification:

V_2 = Manufactured $\frac{\mathbf{0.02}}{\sqrt{\mathbf{6}}}$ = 0.00816mL

Laboratory conditions that affects the volume:

$$V_3 = \frac{2\text{x}2\text{x}10^{-9}}{\sqrt{3}} \text{x } 10 \text{ mL}$$

$$= 0.0024 \text{ mL}$$

Volume Uncertainty of filling the 100 mL volumetric flask

Total volume uncertainty of a 10 mL pipette.

$$UV_{10mL} = \sqrt{(0.0062)^2 + (0.00816)^2 (0.0024)^2}$$

$$= \sqrt{0.000110785}$$

$$= 0.011 \text{ mL}$$

Uncertainty due to standard preparation volume

Manufacturer: States that 100.0 mL ± 0.1 mL at 20 ^{0}C

For three volumetric flasks the mass of the volumes of water at 20^{0}C were measured and the defences was recorded 1 g = 1mL

$V_{1\,=}$ 0.0408 mL

$V_{2\,=}$ 0.020 mL

$V_{3=}$ 0.050mL

$$\mathbf{U\ (V)}_{\mathbf{100\ mL}} = \sqrt{(0.0408)^2 + (0.020)^2 (0.05)^2}$$

$$= \sqrt{0.00456464}$$

$$= 0.068 \text{ mL for 100 mL}$$

Uncertainty due to CRM

Uncertainty due to mass of the salt used to prepare calibration standard Original mass used to prepare 1000 mg/kg calibration standard

Uncertainty due to reproducibility

2500 mg B/kg QC was diluted to make about 250mg B/kg. The analyst was tasked to perform boron analysis over a large time scale. The 2500 standard was diluted and analysed on the AA on different dates and the results were as follows.

Reading No	Date ran	Results Readings from the Instrument in mg B/kg	Calculated Results = Direct readings multiplied by 10 times dilution factor in mg B /kg
1	2012/12/16	249.9	2499
2	2013/01/12	248.9	2489
3	2013/01/13	250.3	2503
4	2013/01/16	250.2	2502
5	2013/02/03	249.7	2497
6	2013/02/10	250.5	2505
7	2013/02/13	248.9	2489
8	2013/02/15	250.0	2500
9	2013/02/16	251.3	2513
10	2013/02/20	252.8	2528
Average=		250.3	2503
Std dev=		1.145	11.45

Calibration uncertainty

The following table represents the concentration of standard used for calibration and its absorbance.

Concentration(x) In mg B/kg	Absorbance(y)
0	0.00
20	0.008
100	0.032
200	0.064
250	0.079
500	0.15

Sum of x_i =$\sum x_1 + x_2 + x_3 \ldots x_n$

Average of $\bar{x}$ = $\frac{\sum x_1 + x_2 + x_3 \ldots x_n}{n}$

Standard deviation of x_i/Degree of spread= s=$\sqrt{\frac{\sum(x_i-\bar{x})^2}{n-1}}$

x_i	y_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$	$(y_i - \bar{y})$	$(y_i - \bar{y})^2$	$(x_i - \bar{x})(y_i - \bar{y})$
0	0	-178.33	31802,78	-0,0555	0,0030803	9,8975
20	0,008	-158.33	25069,44	-0,0475	0,0022563	7,520833333
100	0,032	-78.33	6136,111	-0,0235	0,0005523	1,840833333
200	0,064	21.67	469,4444	0,0085	7,225E-05	0,184166667
250	0,079	71.67	5136,111	0,0235	0,0005523	1,684166667
500	0,15	321.67	103469,4	0,0945	0.0089303	30,3975
$\sum$ =1070	0,333	0	172083,3	0	0.0154435	51,525
Mean= 178.33	0,0555					

Evaluation of the calibration curve

Is the calibration plot linear? We assume that the plot is a straight line and takes the algebraic form of:

Y=bx + a

In order to estimate how well the calibration standard fit the straight line, we calculate the correlation coefficient, r.

The value of r is given by:

$$r = \frac{(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{(x_i - \bar{x})^2 \, (y_i - \bar{y})^2}}$$

$$= \frac{51.525}{\sqrt{(172083.3)(0.015444)}}$$

$$= \frac{51.52}{51.552}$$

$$= 0.9994$$

$r^2 = 0.9989$

The slope b is given by:

$$\mathrm{b} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sum(x_i - \bar{x})^2}$$

$$= \frac{51.525}{172083.3}$$

$$= 0.000299$$

For the equation $y = bx + a$ we need to know the value of a .

At the centroid we can calculate the intercept

$$\bar{y} = b\bar{x} + a$$

$$\therefore 0.0555 = (000299)178.33 + a$$

$$\therefore 0.0555 = 0.0534 + a$$

$$\therefore a = 0.0555 - 0.0534$$

$$\therefore a = 0.002104$$

Since we have got the values of the slope (b) and the intercept (a) the ŷ residuals may be calculated by substituting from the equation; y=bx +c

y_i is an observed result and $\widehat{y_i}$ is a predicted value. The difference between the observed and predicted values is called residuals and is presented as follows: Y residuals = $y_i - \widehat{y_i}$

x_i	${x_i}^2$	y_i	$\hat{y}_i$	$\lvert y_i - \hat{y}_i \rvert$	$(y_i - \hat{y}_i)^2$
0	0	0	0.002104	0.0021	4.427E-06
20	400	0.008	0.008084	8.4E-05	7.056E-09
100	10000	0.032	0.032004	4E-06	1.6E-11
200	40000	0.064	0.061904	0.002096	4.393E-06
250	62500	0.079	0.076854	0.002146	4.605E-06
500	250000	0.15	0.151604	0.0016	2.573E-06
$\sum$ =1070	362900				1.601E-05

We can calculate the errors in the intercept and of the regression line, y=bx +c by using the following formulae:

Standard error of regression/ random calibration uncertainty = $s_{y/x}$

$$s_{y/x} = \sqrt{\frac{\sum(y_i - \hat{y}_i)^2}{n-2}}$$

$$= \sqrt{\frac{1.601\text{x}10^{-5}}{6-2}}$$

$$= \sqrt{\frac{1.601\text{x}10^{-5}}{4}}$$

$$= 0.0020$$

Uncertainty in the slope s_b:

$$s_b = \frac{s_{y/x}}{\sqrt{\sum_i^n (x_i - \bar{x})^2}}$$

$$= \frac{0.0020}{\sqrt{172083.3}}$$

$$= \frac{0.0020}{414.83}$$

$$= 4.84 \text{ x} 10^{-6}$$

Uncertainty in the intercept

$$s_a = s_{y/x} \sqrt{\frac{\sum x_i{}^2}{n\sum(x_i - \bar{x})^2}}$$

$$s_a = 0.0020 \sqrt{\frac{362900}{6(172083.3)}}$$

$$= 0.0020\sqrt{0.35147}$$

$$= 0.0020\ (0.592849053)$$

=0.0012

Regression Uncertainty in Sample analysis: s_{x0}

The prepared sample was analysed under the same calibration condition and the absorbance for the sample were as follows: 0.0792; 0.0793 and 0.0793 resulted in the average of 0.0792 for the sample mean response.

$$s_{x0} = \frac{s_{y/x}}{b} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum(x_i - \bar{x})^2}}$$

$$= \frac{0.002}{0.000299} \sqrt{\frac{1}{3} + \frac{1}{6} + \frac{(0.0792 - 0.0555)^2}{0.000299^2\ (172083.3)}}$$

$$= 6.69\sqrt{0.5 + \frac{5.62x10-4}{0.0154}}$$

$$= 6.69\sqrt{0.5 + 0.03647}$$

$$= 6.69\sqrt{0.536}$$

$$= 4.90$$

Total Uncertainty Calculation at 95% confidence level.

$$\frac{\mathrm{U(t)}}{XO}=\sqrt{\left(\frac{u(P)}{P}\right)^2+\left(\frac{U(m)}{m}\right)^2+\left(\frac{U(v1)}{v1}\right)^2+\left(\frac{U(v2)}{v2}\right)^2+\left(\frac{U(Crm)}{Crm}\right)^2+\left(\frac{S(x0)}{xo}\right)^2+\left(\frac{SIP}{S}\right)^2}$$

$$\frac{\mathrm{U(t)}}{XO}=\sqrt{\left(\frac{o.115\%}{100\%}\right)^2+\left(\frac{8.7x10-5g}{5.7193g}\right)^2+\left(\frac{0.011ml}{10\,ml}\right)^2+\left(\frac{0.068\,ml}{100ml}\right)^2+\left(\frac{1.16}{1000}\right)^2+\left(\frac{4.90}{247}\right)^2+\left(\frac{11.45}{2500}\right)^2}$$

$$=\sqrt{\left(\frac{o.115\%}{100\%}\right)^2+\left(\frac{8.7x10-5g}{5.7193g}\right)^2+\left(\frac{0.011ml}{10\,ml}\right)^2+\left(\frac{0.068\,ml}{100ml}\right)^2+\left(\frac{1.16}{1000}\right)^2+\left(\frac{4.90}{247}\right)^2+\left(\frac{11.45}{2500}\right)^2}$$

$$\frac{\mathrm{U(t)}}{XO}=0.02045$$

$$\therefore \mathrm{U(t)}=0.02045X\ 25OO\ mgB/kg$$

$$=51\ \ mgB/kg$$

The total uncertainty for Boron analysis using the AA at 2500 mg B /kg was found to be 51mg B /kg.

Using the analytical Methodology developed and employing ISO guidelines combined relative uncertainty and expanded/extended relative uncertainty (with coverage factor k =2) of measurement were calculated to be 102 mg B /kg.

Therefore, when reporting the results in 2500 mg B using AA method.
We accept 2500mgB/kg ± 102mg B/kg
2500± 4.1%

3.3.5 Accuracy calculations for boron measurements using AA flame

$$\text{Accuracy}=\frac{2500mg/Bkg-2502mgB/kg}{2500}\ X\,100$$

$$=\frac{3\,mgB/kg}{2500}X\,100$$

$$=0.0008X\,100$$

$$=0.12\%$$

3.3.6 Precision calculations for boron measurements using AA flame

$$\text{Precision} = \frac{11.45\ mg\ B/kg}{2503\ mgB/kg} x\ 100$$

$$= 0.0046x\ 100$$

$$= 0.46\%$$

3.3.7 Advantages of using AA for boron analysis.

AA flame is easy to use. Once the method is set up and optimised, the sample analyses time is between 3-10 seconds. With AA flame, samples with wide range of pH and complex matrix can be analysed and the level of precision and accuracy can be determined and accepted.

3.3.8 Disadvantages of AA for boron determination

A significant disadvantage of boron determination by flame is that the efficiency of atomisation may be quite poor leading to poor sensitivity. There are two reasons for poor atomisation efficiency. First, the majority of the aerosol droplets produced during nebulisation is too large to be carried to the flame by the combustion gases. Consequently, as much as 95% of the sample never reaches the flame. A second reason for poor atomisation efficiency is that the large volume of combustion gases significantly dilutes the sample. Together, these contributions to the efficiency of atomisation reduce sensitivity because the analyte’s concentration in the flame may be than that in solution. Continuous aspiration of samples and standards containing a high concentration of boron may build-up a solid deposit on the burner head that obstructs the flame and that lowers the absorbance that could lead to erratic results.For the laboratories to use this technique, it required to have fume extraction and enough space for gases waste etc. The AA flame technique or method may not be left unattended while the sample analysis is in progress because of the fire hazard.

3.4 Determination of isotopic boron by Inductively Coupled Plasma- Mass Spectrometry (ICP-MS)

3.4.1 ICP -MS Principle

The ICP-MS consist of an auto sampler with peristaltic pump to move a sample to a nebuliser, which converts the liquid sample into an aerosol using argon gas stream. The aerosol is passed through a Scott double bypass spray chamber of a borosilicate glass to remove larger aerosol particles and some of the water load as the spray chamber is cooled to 6^0C. Boron contamination from the glass spray chamber seems to be minor when compared to boron contamination in acid blanks. The aerosol then flows into a quartz torch where a radio frequency (RF) field supports argon plasma in which the sample is ionized in a 7500-K plasma and is extracted from the plasma with the use of two cones, a sample and a skimmer cone. The cones feed the sample into a vacuum system and through a lens stack, which focuses the ion beam into the quadrupole mass selector. The quadrupole passes ions of specific charge into an electron multiplier from which the signal is passed to an amplifier, multichannel analyser and finally a computer for storage retrieval and analysis. The sample goes through the following steps before it is introduced into the mass analyser:Nebulisation, Desolvation, Vaporisation, Atomisation, Ionisation as shown on the diagram below.

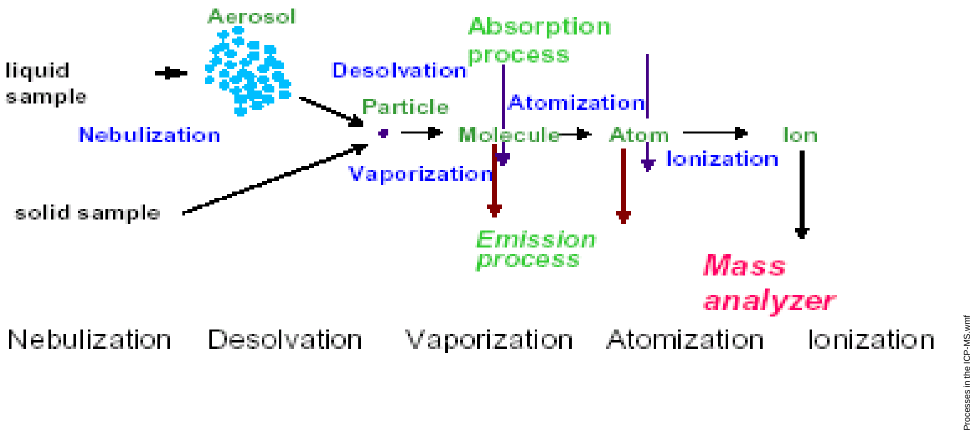


Figure 3.4.1 represention of the processes in the ICP-MS [61]

3.4.2 Interferences associated with isotopic boron analysis by ICP-MS

The sample matrices, memory effects, and some instrument parameters affect the accuracy and precision of B isotope ratio determination if adequate precautions are not taken. New generations of plasma-source MS instruments using high-resolution mass analysers provide better sensitivity and precision than the currently used quadrupole ICP-MS. Because of the convenience and high sample throughput, the high-resolution ICP-MS is expected to be the method of choice for B isotope ratio determination. The current state of instrumental capabilities is adequate for B isotope determination. However, precision and accuracy are primarily limited by sample preparation, introduction, and analytical methodology, including

- Analyte loss and isotope fractionation during sample preparation.
- The precision of B isotope determination in small samples, especially those containing low concentrations.
- Difficult matrices.
- Memory effects and Mass bias

At Koeberg Nuclear Power station, the ICP-MS is also used to determine trace metals in highly borated water. When analysing those highly borated samples high boron content is left on the instrument components and this results in high boron background (memory effect). Memory effects of B that occur during sample determination may cause serious errors in B isotope ratio determination.

Although the utilisation of high-resolution plasma-source MS will undoubtedly improve analytical precision, it is the sample preparation, sample introduction, and analytical methodology that represent the primary limitation to accurate and precise B isotope ratio determination. ICP-MS matrix effects can be classified into two categories spectroscopic interference (matrix induced spectral overlap) and non-spectroscopic interferences(matrix induced signal intensity changes) [69].Spectral interferences occur in isotopic boron analysis. The large $^{12}C^+$ peak from carbon containing impurities in the plasma gas contributes to the intensity of ^{11}B [68]. Non spectroscopic interferences are characterised by reduction or enhancement of analyte signal caused by factors that influence the sample transport, ionisation in the plasma, ion extraction or ion throughput in the resulting beam. The severity of the effects is dependent on the nature and concentration of sample matrix.

Suppression of the analyte signal can also be caused by the deposit of salt on the sampler skimmer cones. This leads to the clogging of orifices which not only reduces the number of ion optics region and the mass spectrometer but also affets the sampling process. This can cause serious drift problems [67]. The two main concerns about isotopic boron analysis by ICP MS are memory effects and mass bias. Boron tends to raise the the background of analytical instruments by adhering to the instrument components thereby affecting subsequent determinations. This phenomenon is called “memory effect” and is a major problem. Mass bias occurs when ions of different masses are transmitted with different efficiencies from the point at which they enter the surface until they are finally detected, this results in a non-uniform sensitivity across the mass the mass range that results into in accurate isotopic boron analysis results.

3.4.3 Optimisation of the ICP-MS for isotopic analysis

The operating experience shared in 1.9.3 resulted in investigative work and optimisation of the boron isotopic measurement process. It was found that the instrument response was at least 10 times lower than it should be for the tuning solution. The tuning file showed counts of 700 cps (counts per second) while the normal counts average 6000 to 10000 cps, for the tuning solution. When the “normal parameters” were adjusted there was no improvement on the sensitivity of the instrument. The detector parameters were then adjusted which led to an immediate increase in the sensitivity of the instrument. The counts for the tuning solution then increased to approximately 7000 cps. The change in instrument settings was not noticed by the Analyst and expected tuning counts range is not mentioned in the procedure.

The quality control check is done by analysing an independently prepared standard (ERM), boric acid water enriched with 22% ^{10}B.This solution appeared to be very stable. An additional QC check for ^{10}B need to be devised with the same matrix and concentration as samples analysed in the lab. Analysing the sample in the same matrix and concentration for QC check will help to minimise the analytical error.

The pre-analysis start-up time changed from 15 minutes to 30 minutes. These eliminated instrument drift. Majority of adjustable parameters were kept constant (at optimum settings). After investigation and interventions, samples analysed produced expected results. ERM was still reading within the acceptable limits.

3.4.4 Uncertainty calculation for isotopic boron analyses using ICP-MS

To assess the final uncertainties of isotopic boron 10 after optimisation of the measurement method, an experimental methodology of estimating the measurement uncertainty has been therefore established.

This method was established on the implementation of a series of measurements on the standard that is used as QC sample analysed on routine basis. The QC standard that was used is a certified reference material that is analysed prior to sample analysis.
The data used was extracted from the LIMS (Laboratory Information Management System).

DATE	B10-ISOTOPE
2015/01/19 15:51	21.95
2015/01/26 09:34	22.03
2015/01/27 09:42	22.03
2015/02/02 14:48	21.98
2015/02/11 16:29	22.04
2015/02/17 15:09	21.93
2015/02/24 16:14	21.93
2015/03/03 11:36	22.00
2015/03/09 15:01	21.95
2015/03/16 16:02	21.98
2015/03/24 12:31	22.04
2015/04/01 08:00	21.99
2015/04/07 11:07	21.97
2015/04/13 15:34	21.98
2015/04/14 09:34	22.02
2015/04/21 11:56	21.95
2015/04/29 11:35	21.99
2015/05/04 14:35	22.03
2015/05/11 11:19	22.03
2015/05/19 11:15	21.95
2015/05/26 09:13	21.98
2015/05/27 11:03	22.05
2015/05/28 14:02	21.95
2015/06/03 08:46	22.01
2015/06/09 08:01	22.06

2015/06/10 15:30	21.96
2015/06/13 13:18	21.96
2015/06/17 09:42	21.98
2015/06/22 16:18	21.94
2015/07/07 10:23	22.01
2015/07/08 12:19	21.97
2015/07/15 11:56	21.99
2015/08/05 13:25	21.98
2015/08/06 13:10	22.00
2015/08/14 12:00	22.08
2015/08/25 12:04	21.97
2015/09/02 10:57	21.98
2015/09/30 07:16	21.99
2015/10/15 16:23	21.98
Average=	21.99
RSD=	0.03677814

Table 3.4.4 Historic results for 22% boron- 10 standard

$$\mathrm{U} = 2\, x\sqrt{U\, precision^2 + Ureference^2} + Bias$$

With U absolute: Expanded absolute uncertainty to k=2

The standard uncertainty U precision and U reference is representative of potential sources of uncertainties due to:

Variability of measurement (RSD) U precision

This is quantified as standard deviation of the isotopic boron 10 analysis from the QC standard.

The Uncertainty on the reference value of the b isotopic boron 10 analysed: U reference.

This standard uncertainty is quantified according to the solution tested, from the certificate provided by manufactures or from the method of preparation of this solution (together with the certificate of chemicals used and the certificates of verification or calibration of the measuring equipment.

The bias is a representative of the trueness of measurements (Difference between the average value of measured total boron and the reference value of the total boron concentration.

$$= 2\ x\sqrt{U\ precision^2 + Ureference^2} + Bias$$

=2 [$\sqrt{0.037^2 + 0.05^2} + 0.01^2$]

= 2 [$\sqrt{0.003869}$ +0001]

=-2 [0.06220+0.0001]

=2 [0.06230]

=0.125

3.4.5 Accuracy calculation for isotopic boron analysis using ICP-MS

A= $\frac{Average-true\ value}{tue\ value}$

= $\frac{21.99-22}{22}\ x\ 100$

=0.05%

3.4.6 Precision calculation for isotopic boron analyses using ICP - MS

Precision= $\frac{RSD}{tue\ value}X100$

= $\frac{0.037}{22}\ x\ 100$

=0.17%

3.4.7 Advantages of using ICP MS for isotopic boron analysis

ICP- Ms has high sensitivity and that makes it suitable and reliable method for isotopic boron analysis. This technique requires a small sample size and provides high sample throughout.

3.4.8 Disadvantages of using ICP MS for isotopic boron analysis

The current state of instrumental capabilities is adequate for B isotope determination. However, precision and accuracy are primarily limited by:

- sample introduction (samples are aspirated manually)
- Analytical methodology (incorrect calibration standard range being used with quality control standards falling out of sample analysis).

Since the ICP- MS at Koeberg is also used for the determination of trace cations in high boric acid samples, the method suffers memory effect of boron.

The ICP MS costly in terms of purchase spares and operation, it has high consumption of career gas argon.

CHAPTER FOUR: DISCUSSION, INTERPRETATION OF RESULTS, RECOMMENDATIONS AND CONCLUSION

4.1 Discussion for boron analysis

Three techniques available for boron analysis and one technique for isotopic boron analysis are available for use at KNPS. These techniques were optimised, calibrated and evaluated for, the range of analysis, precision, accuracy and the level of uncertainty contributed on each. The techniques/ methods were also evaluated for the type of samples that can be analysed on. This was done to find the most appropriate method for different type of samples available for boron analysis.

Titration technique

Titration technique has two methods. The first method is manual titration and the second method is Potentiometric Titration method. The titration technique is known to be used for boron analysis in boric acid samples, thus titration of the boron / mannitol complex. The technique is set up to analyse samples with boric acid only. Should samples contain other salts either than boric acid; the boron concentration result will be incorrect resulting on the wrong results being reported. Mannitol is added to complex boric acid. The solution is then titrated with basic sodium hydroxide to determine boron. Manual titration method was optimised and evaluated. It was suggested that the manual titration be used as a backup method when the automatic titration is not available. The reason for manual titration to be used as a backup method to Potentiometric Titration is that it takes time to analyse the samples and this method is prone to errors. The manual titration method has also been proven to be less precise than the automatic titration when comparing the results in appendix D and appendix I.

Potentiometric Titration

Potentiometric Titration has been used in the past for boron concentration. The reason why this method was chosen to be used in this project is that it produces rapid and reliable results. The accuracy, precision, reproducibility and speed of analysis is satisfactory and acceptable in a Pressurised Water Reactor Plant. The procedure for Potentiometric Titration allows a monthly standardisation of sodium hydroxide solution or once a fresh sodium hydroxide has been prepared.

Optimisation of this method involved replacement of a 10 mL pipette with a 20mL pipette to avoid refilling of 10 mL pipette during the analysis that could cause air bubbles during sample analysis. The 1 L Sodium Hydroxide container was replaced with a 5L container to minimise the frequent sodium hydroxide standardisation. The sample volumes to be used were optimised and tabulated according to the sample boron concentration.

This method requires a pH electrode to be calibrated to enhance the sensitivity of the method then sodium hydroxide to be standardised with a primary standard (Potassium Hydrogen Phthalate). Then the standardised Sodium Hydroxide solution will be used for boron analysis via acid base titration (Boric acid and Sodium hydroxide). Sample analysis involves the addition of mannitol to form a complex with boric acid and weighing of samples prior to boron analysis. This method assumes that the samples to be analysed are at neutral pH with no buffering capacity. This method can be used to analyse boric acid samples within 5 mg B/kg - 8000 mg B/kg. Pressurised Water Reactors system samples are a combination of demineralised and boric acid, which makes it easy to determine boron concentration in most Pressurised Water Reactor Systems water samples using this method. The 2500 mg B/kg standard was prepared and analysed using this method.

Then the results produced after optimisation of the process were used for comparison with other techniques for accuracy precision and Uncertainty of measurement.

The second technique tested was UV Azomethine H method

Two reagents were available to be employed for the spectrophotometric determination of boron at Koeberg Nuclear Power Station. The first being the carminic acid and the second one being the Azomethine 4hydroxy-5 [(2hydroxyphenyl) methylene amino]-2,7napththalene disulphonic acid. The carminic acid method requires use of concentrated sulphuric acid and a lengthy equilibration step. The carminic acid method was not suited for rapid analysis because it contains hazardous chemicals like concentrated sulphuric, for those reasons it was discontinued to be used in this work.

The azomethine H method is the method that was evaluated against other techniques. This method is available and has never been used to report boron results at Koeberg Nuclear Power Station. In an attempt to optimise the process, the use of same volume volumetric flasks and use of auto pipettes for preparation of standards and sample preparation was encouraged. The time intervals of adding reagents was optimised and adhered to. The Azomethine H method calibration range was (0 - 5) mg B/kg any samples with higher than this range need to have a dilution. For sample concentration of higher than this range, dilution of the samples would be required. The dilution of samples to fit within the reporting range could cause too much experimental error. This method would be suitable for laboratories that need to know the boron concentration less than 5mgB/kg. This method can be used at Koeberg Nuclear Power Station for investigation purposes like leak detection.
The 2500mg B/kg standard was prepared, diluted and analysed using this method.
Then the results produced after optimisation of the process were used for comparison with other techniques.

Atomic Absorption Spectrophotometry (Flame)

Atomic Absorption Spectrophotometry (Flame**)** method for boron analysis has been used at Koeberg for analysis of waste treatment boron samples. This method was operated with reducing nitrous oxide-acetylene flame at 249.8 nm and a lamp current of 15 mA. The boron specific lamp required 15 **-** 20 minutes to warm up before stable readings could be achieved. Aspirating high concentration of boron samples and standards caused carbon to build up on the burner head, requiring the head to be cleaned up regularly. The instrument could only be used to report boron results within the measuring range of (20 **-** 500) mg B/kg. For sample concentration of higher than this range, dilution of the samples would be required. The dilution of samples to fit within the reporting range could cause too much experimental error. The instrument was only giving acceptable results when the instrument has shut down during analyses process and between sample analysis and the burner head required cleaning during analysis of two to three samples. With regular clean-up of the burner head, switching off and on of the flame during the analysis, the method produced results with improved accuracy, precision and the acceptable level of uncertainty measurements. The 2500 mg B/kg standard was prepared diluted and analysed using this method.Then the results produced after optimisation of the process were used for comparison with other techniques for accuracy precision and Uncertainty of measurement.

4.2 Presentation of results for boron analysis (Table 4.1)

Three Techniques were optimised and evaluated to determine the level of capability in order to choose the technique that will be best suited for boron analysis in Pressurised Water Reactor water systems. The table below has the results calculated and found on each technique for comparison purposes. The table 4.1 below presents 10 results produced by each technique or method to evaluate and compare accuracy and precision.

In the Potentiometric titration method, there was no dilution but a specific mass of sample was weighed. For UV-Vis and AA samples standard dilution had to be performed to fit in the calibration curves obtained.

Sample	**Potentiometric Titration**	**UV-VIS**	**AAs**
1	2501	2515	2499
2	2504	2490	2489
3	2504	2500	2503
4	2508	2505	2502
5	2503	2515	2497
6	2503	2485	2505
7	2505	2510	2489
8	2505	2495	2500
9	2507	2515	2513
10	2505	2490	2528
Mean=	2505	2502	2503
Std dev=	2	11	11

Table 4.1: Table of results for analysis of 2500mgB/kg standard.

	Potentiometric Titration	UV Azomethine H	AA Flame
Accuracy	0.2mgB/kg	0.08 mg B/kg	0.12 mg B/kg
Precision	0.08 mg B/kg	0.44 mg B/kg	0.44 mg B/kg
Range	5-8000 mg B/kg	0 - 10 mg B/kg	0 - 500 mg B/kg
Uncertainty	2500mgB/kg ±16mgB/kg	2500 mg B/kg ±72 mg B/kg	2500 mg B/kg ± 51 mg B/kg

Table 4.2 of calculated technical data for techniques/methods tested.

4.3 Interpretation of results for boron analysis

Accuracy of the results produced by three techniques (Table 4.2)

The three techniques were evaluated for accuracy of measurement. The approach used was that a known boron standard of 2500 mg B/kg was analysed and the percentage difference in results were calculated and presented. The results for Potentiometric Titration, UV-VIS and AA were 0.2 mg B/kg, 0.08 mg B/kg and 0.12 mg B/kg respectively. According to the accuracy criterion set by the NWT PWR/Q-Chem which is INPO's 95% confidence level for boron concentration analysis of ± 1% [70]. The results produced by three methods are well within the acceptable limits.

Precision of the results produced by three techniques

The three techniques were evaluated for precision of measurement. The approach used was that a known boron standard of 2500 mg B/kg was analysed and the spread within the results of different instrument was calculated and presented. The results for Potentiometric Titration, UV-VIS and AA were 0.08 mg B/kg, 0.46 mg B/kg and 0.46 mg B/kg respectively.
From the precision results obtained, it is evident that the Potentiometric Titration method is more precise than the UV-VIS and AAs.

Range of analysis

The three techniques were evaluated for the range of analysis. The criterion used to identify the range of measurement was the supplier recommendation and calibration curve range applied on each method. For Potentiometric titration, the instrument supplier quoted on the instrument document that the low level of analyses was that the instrument can quantify is 5mgB/kg and the high level can be determined to up to 8000mgB/kg. For Atomic Absorption Spectrophotometry the calibration was done from 0-500 mg B/kg and for UV VIS the supplier recommended measurement range of 0-10mgB/kg. Potentiometric Titration method has a wide range of analyses; this is an advantage over other analysis methods for boric acid analysis.

Uncertainty of analysis

The sources of uncertainty identified in the cause-and effect diagrams were calculated and the values of the magnitude of uncertainty components were obtained.

The tables on Appendix L show the uncertainty values calculated for each technique. These tables show which sources are the main contributors to uncertainty for each technique before the sum of square root has been applied on uncertainty calculations.Table 4.2 shows the uncertainties of measurement for three techniques tested. The uncertainty estimations for Potentiometric Titration, Atomic Absorption Spectrophotometry (Flame) and UV-VIS Azomethine-H method were determined and were 2500 mg B/kg±16 mg B/kg, 2500 mg B/kg±51 mg B/kg and 2500 mg B/kg±72 mg B/kg respectively (at a 95% confidence level).

For Potentiometric titration, the main contributor to uncertainty was purity of the salt. For AA and UV-VIS it was the calibration curve. The Potentiometric Titration method had lower uncertainty of measurement than the UV-VIS method or the AAs. Since all known uncertainty sources were taken into account for all the methods and Potentiometric Titration had very low uncertainty. The Potentiometric titration method will be preferred over the UV-VIS and AA method.

4.4 Conclusion for boron analysis

The Objective of this study was to optimise the currently employed methods /techniques for boron analysis available at Koeberg Power Station and to determine which method/ technique is more applicable and appropriate for producing precise and accurate results with minimum measurement of uncertainty for use in Pressurised Water Reactor Plants for boron analysis. The methods for boron analysis have been optimised and evaluated for the measurement uncertainty, accuracy and precision. The accuracy and precision criterion set by the NWT PWR/Q-Chem which is INPO's 95% confidence level for boron concentration analysis is ± 1% [70]. This criterion is set for all PWR laboratories performing boron analysis. The methods/techniques were assessed based on this the INPO's 95% confidence level for boron analysis. The three techniques were assessed and found to be well within the acceptance level for accuracy and precision. Of the three methods tested, the Potentiometric Titration method was found to be more applicable and more appropriate to be used by Pressurised Water Reactor Water plants than the other two methods because it has been scientifically proven using the uncertainty of measurements test that, it has the lowest level of uncertainty. With Reactor coolant system boron dynamic concentration, Potentiometric titration is still a preferred method in terms of speed, reliability and range of measurements. This method can be used to analyse one sample within three minutes after being sampled, and can analyse a range 5-8000mgB/kg for a month without requiring recalibration. Other reasons why this method is preferred is that instrument setup and operation is simple and sample preparation and analysis time is minimal.

4.5 Recommendations for boron analysis

For boron analysis, since three methods meet the INPO's criteria of accuracy and precision, it is therefore recommended that Potentiometric Titration be used as a primary method for boron in PWR power plants. The AA flame method is recommended to be used for waste treatment samples with complex matrix. The UV azomethine-H method can be used to determine trace boron concentration when investigating the leaks in primary system water.

It is recommended that further investigation for the determination of the measurement of uncertainty, accuracy and precision be carried out in the range of 7000mgB/kg -8000 mg B/kg for the laboratory to be able to have confidence in reporting the results at this high range.

It is also recommended that the results produced in this work be documented and archived as part of laboratory's quality control that can be also be used by customers who have best interest at heart for boron analysis results.

4.6 Isotopic boron (^{10}B) analysis Discussion

Determination of isotopic boron at Koeberg Nuclear Power Station is achieved by the use of Inductively Coupled Plasma (ICP- MS). This is the only technique that is available for isotopic boron (^{10}B) analysis at Koreberg Nuclear Power Station. According to the literature reviewed, there are other techniques / instruments that can be used for isotopic boron analysis. The process involved determination in isotopic boron (^{10}B) was optimised and evaluated for measurement uncertainty, accuracy and precision. The results showed that uncertainty of measurement = 22% ± 0.125%, accuracy 22%± 0.05 and precision 22% ±0.17. The results obtained show that the method used for isotopic boron 10 analyses is acceptable and the results obtained are reliable.

4.7 Isotopic boron (^{10}B) analysis Conclusion

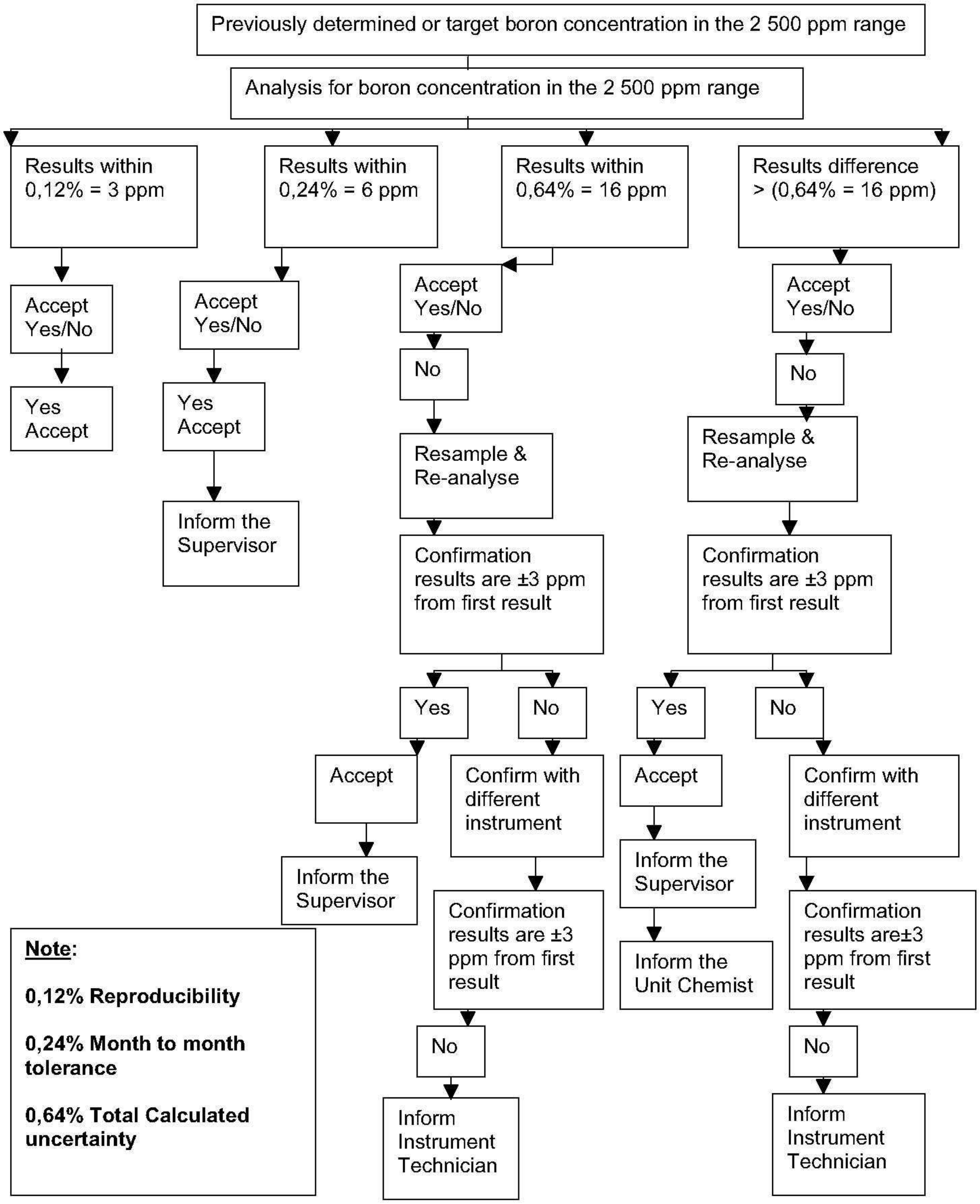
The method used for isotopic boron (^{10}B) analysis used at Koeberg Power Station has been developed optimised and evaluated. The uncertainty of measurement, accuracy and precision has been determined and according to the INPO’s 95% criteria of acceptance these results are within the acceptable limits.

4.8 Isotopic boron (^{10}B) analysis Recommendations

Although the current state of instrumental capabilities is adequate for ^{10}B isotope determination, further work of optimising the methodology for even better results is recommended. Since the ^{10}B depletes gradually with the use of boron through the cycle, lower than 20% calibration standards and quality control standard are necessary to be used to ensure more reliable results.

APPENDIX

Appendix A: Criteria of reporting boron results in 2500 range



Note:

0,12% Reproducibility

0,24% Month to month tolerance

0,64% Total Calculated uncertainty

Appendix B: Zinc Acetate investigation report

Zinc Boron effect: analysis using Potentiometric Titration method

Introduction:

Koeberg Nuclear Power station is about to inject zinc acetate on both reactors for dose reduction purposes. Analytical laboratory need to establish before commencing with this project that the methods used are not affected or the extent to which they are affected is known in advance.

Objective:

To provide a report on the boron analysis method (alkali metric titration method), when analysing boron samples with added different concentrations of zinc acetate.

Experimental:

Reagents:

7000 mg B/kg stock standard was prepared from boric acid salt

1000 mg Zn/kg stock was prepared from zinc acetate salt

1000 µg Zn/kg intermediate was prepared from the1000 µg Zn/kg stock

Milli Q water

Instruments and Equipment used:

Balance

100mL poly bottles

Eppendorf transfer pipettes

Sample preparation:

The samples with 500 mg B / kg and different concentration of zinc were prepared by tarring a 100 mL poly bottle, added 7.143 g of 7000 mg B / kg and addition of a required mass of 1000 µg Zn / kg to prepare different concentrations of zinc concentrations.

The samples with 1000 mg B / kg and different concentration of zinc were prepared by tarring a 100 mL poly bottle, added 14.29 g of 7000 mg B / kg and addition of a required mass of 1000 µg Zn / kg to prepare different concentrations of zinc concentrations.

The sample with 100 mg B / kg and 100 µg Zn / kg was prepared by tarring a 100 mL poly bottle, added 1.43 g of 7000 mg B / kg and addition of a 10 g of 1000 µg Zn / kg to prepare 100 concentrations of zinc concentrations.

Effect of zinc acetate on boron analysis using Potentiometric Titration method (continues)

The sample with 100 mg B / kg and 3 mg Zn / kg was prepared by tarring a 100 mL poly bottle, added 1.43 g of 7000 mg B/ kg and addition of a 0.3 g of 1000 mg Zn / kg to prepare 3 mg Zn / kg concentration of zinc concentrations.

METTLER T50 was used to determine the boron concentration in accordance with KWC-AC-ANA-025 (more equipment instruments and reagents are mentioned on the procedure)

Table of Results

Original Prepared in mg B / kg	Prepared zinc in µg Zn / kg	Boron analysis results before addition of zinc	Boron analysis results after addition of zinc
500	5	500	498
500	10	500	498
500	20	500	501
500	30	501	500
500	50	500	502
500	100	499	499
500	1000	500	499
500	3000	500	501
1000	1000	1001	1000
1000	3000	1003	1000

Testing for statistical significance using only boron standards with different concentration of Zinc

Original Prepared in mg B / kg	Prepared zinc in µg Zn / kg	Boron analysis results before addition of zinc	Boron analysis results after addition of zinc
500	5	500	498
500	10	500	498
500	20	500	501
500	30	501	500
500	50	500	502
500	100	499	499
500	1000	500	499
500	3000	500	501
Average		500	500

Number of clean B sample analysed: n=8 on T50

Mean /Average results: $\overline{x}B$ = 500

Standard deviation: s = 0.53

To verify that there is significant difference in results

Number of Zn/ B sample analysed: n = 8 on T50

Mean /Average results: $\overline{x}$ Zn B = 499.8

Standard deviation: s = 1.5

To verify that there is significant difference in results

The hypothesis are : H_0 $\overline{x}B = \overline{x}$ Zn B

H_1 $\overline{x}B \neq$ Zn B

The t-test must be performed to verify.

$$T_{calc} = \frac{/\,\overline{x} - \mu\,/}{\frac{s}{\sqrt{8}}}$$

$$= \frac{/499.8 - 500\,/}{\frac{1.5}{\sqrt{8}}}$$

$$= \frac{0.2}{\mathbf{0.53}}$$

= 0.38

$T_{critical}$ for df = n-1 = 8 - 1 = 7 at 95 % confidence, the t value is=2.36

$T_{calc} < T_{critical}$, so we accept $H_0 : \overline{x}B = \overline{x}$ Zn B

Conclusion

From the experimental results obtained after addition of different zinc acetate standards in known concentration of boron samples, it is evident that there is no effect of zinc acetate on the determination of boron by alkali metric method.

Appendix C: Samples bottles and laboratory ware preparation for boron analysis boron analysis.

Sample bottle preparation for boron analysis

- 250 mL plastic bottles were used to take the samples.
- Bottles were soaked with nitric acid for 24 hours and thoroughly rinsed with demineralised water before use.
- Samples were collected in duplicate for confirmation purposes.
- Bottles were filled to just overflow.
- There were no air bubbles in the bottle when sealed.

Laboratory ware preparation for boron analysis

- 1000 mL, 250 mL or 100 mL volumetric flasks were used to prepare standards Volumetric flasks were soaked with nitric acid for twenty four hours and thoroughly rinsed with demineralised water.
- 5 mL and 1 mL auto pipettes are used to transfer volumes of solution needed
- 10 mL glass pipette is soaked in nitric acid and rinsed with water before use.

Appendix D: Boron determination by manual titration

Reagents used

Demineralised water (Milli -Q)

Sodium hydroxide (NaOH) 0.1 M

Potassium hydrogen phthalate ($C_8H_5KO_4$) 1%; 0.1 M

Boron (B) salt that is used to prepare control solutions (10 – 7000) mg B / kg

Mannitol ($C_6H_{14}O_6$)

Phenolphthalein indicator

Apparatus

METTLER balance AB 204-S FACT

25 mL “A” grade burette

10 mL “A” grade pipette

5 mL Eppendorf pipette

100 mL Erlenmeyer flask

Instructions for Manual Titration

Standardisation of NaOH Solution (0.1 M)

NOTE: Standardisation is performed in triplicate.

- Transfer accurately (by means of a volumetric pipette) 10 mL of 0.1 M PHP solution into a titration vessel.
- Add 3 to 5 drops of phenolphthalein indicator.
- Titrate against the 0.1 M NaOH solution to be standardised to the end point (which is pale pink in colour).
- Calculation of NaOH concentration:

$$C_{(NaOH)} = \frac{C_{(PHP)} \times V_{(PHP)}}{V_{(NaOH)}}$$

Where:

$C_{(NaOH)}$: Concentration of NaOH in mol/ℓ or M

$V_{(NaOH)}$: Volume of NaOH used in mL

$V_{(PHP)}$: Volume of PHP in mL

$C_{(PHP)}$: Concentration of PHP in mol/l or M

Analysis of Boron Samples

- Transfer a suitable amount of sample solution into the titration vessel (see Appendix1).
- Note the weight of the sample to 4 decimals (n.nnnn g).
- Add 2.5 g – 3.0 g mannitol.

NOTE: Make sure that the mannitol dissolves completely. (Dilute to approximately 60 mL with demineralised water to facilitate the dissolving of the mannitol.)

- Add 3 – 5 drops phenolphthalein indicator
- Titrate against standardised 0.1 M NaOH solution to the end point (which is pale pink in colour).
- Record the volume of the NaOH solution used.

Calculation of Boron concentration:

$$\text{mg B/kg} = \frac{V_{(NaOH)} \times C_{(NaOH)} \times 10{,}811 \times 1000}{W_{(Sample)}}$$

Where:

$V_{(NaOH)}$: Volume of NaOH used in mL

$C_{(NaOH)}$: Concentration of NaOH mol/l or M

$W_{(sample)}$: Mass of sample (n,nnnn g)

***NOTE:** Perform the sample analysis in duplicate and report the mean boron results.*

Results of 2500 mg B /kg Standard analysed using Manual titration method

		Mass in g	Volume mL	Conc mgB/kg
	1	*4.0755*	*9.42*	*2506*
	2	*4.0876*	*9.5*	*2520*
	3	*4.0104*	*9.22*	*2493*
	4	*4.0195*	*9.26*	*2498*
	5	*4.0203*	*9.25*	*2494*
	6	*4.0541*	*9.37*	*2507*
	7	*4.0103*	*9.23*	*2496*
	8	*4.0303*	*9.3*	*2502*
	9	*4.0511*	*9.31*	*2492*
	10	*4.0412*	*9.35*	*2508*
Mean				*2502*
std dev				*8.8*

Appendix E: Basic parts of the auto-titrator and their uses and explanations

The Autotitrator consists of the following:
A control unit consisting of a calibrated potentiometer, an amplifier and a circuit.
Delivery unit which comprises a burette and a solenoid valve
An electrode assembly, which includes an indicator and reference electrode.

Operation of a control unit:

The titration proceeds at a fast rate until a predetermined distance from the end point when the anticipation control automatically slows the delivery of a titrant. At the end point the delivery is stopped. The anticipation control is the key to highly precise automatic operation. It is set to anticipate the end point (pre-set on METTLER Autotitrator) by a chosen number of pH units.
Controlling the rate of reagent delivery has two advantages:

- Prevents overstepping the **pre-set endpoint**.
- Permits a **rapid delivery of titrant** during the initial stages of the titration.

Operation of the delivery unit:

In the delivery unit with no current passing through the solenoid, a short length of flexible tubing (burette) is squeezed shut. When the solenoid is energized, the pressure on the tubing is released and the titrant is allowed to flow through the delivery tip.

The electrode assembly:
The electrode assembly consists of an indicator (usually glass electrode) and a reference electrode. To ensure a rapid signal the delivery unit is placed close to the indicating electrode and in front, with respect to the direction of stirring, so that the indicating electrode is bathed by solution at a more advanced stage of titration.

The **analytical balance** (used to record the weight of the sample) and **the printer** (to print out the results and calibration results) are directly connected to the Autotitrator. The METTLER Autotitrator is operated by means of a key board. By pressing the number of keypads the METTLER Autotitrator can be manipulated to perform a number of functions.
The procedure for the determination of boron illustrates the basic operating steps when using the key board.

Basic parts of the auto-titrator and their uses and explanations (continues)

The principle of operation of METTLER Autotitrator:

The potentiometer is set at predetermined pH or potential which is the end point. The electrode assembly is immersed in the sample solution and the operating switch is depressed. Once switched on the pre-set equivalence point potential is applied across the electrodes by the calibrated potentiometer. If a difference exists between the potential and that of electrodes an error signal results .The signal is the amplified and then closes an electronic switch that permits a flow of electricity through the solenoid operated valve of the burette. As the end point is approached the error signal becomes smaller.

Instrument Calibration:

The most important part of METTLER Autotitrator that needs to be calibrated is the pH glass electrode. The potential of a measuring electrode can always only be given relative to that of a reference electrode. To be able to compare systems, the electrode zero point is defined as being 0 mV for pH = 7 and 298.15 K or 25 ℃. The electrode slope, i.e. the alteration in the measured value with the pH, is given by the Nernst equation and at 25 ℃ is 0.059 V per pH= These are ideal values from which Metro sensor electrodes only differ slightly.

The electrode zero point is ±0.015 V. The electrode zero point and the electrode slope may change as a result of the aging of the glass membrane or contamination of the diaphragm. For this reason, the pH meter must be adapted to the characteristics of the electrode, i.e. calibrated, at regular intervals by using buffer solutions. The electrode zero point is set first (pH = 7 corresponding to 0 mV for Metro sensor pH electrodes). The second and further buffer solutions are used to determine the slope of the pH electrode. This slope is expressed as a percentage of the theoretical value100% = 0.059 V per pH = 1). In order to minimize subsequent measuring errors, care should be taken that the expected measured value of the sample solution always lies within the pH range covered by the buffer solutions.

In the first calibration step with buffer pH = 7 the variation from the electrode zero point (asymmetry potential) is determined and corrected. In the second calibration step with another buffer solution the electrode slope is determined and expressed as a percentage of the theoretical value of 0.059 V (at 25 ℃).

Basic parts of the auto-titrator and their uses and explanations (continues)

Calibration always includes a check of the measuring electrode. The calibration buffers have a medium acid-base concentration and their ionic strength is approximately that of the most common sample solutions. The dependency of the electrode slope on the temperature means that the calibration and measuring temperatures must be known. Information about the electrode condition is provided by the electrode slope, electrode zero point, response time of the signal and its streaming dependency.

Appendix F: Determination of boron by titration (PotentiometerT50 MODEL)

Reagents used

Demineralised water (Milli -Q)

Sodium Hydroxide (NaOH) 0.1 M

Potassium Hydrogen Phthalate ($C_8H_5KO_4$) 1%; 0.1 M

pH buffers 7, 10 for the calibration of pH electrode and 9.18 for Quality control check

Boron (B) salt that is used to prepare control solutions 10 – 7000 mg B/kg

Mannitol ($C_6H_{14}O_6$)

Phenolphthalein indicator (for manual titration only).

Apparatus

METTLER T 50 Auto Titrator

METTLER balance AB 204-S FACT

25 mL “A” grade burette (for manual titration only).

10 mL “A” grade pipette

5 mL Eppendorf pipette

100 mL Erlenmeyer flask (for manual titration only).

Standardisation of the pH Electrode:

- The pH standardisation is done with pH 7 and pH 10 buffer solutions. On the screen touch the icon pH calibration (sensor Cal).
- When the message add sample 1/2 appears, rinse the electrode with the pH buffer solution, then fill 1/3 of a titration cup with the pH 7 buffer solution and secure it to t the titration assembly .
- Press OK.
- When the message add sample 2/2 appears, rinse the electrode with the pH10 buffer solution, then fill 1/3 of a titration cup with the pH 10 buffer solution and secure it to the titration assembly.
- Press OK.
- On completion of the measurement, the results will be printed.

Determination of boron by auto-titrator T50 MODEL(continues)

Standardisation of 0.1 M NaOH Solution with a (1% mass/volume) PHP Solution

NOTE: *Standardisation is performed in triplicate.*

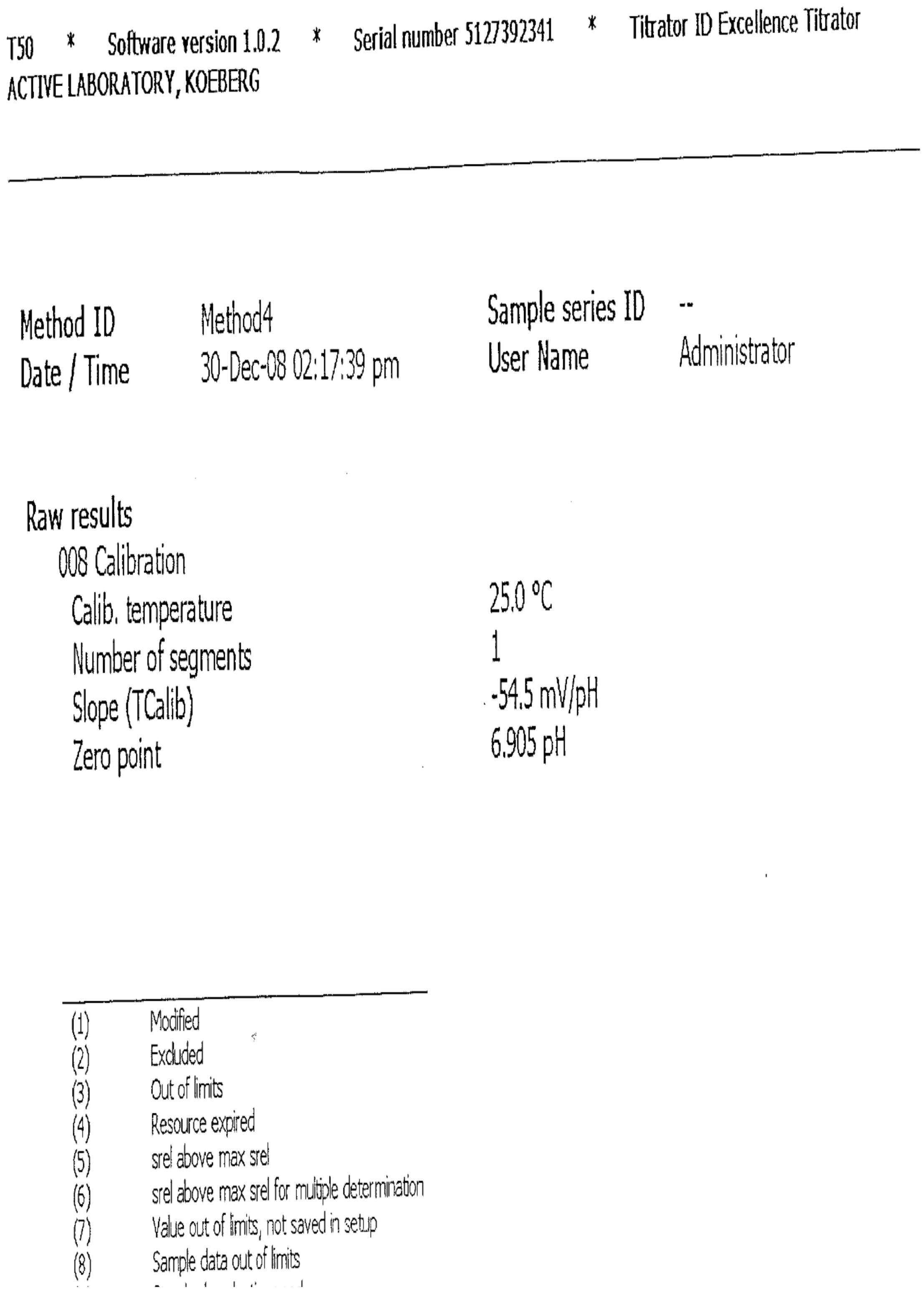
- Flush the burette with NaOH solution after changing the NaOH solution
- On the screen, touch the icon Std 0.1M
- Enter the number of samples to be run (n = 3)
- Press Start
- Pipette 10 mL 1% PHP solution in to a titration cup
- Dilute to approximately 60 mL with Milli-Q water in to the titration cup
- Press Start
- The software will prompt the operator to add the next sample
- On completion of the analysis, the results are printed and the new NaOH concentration is stored

Analysis of Boron Samples
NOTE: *Perform sample analysis in duplicate and report the mean boron results.*

- Touch the icon Method 1 or Method 2. Method 1 for the high range (50-8000) method 2 for low range (50-5) mg B/kg
- Enter the number of samples to be run
- A full sample description can be entered, using the touch screen alphanumeric keypad
- Weigh 2.5 – 3.0 g Mannitol in a titration cup and tare the balance
- Weigh an appropriate mass of sample (see appendix 1 of KWC-AC-ANA-025)
- Accept the sample mass on the touch screen by pressing ACCEPT then OK
- Add demineralised water to the titration cup to approximately 60 mL
- Secure the titration cup to the titration assembly and press OK
- The software will prompt the operator to add the next samples
- On completion of the sequence, the results are printed

Determination of boron by auto-titrator T50 MODEL(continues)

<u>Calibration and sample analysis printouts for Auto titrator T50 model</u>



T50 * Software version 1.0.2 * Serial number 5127392341 * Titrator ID Excellence Titrator
ACTIVE LABORATORY, KOEBERG

Method ID	Method4	Sample series ID	--
Date / Time	30-Dec-08 02:17:39 pm	User Name	Administrator

Raw results

008 Calibration

Calib. temperature	25.0 °C
Number of segments	1
Slope (TCalib)	-54.5 mV/pH
Zero point	6.905 pH

(1)	Modified
(2)	Excluded
(3)	Out of limits
(4)	Resource expired
(5)	srel above max srel
(6)	srel above max srel for multiple determination
(7)	Value out of limits, not saved in setup
(8)	Sample data out of limits

T50 * Software version 1.0.2 * Serial number 5127392341 * Titrator ID Excellence Titrator
ACTIVE LABORATORY, KOEBERG

Method ID	Method3	Sample series ID	--
Date / Time	30-Dec-08 02:22:07 pm	User Name	Administrator

All results

Sample	Sample 1/3
R1 (Titer)	0.97454 mol/L
Sample	Sample 2/3
R1 (Titer)	0.97197 mol/L
Sample	Sample 3/3
R1 (Titer)	0.96991 mol/L

Statistics

R1	Titer
Number of samples	3
Mean value	0.97214 mol/L
s	0.00232 mol/L
srel	0.239 %

---

(1)	Modified
(2)	Excluded
(3)	Out of limits
(4)	Resource expired
(5)	srel above max srel
(6)	srel above max srel for multiple determination
(7)	Value out of limits, not saved in setup
(8)	Sample data out of limits
(9)	Standard evaluation used

```
T50     *     Software version 1.0.2     *     Serial number 5127392341     *     Titrator ID Excellence Titrator
ACTIVE LABORATORY, KOEBERG
-------------------------------------------------------------------------------------------------------------

 Method ID          Method1                        Sample series ID    --
 Date / Time        30-Dec-08 03:30:52 pm          User Name           Administrator

 All results
      Sample                                       FB (Sample 1/5)
        R1 (Content)                               2656 mg/kg
        R2 (Content)                               9.7 mL
      Sample                                  2500 -- (Sample 2/5)
        R1 (Content)                               2503 mg/kg
        R2 (Content)                               9.6 mL
      Sample                                       500 (Sample 3/5)
        R1 (Content)                               499 mg/kg
        R2 (Content)                               9.6 mL
      Sample                                       100 (Sample 4/5)
        R1 (Content)                               101 mg/kg
        R2 (Content)                               5.1 mL
      Sample                                       7000 (Sample 5/5)
        R1 (Content)                               6997 mg/kg
        R2 (Content)                               20.2 mL

 Statistics
      R1                                           Content
        Number of samples                          5
        Mean value                                 2551 mg/kg
        s                                          2738 mg/kg
        srel                                       107.334 %
      R2                                           Content
        Number of samples                          5
        Mean value                                 10.8 mL
        s                                          5.6 mL
        srel                                       51.556 %

      ------------------------------------------------
      (1)          Modified
      (2)          Excluded
      (3)          Out of limits
      (4)          Resource expired
      (5)          srel above max srel
      (6)          srel above max srel for multiple determination
      (7)          Value out of limits, not saved in setup
      (8)          Sample data out of limits
      (9)          Standard evaluation used
```

Appendix G: Determination of boron concentration in water for by UV Methods

Method for determination of boron in water for concentrations less than
5 mg /kg at the wavelength 415nm using Azomethine H reagent**.**

Apparatus

UV-VIS Spectrophotometer Hach DR5000 spectrophotometer
20 mm Cuvettes
50 mL stoppered glass measuring cylinders
100 mL volumetric flasks
Volumetric pipettes
Auto pipette and pipette tips
Plastic beaker and Plastic measuring cylinders

Reagents used

Buffer Masking Solution
Azomethine-H reagent
28% m/v tartaric acid
10 mg B/kg boron standard and 2.5 mg B/kg Control

Determination of Boron (concentration less than 5 mg/kg) in water

Standard solutions containing 0; 1; 2; 3; 4 and 5 mg B / kg were prepared by diluting 10 mg B / kg to 100 mL different volumes of 0; 10; 20; 30; 40 and 50 mL were added into different 100 mL flasks and diluted to the mark

NOTE:

1. Samples with greater than 5 mg B / kg must be diluted appropriately
2. Samples standards and blanks are treated the same in the process

- Using a volumetric pipette, transfer 50 mL of the sample into a 100 mL plastic measuring cylinder
- Use 50 mL of Milli-Q water for the blank
- Choose a suitable time-interval (e.g. 3 minutes for the blank and 1-minute intervals for the samples)

NOTE: *It is important to adhere to the chosen time-interval throughout the rest of the procedure*

Add 4 mL buffer masking solution to each solution

NOTE: *Clean and dry the stirring rod between each use*

- Immediately add 2 mL of Azomethine-H reagent to each solution at the chosen time interval and mix well
- Stir after 15 minutes, at the appropriate time intervals
- Thirty minutes after the addition of the Azomethine-H, at the chosen time interval, add 2 mL of tartaric acid to each solution
- Mix well and allow each solution to stand for exactly 10 minutes
- Zero the spectrophotometer with the blank
- At the appropriate time intervals, measure the absorbance/ concentration of the samples and control against the blank at wavelength of 415 nm
- Analyse according to steps: when using the Hach DR 5000 .

Determination of Boron using: Carminic acid - Sulphuric acid method for boric acid determination in high purity water. 0.2 - 20 mg (H_3BO_3) /kg 600nm. (it does not make sense) [9]

Apparatus

5 mL; 10 mL and 25 mL volumetric pipets

200 mL Beakers 7x

Reagents used

Concentrated Sulphuric acid

Concentrated Hydrochloric acid

Carminic acid- sulphuric acid reagent (0.5g carminic acid powder in 1L sulphuric acid)

100 mg H_3BO_3 / kg boron standard and 10 mg H_3BO_3 / kg Control

Standard solutions containing 0; 5; 10; 15; 20 mg H_3BO_3 / kg were prepared by diluting 100 mg B/kg to 100 mL different volumes of 0; 5; 10; 15; 20 mL were added into different 100 mL flasks and diluted to the mark

Notes

1. The sensitivity of the colour reaction is a function of the total water content of the reaction medium.

2. The accuracy of the standard curves should be checked whenever

It is important that the boron free beakers and 50 mm cells be absolutely dry before they are used. A rinse with acetone followed by air drying is generally satisfactory

The method proceeded as follows

- Pipet 5 mL standard into a dry, boron free beaker
- Add 6 drops of concentrated HCl (Caution acid)
- Pipet 25 mL of concentrated H_2SO_4 (Caution acid) into the beaker in a room temperature water bath for about 3 min
- Pipet 10 mL of the carminic acid - sulphuric acid (Caution acid) - into the beaker, S swirl and let stand at room temperature for 30 min
- After 30 minutes read the absorbance against a reagent blank at 60 nm using 50 mm matched absorption cells.
- The standards were treated the same as samples to produce a calibration curve.

Operation and use of UV HACH DR 5000 Instrument

- Remove the protective cover
- Make sure the instrument is switched on at the power supply.
- Switch on the instrument by pressing the power switch at the back of the instrument.

NOTE: *Do not turn the instrument off and on in rapid succession. Always wait about 20 seconds before turning the instrument on again, otherwise the electronic and mechanical systems will be damaged.*

Each time the instrument is powered up, a series of diagnostic tests are performed automatically to ensure operation of major system components.

This procedure, which takes approximately two minutes, checks the system lamp, filter adjustment, wavelength calibration and voltage. Each test which functions correctly is confirmed with a check mark. The ***Main Menu*** *is displayed when power up diagnostics are completed.*

- On the **Main Menu** select **User Program**
- Select the required **method or parameter**

NOTE: *The screen for the parameter to be analyzed will appear.All corresponding data (wavelength, factors and constants) are already set*

- Press **Start**
- Rinse the required cuvette with Mill-Q Water.
- Rinse the cuvette with the reagent blank to be used and fill the cuvette with reagent blank.
- Wipe the cuvette containing the reagent blank and insert the cuvette into the sample cell holder and press **Zero. (The instrument will be Zeroed)**

- For control or sample, rinse the cuvette with Mill-Q Water, rinse the cuvette with the control or sample to be analysed and fill the cuvette with the control or sample, wipe the cuvette and insert the cuvette with sample or control into the sample cell holder and press **Read**.
- Concentration or results will be displayed on the screen.
- Record the results and remove the cuvette.

Appendix H: Boron determination using AA flame AA(PE 700)

Flame Setup

- Switch the PC on.
- Click on the ***User*** icon to log on to the PC.
- Click on the ***WinLab32 for AA*** icon to open the programme.
- The system will initialise all the installed components.
- If the furnace is installed, do the following:

REMOVE THE AUTOSAMPLER

(1) Loosen the locking nut, located under the sample tray on the lower left hand side, by turning it anti-clockwise, until it is unlocked.

(2) Gently swing the autosampler to the right until it stops.

On the menu bar, click on ***File>Change Technique>>Flame***.

- A pop-up window appears, informing you that the technique will be changed.
- Click on ***Ok***.
- Another pop-up window appears, informing you that the atomiser will be changed and reminding you to move the autosampler.
- Click on ***Ok***.
- The burner moves into position.
- Select a workspace by clicking on ***File>Open>>Workspace***.
- Select a workspace to be used.
- Select the method to be used by clicking on ***File>Open>>Method***.*KWC-AC-ANA-020 Rev 5a Page 7*

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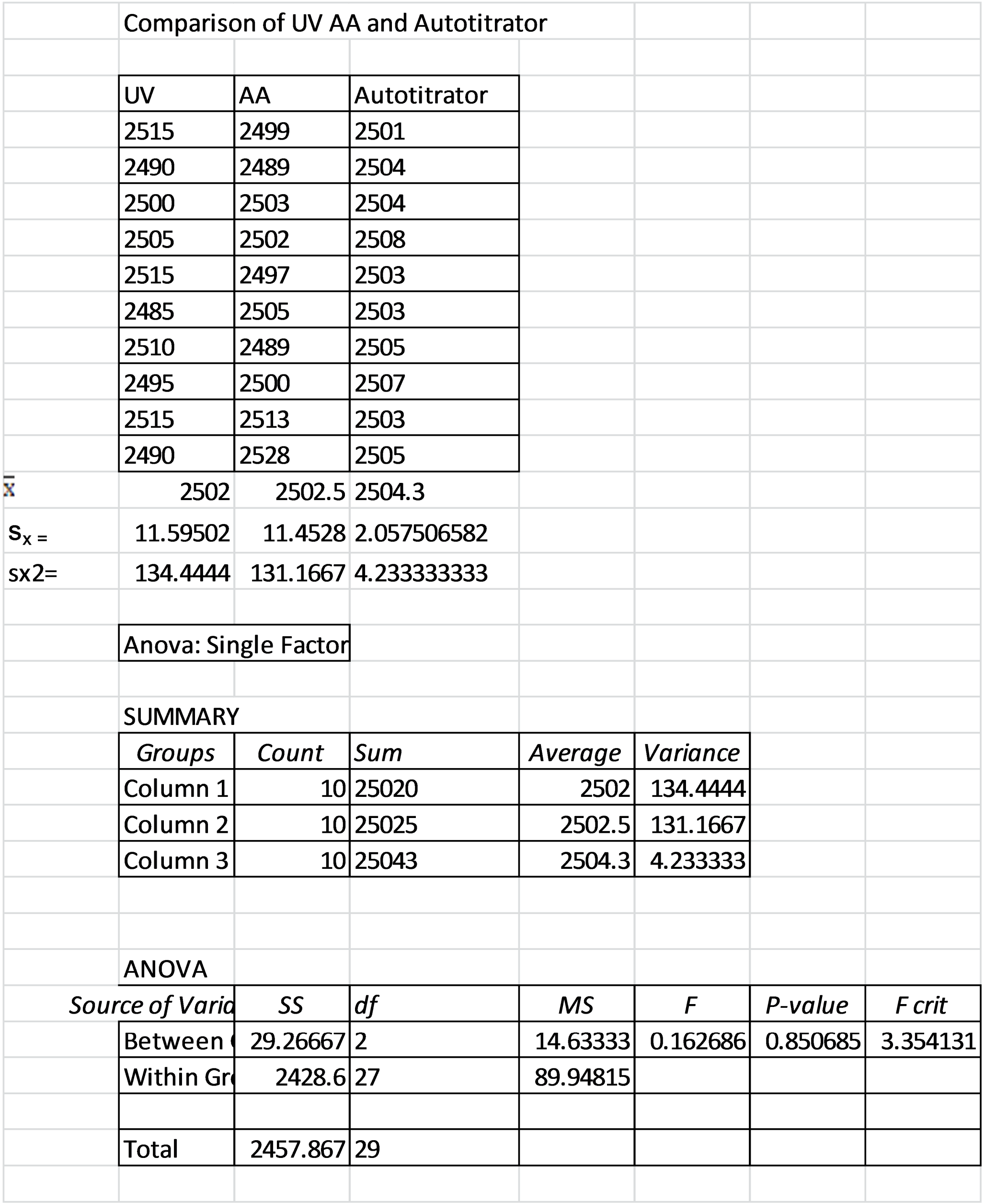
- Select a method from the list.
- Click on the ***Lamp*** icon.
- Click the ***On/Off*** button to switch on the required lamp.
- Allow the lamp to warm up for 15 minutes.
- Click on the ***Setup*** button to optimise the lamp.
- When the setup is complete, close the window.
- Check the burner head position optimisation by doing the following:
- Ignite the flame by clicking on the ***On/Off*** switch in the ***Flame Control*** window.
- Allow the flame to burn for 5 minutes to allow the burner head to reach optimum conditions.
- Click on the ***Cont.*** tab to see the absorbance display.
- Aspirate a blank to auto zero the instrument.
- Aspirate a standard solution that will give 0.2 absorbance units. Refer to appendix 1 for the concentration of the solution to be used as the sensitivity check for the element of interest. The sensitivity check solution will give 0.2 absorbance units.
  If the absorbance of the sensitivity check solution is not within this (0,195 – 0,205) range the nebulizer adjustment and/or burner alignment needs to be performed.
- The burner alignment is done as follows:
- Extinguish the flame by clicking the ***On/Off*** switch in R in the ***Flame Control*** window.
- Click on the ***Align Burner*** button in the ***Burner Control*** window.
- Follow the instructions in the pop-up window.
- The burner head optimal position is automatically stored at the end of the alignment process.
- Extinguish the flame by clicking the ***On/Off*** switch in the ***Flame Control*** window.
- Enter the sample details in the ***Sample Information Editor*** window.

Analysis

- Aspirate deionised water.
- Click on the ***Cont.*** tab to see the absorbance display.
- Autozero the graph.
- Close the window.
- Start the analysis. This is done in the ***Manual Analysis Control*** window.
- Click on the ***Analyse Blank*** button for the blank.
- Click on the ***Analyse Standard*** button for the standards.
- Click on the ***Analyse Sample*** button for the samples and QC solutions.
- On completion of the analysis, the results can be printed.

- Click on the ***Results*** window.
- Click on ***File>Print>>Active Window***.
- Extinguish the flame by clicking the ***On/Off*** switch in the ***Flame Control*** window.
- Click on the ***Lamp*** icon.
- Click the ***On/Off*** button to switch off the lamp.

Appendix I: Comparison of three techniques



Comparison of UV AA and Autotitrator

	UV	AA	Autotitrator
	2515	2499	2501
	2490	2489	2504
	2500	2503	2504
	2505	2502	2508
	2515	2497	2503
	2485	2505	2503
	2510	2489	2505
	2495	2500	2507
	2515	2513	2503
	2490	2528	2505
$\bar{x}$	2502	2502.5	2504.3
s_x =	11.59502	11.4528	2.057506582
sx2=	134.4444	131.1667	4.233333333

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	10	25020	2502	134.4444
Column 2	10	25025	2502.5	131.1667
Column 3	10	25043	2504.3	4.233333

ANOVA

Source of Varia	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between (	29.26667	2	14.63333	0.162686	0.850685	3.354131
Within Gr	2428.6	27	89.94815			
Total	2457.867	29				

Appendix J: Agilent 7500 ce Inductively Coupled Plasma Spectrometer Operation

Boron Isotopic Ratio (B10)

- Install the dedicated spray chamber, sample transfer tube and plasma torch.
- Install the sample and skimmer cones as per step
- Configure the ALS (autosampler) and enable it. Refer to step
- At the ICP-MS top window, select a method to be run by clicking Methods>>Load.
- Ensure that the sample introduction tip of the autosampler is immersed in either a rinsing solution or in Milli-Q water.
- At the ICP-MS top window click Plasma>>Plasma on to ignite the plasma.
- Allow the instrument to run for 10-15 minutes before proceeding with sample analysis.
- At the ICP-MS top window select Instrument>>Tune. >>Select tune file B-IRJWX.u

NOTE: *Unlike Full and Semiquant analyses where auto-tuning is recommended, Boron isotopic ratio utilises a defined set of pre-determined values for some key parameters. The only variables are detector parameters and carrier gas flow-rate which is independently adjusted (by the operator) to give the best counts per second to interferences ratio. It was found that values in the range of 0.95 – 1.05L/min yielded favourable results.*

- Arrange all samples in the vial rack of the autosampler. At the Data Acquisition top window click ALS>>Go to and select the desired sample to be analysed.

NOTE: *Unlike Full and Semiquant analyses that utilise the autosampler for sequential analyses (as per operator needs), Boron isotopic ratio uses a single data acquisition mode. This allows the operator to monitor any erratic changes that may arise (cross-contamination, etc) in samples without having to abort lengthy samples sequences. KWC-AC-ANA-084 Rev 3 Page 16 j:\kwc\ac\ana\authorised\kwc-ac-ana-084 rev 3.doc Eskom – 2014*

- At the Data Acquisition top window click Acquire Data and insert the file, operator and sample names into the designated fields. Finally click Acquire to start sample analysis.
- Finally, click Data Analysis>>Main Panel to open the Data Analysis top page. Here data can be retrieved, reprocessed and interpreted.

Shutdown

Analysis to Standby Mode

- In the ICP-MS Top window, select *Instrument>>Instrument Control*.
- Select *Plasma Off.*
- Click *Yes* in the dialog box.
- The plasma is shut off.
- All gasses, the RF generator, the peripump and the cooling water flow is automatically shut off.
- The vacuum pumps remain on.
- Switch off the chiller.

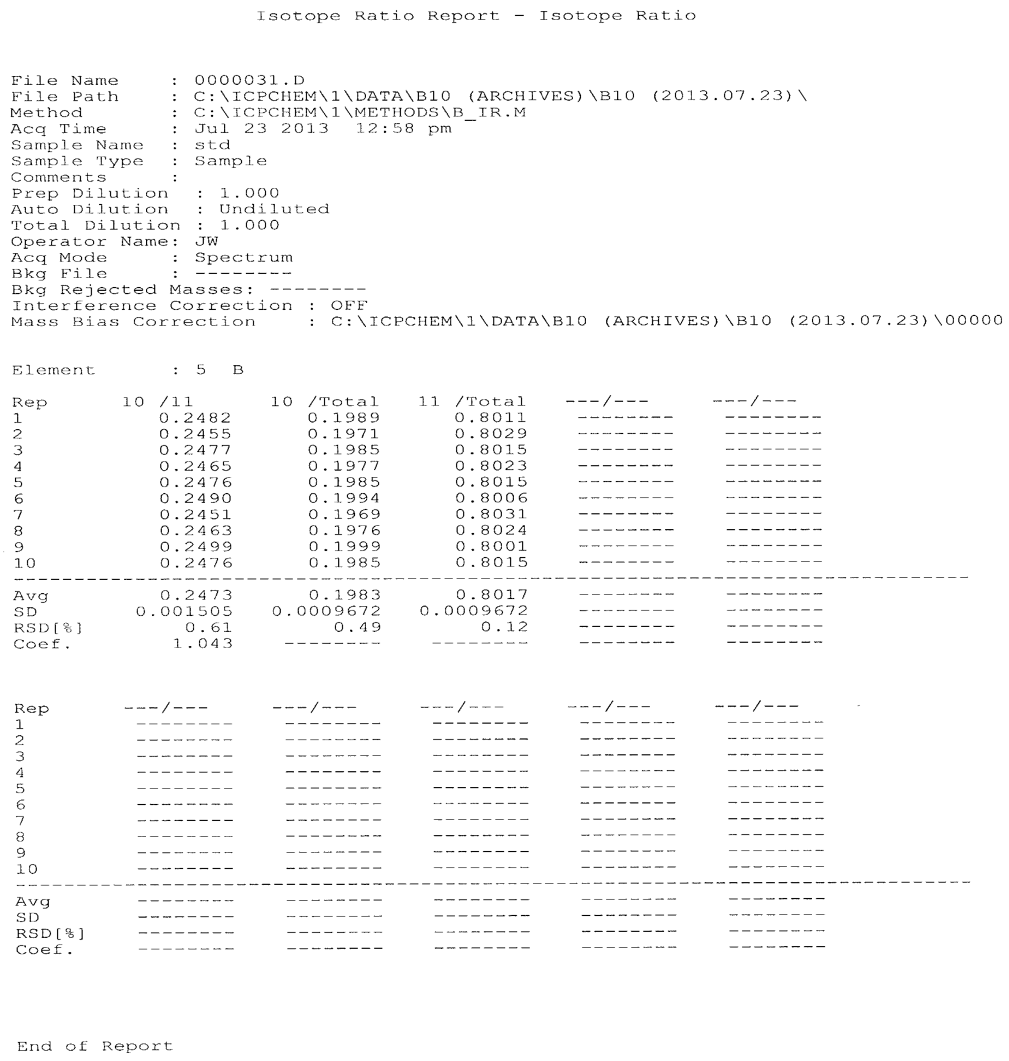
Standby to Shutdown Mode

- Put the instrument in standby mode.
- Ensure that the Argon gas is open.
- When the instrument is changing to Shutdown mode, argon gas is introduced into the vacuum chamber.
- Select *Vacuum>>Vacuum Off.*
- The turbo and rotary pumps are turned off.
- The title bar of the *Instrument Control* window shows that the instrument is in *Shutdown* mode.

QUALITY CONTROL

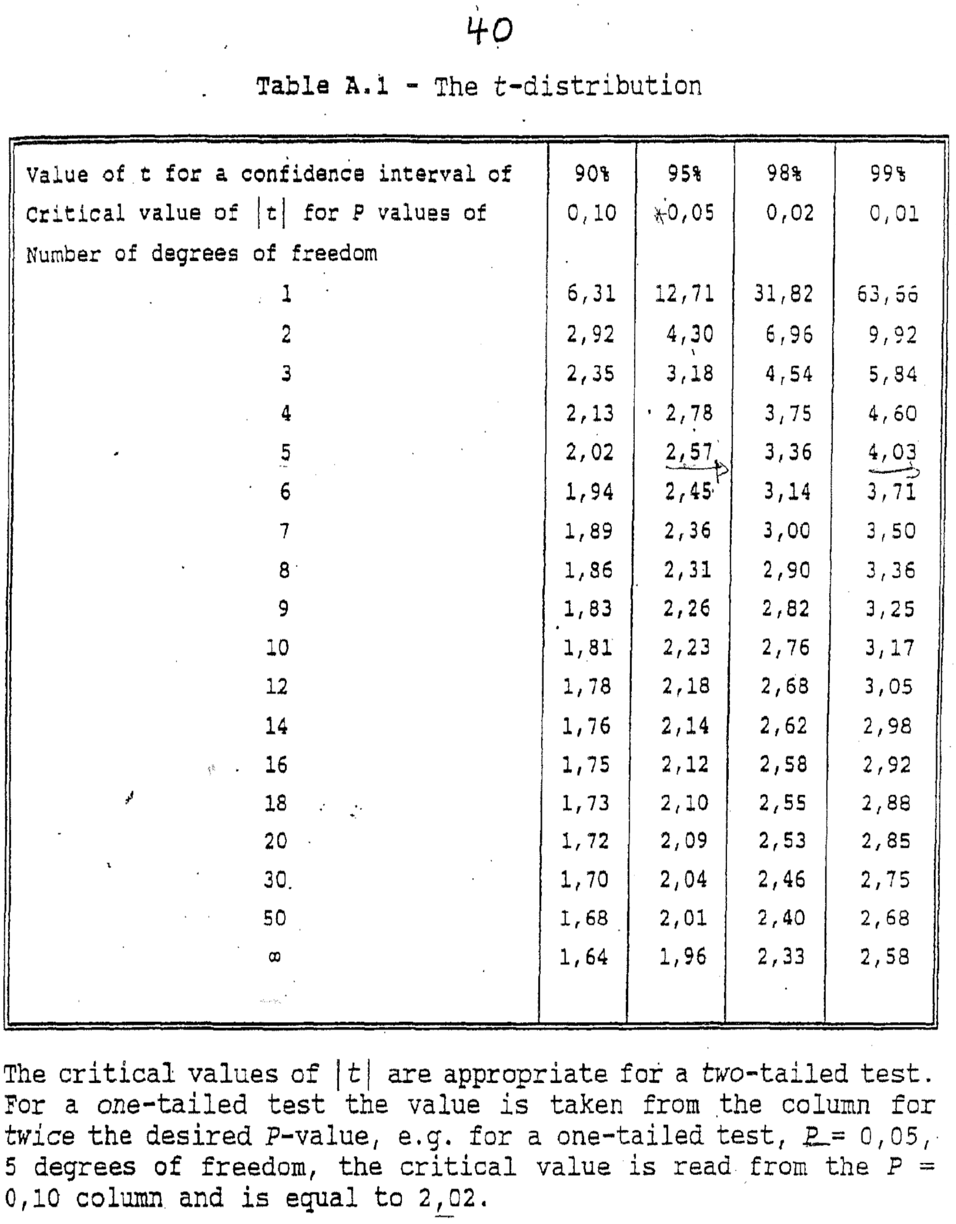
- The quality control must be within the control limits before the results for the sample can be reported.
- The value for the control must be plotted on the quality control chart

Isotopic Boron analysis report sheet by ICP -MS



```
                    Isotope Ratio Report - Isotope Ratio


File Name     : 0000031.D
File Path     : C:\ICPCHEM\1\DATA\B10 (ARCHIVES)\B10 (2013.07.23)\
Method        : C:\ICPCHEM\1\METHODS\B_IR.M
Acq Time      : Jul 23 2013  12:58 pm
Sample Name   : std
Sample Type   : Sample
Comments      :
Prep Dilution  : 1.000
Auto Dilution  : Undiluted
Total Dilution : 1.000
Operator Name: JW
Acq Mode      : Spectrum
Bkg File      : --------
Bkg Rejected Masses: --------
Interference Correction : OFF
Mass Bias Correction     : C:\ICPCHEM\1\DATA\B10 (ARCHIVES)\B10 (2013.07.23)\00000

Element       : 5  B

Rep      10 /11       10 /Total    11 /Total    ---/---      ---/---
1           0.2482       0.1989       0.8011    --------     --------
2           0.2455       0.1971       0.8029    --------     --------
3           0.2477       0.1985       0.8015    --------     --------
4           0.2465       0.1977       0.8023    --------     --------
5           0.2476       0.1985       0.8015    --------     --------
6           0.2490       0.1994       0.8006    --------     --------
7           0.2451       0.1969       0.8031    --------     --------
8           0.2463       0.1976       0.8024    --------     --------
9           0.2499       0.1999       0.8001    --------     --------
10          0.2476       0.1985       0.8015    --------     --------
-----------------------------------------------------------------------------
Avg         0.2473       0.1983       0.8017    --------     --------
SD        0.001505    0.0009672    0.0009672    --------     --------
RSD[%]        0.61         0.49         0.12    --------     --------
Coef.        1.043     --------     --------    --------     --------


Rep       ---/---      ---/---      ---/---      ---/---      ---/---
1         --------     --------     --------     --------     --------
2         --------     --------     --------     --------     --------
3         --------     --------     --------     --------     --------
4         --------     --------     --------     --------     --------
5         --------     --------     --------     --------     --------
6         --------     --------     --------     --------     --------
7         --------     --------     --------     --------     --------
8         --------     --------     --------     --------     --------
9         --------     --------     --------     --------     --------
10        --------     --------     --------     --------     --------
-----------------------------------------------------------------------------
Avg       --------     --------     --------     --------     --------
SD        --------     --------     --------     --------     --------
RSD[%]    --------     --------     --------     --------     --------
Coef.     --------     --------     --------     --------     --------


End of Report
```

Appendix K: The t distribution table [12]



40

Table A.1 - The *t*-distribution

Value of t for a confidence interval of	90%	95%	98%	99%
Critical value of |t| for *P* values of	0,10	*0,05	0,02	0,01
Number of degrees of freedom				
1	6,31	12,71	31,82	63,66
2	2,92	4,30	6,96	9,92
3	2,35	3,18	4,54	5,84
4	2,13	2,78	3,75	4,60
5	2,02	2,57	3,36	4,03
6	1,94	2,45	3,14	3,71
7	1,89	2,36	3,00	3,50
8	1,86	2,31	2,90	3,36
9	1,83	2,26	2,82	3,25
10	1,81	2,23	2,76	3,17
12	1,78	2,18	2,68	3,05
14	1,76	2,14	2,62	2,98
16	1,75	2,12	2,58	2,92
18	1,73	2,10	2,55	2,88
20	1,72	2,09	2,53	2,85
30	1,70	2,04	2,46	2,75
50	1,68	2,01	2,40	2,68
∞	1,64	1,96	2,33	2,58

The critical values of $|t|$ are appropriate for a *two*-tailed test. For a *one*-tailed test the value is taken from the column for *twice* the desired *P*-value, e.g. for a one-tailed test, $P = 0{,}05$, 5 degrees of freedom, the critical value is read from the P = 0,10 column and is equal to 2,02.

Appendix L: Uncertainty sources and % Contributions [12]

Uncertainty table for Automatic titration by Potentiometer

Source of Uncertainty	Value	% Contribution to total
Purity	$8.41\text{x}10^{-6}$	83.5
Reapeatability	$2.91\text{x}10^{-7}$	2.88
Salt mass	$1\text{x}10^{-9}$	0.01
Sample mass	$2\text{x}10^{-9}$	0.02
Volume pipette	$1.21\text{x}10^{-6}$	12.01
Volume volumetric flask	$1.6\text{x}10^{-7}$	1.59
Total uncertainty	$1.0074\text{x}10^{-5}$	100%|

Uncertainty table for UV VIS

Source of Uncertainty	Value	% Contribution to total
Purity	$1.322\text{x}10^{-6}$	0.16
Repeatability	$2.1529\text{x}10^{-5}$	2.63
Salt mass	$2.314\text{x}10^{-10}$	0
CRM	$1.35\text{x}10^{-6}$	0.17
Volume pipette	$1.21\text{x}10^{-6}$	0.15
Volume volumetric flask	$4.62\text{x}10^{-7}$	0.06
Calibration Uncertainty	$7.9\text{x}10^{-4}$	96.6
Total uncertainty	$8.1818\text{x}10^{-4}$	100%|

Uncertainty table for Atomic absorption flame

Source of Uncertainty	Value	% Contribution to total
Purity	$1.322\text{x}10^{-6}$	0.32
Repeatability	$2.09\text{x}10^{-5}$	5
Salt mass	$2.314\text{x}10^{-10}$	0
CRM	$1.35\text{x}10^{-6}$	0.32
Volume pipette	$1.21\text{x}10^{-6}$	0.30
Volume volumetric flask	$4.62\text{x}10^{-7}$	0.11
Calibration Uncertainty	$3.94\text{x}10^{-4}$	94.26
Total uncertainty	$4.18\text{x}10^{-4}$	100%|

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