IDENTIFICATION AND QUANTIFICATION OF ORGANIC SPECIES IN POWER STATION FEEDWATER

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Cape Peninsula
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By

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Thesis submitted in fulfilment of the requirements for the degree

Master of Technology in Chemistry

In the Faculty of Applied Science
at the Cape Peninsula University of Technology

Supervisor: Prof. Tjaart Nicolaas van der Walt

Co-supervisor: Dr. Nestor van Eeden

Bellville
Date submitted on the 15 March 2013

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DECLARATION

I, Mandisi Buntu Stwayi, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/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.

MB _____   16 September 2013

Signed   **Date**

ABSTRACT

It is possible for organic material to enter the steam/water cycle of a power station in number of ways. Make-up water, chemical additives and ion exchange resin leachates are usual sources of organics entering the system during normal power operation. Other sources include cleaning agents, lubricants, bacteria and condenser inleakage that can enter the steam/water by contamination during outages or damaged plant during operation.

Although the steam/water cycle is a closed loop, water and steam is lost by imperfection in design and construction, material degradation and defective components. Normal operation includes interventions that occasionally require or result in a loss of steam and / or water from the secondary system. From several strategic positions on the secondary cycle on both the water and steam lines, continuous sample flows via the sampling system to the online analysers and grab sampling points. All of operational losses of steam and water require the secondary system to be made-up. Make-up water is the source of natural organic matter (NOM) that enters the system during normal operation. Water treatment that includes chlorination for disinfection causes the formation of disinfection by-products (DBP) and of specific interest are organochlorides such as chloroform as a product from reaction of chlorine with NOM and microorganisms.

Organochloride breaks down under the plant thermohydraulic conditions resulting in the ,increase of the chloride ion concentration. Chloride in contact with metal surfaces has a detrimental effect on the structural integrity for power plants. Inconel, a metal alloy consisting of nickel, chromium and iron is used for the manufacture of steam generator (SG) tubes of PWRs worldwide because of its physical properties. SG tubing is by far the most vital component of this type of nuclear power plant and Inconel is susceptible to chloride induces pitting corrosion. Chloride also causes stress corrosion cracking (SCC) in austenitic stainless steels that constitute the balance of the plant systems. For these reasons it is imperative that plant chemists must continue to strive to keep the chloride concentration as low as achievable.

Over the years it has been observed that high secondary make-up at Koeberg Nuclear Power Station (KNPS) results in corresponding increased chloride levels in the steam generators even though the make-up water tanks chloride analysis is low. The elevated chloride concentration following high system make-up has been attributed to trihalomethanes (THM) being present in the make-up water.

Chemicals are added to the secondary circuit with the intent to establish the most favourable chemical condition that will mitigate plant degradation by limiting corrosion mechanisms. It is usual to have additives that control pH and dissolved oxygen in the secondary system of a pressurised water reactor (PWR). Historically inorganic additives such as trisodium phosphate and later ammonia have been used to control pH. Recent developments have established that organic amines have superior properties and are often the preferred additive. Plants that use amines add to the organic loading and this has consequences that are important to consider.

In power plant chemistry ion exchange (IX) resins are used to remove impurities from the process water. Ion exchange is extremely effective for retaining inorganic ionic species but organic compounds are not readily retained. These IX resins are organic polymers and under certain physical conditions break down resulting in the leaching of organic material into the process water increasing the organic load.

For this work, water samples of the secondary cycle from PWR, KNPS, have been analysed to gain a better understanding of the overall effect of organic material on the system chemistry. During normal plant operation sources include NOM, chemical additives and ion exchange resin leachates. This work focuses on the analysis and profiling of organic material entering the system during normal operation with more specific focus on organochlorides because of its potential detrimental effect on the plant construction materials.

In the attempt to identify and quantify organic species at KNPS methods for identification and quantification of organic species at KNPS were developed and implemented. This was achieved by purchasing Total Organic Carbon (TOC) analyser and also specific analytical column were purchased and installed in the Ion Chromatography (IC) System to enable it to have capabilities to quantify organic anions such as formate, acetate, oxalate and glycolate in single run along with the inorganic anions. The TOC and IC work was performed at KNPS while some of the samples were sent to various laboratories for further organic characterisation and also for trihalomethanes (THM) analysis. Koeberg Nuclear Power Station surveillance procedures were updated to reflect a surveillance requirement for TOC in the water production plant systems.

This research project has also initiated various other projects at KNPS. One of the projects was the anion resin routine clean-up process where the organic material, that fouls the anion resins are removed by soaking the resin in a solution containing 5 % sodium chloride and 2 % sodium hydroxide and this process is also known as a "brine washed". Procedures were

compiled and they are currently being utilised by KNPS chemistry staff. Another project that was initiated was to replace the anion resins in the water production plant.

This project has also initiated a strategy and recommendation on how KNPS should deal with poor water quality and these recommendations were communicated to Engineering Group so that appropriate modification may be initiated. TOC analysis was performed at various strategic points around the water production plant and secondary systems to develop an organic profile which had not previously been performed at KNPS.

ACKNOWLEDGEMENTS

DEDICATION

This thesis is dedicated to my late Grandfather Mr Fudumele Felix Stwayi, for being an inspiration to my life and also for affording me an opportunity to seek knowledge and embracing the spirit of academic world.

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GLOSSARY

Acronyms	Explanation
ABP	Low Pressure Feedwater Heater System
ACO	Drain Recovery System
AHP	High Pressure Feedwater Heater System
Alum	Aluminium Sulphate
APA	Motor Driven Feedwater Pump
APP	Turbine Steam Driven Feedwater Pump
AVT	All Volatile Treatment
BA	Tank
BB	Building Blocks
CDOC	Chromatographic Dissolved Organic Carbon
CEX	Condenser Extraction System
CC	Cation Conductivity
CPI	Chemistry Performance Indicator
CPP	Condensate Polishing Plant
CRF	Circulating Water System
CRTC	Continuous Regenerated Trap Column
CS	Carbon Steel
Degas	Degassed
Demin	Demineralised
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DVB	Divinylbenzene
EC	Erosion Corrosion
EdF	Electricite de France
EPRI	Electric Power Research Institute
ETA	Ethanolamine
FAC	Flow Accelerated Corrosion
GAC	Granular Activated Charcoal
GPV	Turbine Valves and Drain System
GC-MS	Gas Chromatography Mass Spectroscopy
HOC	Hydropholic Organic Carbon
HP	High Pressure
HS	Humic Substance
IC	Ion Chromatography
IGA/SCC	Inter Granular Attack / Stress Corrosion Cracking
IX	Ion Exchange
K_{25}	Conductivity
KNPS	Koeberg Nuclear Power Station
LC-OCD-OND	Liquid Chromatography – Organic Carbon Detection – Organic Nitrogen Detection
LIMS	Laboratory Information Management System
LMW A	Low Molecular Weight Acids
LMW N	Low Molecular Weight Neutrals
LP	Low Pressure
MA	Mill-Anneated Alloy
MB	Mixed Bed
Nm	Nano metre

NOM	Natural Organic Matter
NPOC	Non-Purgeable Organic Carbon
Nq	Not Quantifiable
OBS	Organically Bound Sulphate
OD-IGA /SCC	Outer Diameter-inter Granular Attack / Stress Corrosion Cracking
OEM	Original Equipment Manufacture
POC	Particulate Organic Carbon
PPB	Parts Per Billion
PS	Polysaccharide
PWSCC	Primary Water Stress Corrosion Cracking
PWR	Pressurised Water Reactor
RFIC	Reagent Free Ion Chromatography
RO	Reverse Osmosis
RSD	Relative Standard Deviation
SCC	Stress Corrosion Cracking
SDA	Water Production Plant
SEP	Potable water
SED	Demineralised water pH 7
SER	Demineralised water pH 9.5
SIR	Chemical Reagent Injection System
SG	Steam Generator
SRI	Closed Cooling Water System
Spec	Specification
SUVA	Specific Ultraviolet Absorbance
TC	Total Carbon
THM	Trihalomethanes
TIC	Total In-organic Carbon
TSP	Tube Support Plate
TS	Tube Sheet
TTHM	Total Trihalomethanes
TOC	Total Organic Carbon
VOC	Volatile Organic Carbon
VVP	Main Steam
UV	Ultra Violet
WANO	World Association of Nuclear Operators
WTP	Water Treatment Plant

CHAPTER ONE: INTRODUCTION

1.1 General Introduction

Water treatment forms an integral part of thermal electric power generation (coal as well as nuclear stations). There are generally two main cycles associated with thermal power generation, namely the steam/water cycle that uses demineralised water for the production of steam and the cooling water circuit, which is used for condensing the steam back to water. The two cycles are isolated from each other and exchange heat via heat exchanger in a form of condensers.

The power stations make-up water treatment plants have traditionally been designed to produce water of a very high quality (free from inorganic salts) by using synthetic ion exchange resins. Raw water quality (mainly ability to remove total dissolved solids, oxygen absorbed and silica) is the key factor in the design of the water treatment plant. Any deterioration of raw water quality during the life cycle of the plant, which is currently a South African and worldwide phenomenon, will inevitably have a negative impact on treatment plant performance and plant ability to remove impurities. In order to meet the specifications of the water quality required for proper plant operation, an extra burden, as well as associated treatment costs, will therefore have to be placed on existing treatment processes to compensate for change in feed water quality.

Apart from increasing salt concentration in raw waters, there are indications that natural organic matter present in the water is also increasing. This is becoming a concern for industries requiring high purity water and a number of industries, including the power industry, have embarked on programmes to set a maximum target value for total organic carbon (TOC) material in demineralised water. Lowering the target value for TOC might have a negative impact on the costs of demineralised water production, especially if such a decision is not supported by scientific facts. An area that has been a topic of contention for quite some time is the fate of organic matter in the steam/water circuit and the potential damaging impact of these compounds and their breakdown products (organic acids and carbon dioxide) on construction materials.

Raw water used at Koeberg Nuclear Power Station is obtained from the Voëlvlei Dam and contains natural organic matter (NOM). NOM is present in all natural water sources and it originates as a result of the decay of vegetable and animal matter, micro-organisms, oily material and humic matter. NOM is normally quantified and expressed as Total Organic Carbon (TOC), which is defined as the sum of the dissolved organic carbon (DOC), non-

purgeable organic carbon (NPOC), particulate organic carbon (POC) and volatile organic carbon (VOC) fraction [1], [2].

The DOC fraction consist of humic and fulvic acids (collectively known as humic substances and is the predominant fraction of NOM), which are high molecular polyfunctional weak organic acids [3]. Humic substances are responsible for the brown or yellow colour in the surface water containing high levels of NOM (10 – 30 mg/l C). By definition, DOC is classified as that fraction of humic substance that can pass through a 0.45 μm filter. They contribute to 5 – 10 % of all anionic species in natural waters and their anionic character is due to the dissociation of carboxylic acid groups. Humic acid can be divided into three main groups of organic compounds [4].

Humic acid (See Figure 1.1 to view humic acid structure) is that fraction of humic substance that is not soluble in the water under acidic conditions. Fulvic acid is the fraction that is soluble in water under all pH conditions and finally humin is that fraction that is not soluble in water at any pH level and is commonly referred as particulate organic matter (POC).

Humic Acid Structure

Humic Acid Structure proposed by Dragunov
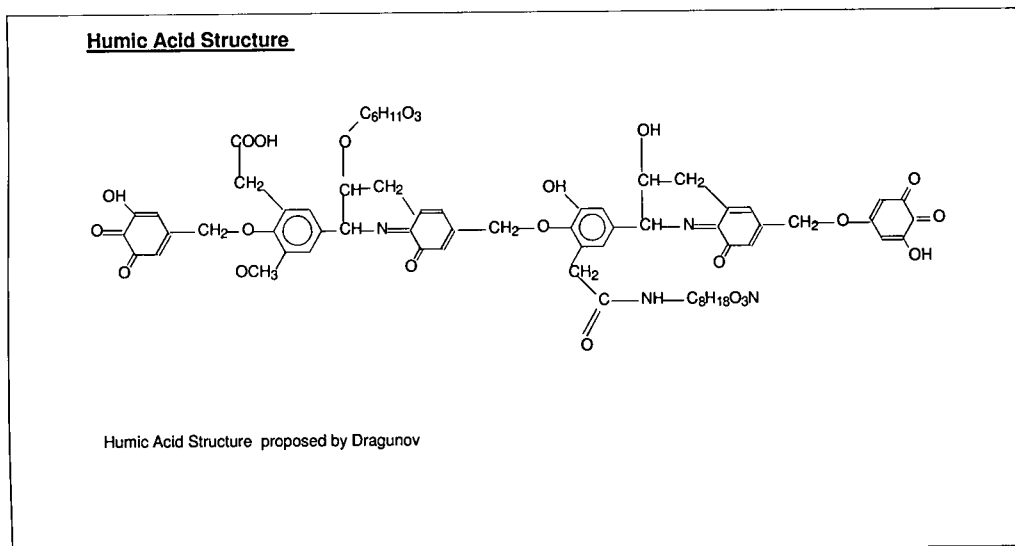
Figure 1.1: Humic Acid Structure

(Source: Presentation at Condensate Polishing Workshop, October 1985 [5])

The presence of humic substances in natural water is undesirable for a number of reasons:

- They possess ion exchange properties.
- They can act as a transport mechanism for toxic and water insoluble compounds.
- They react with chlorine to form chlorinated organic compounds such as trichloromethanes.

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- They stabilise dispersed and colloidal particles during coagulation processes.
- They can precipitate in the water distribution system.

The presence of organic species can therefore be based on the above have a major impact on the performance of a water treatment plant [6].

There are a number of possible sources through which organic matter can enter the steam/water cycle of a power plant. These possible sources are listed below as followings:

- Passage of organic species through the make-up water.
- Passage of organic species through the ion exchange resin.
- Passage of organic species through the pre-treatment of the make-up water, i.e. activated carbon.
- Organic treatment agents.

The above mentioned passage route of organics to the water cycle of a power plant will be discussed further later but it is important to understand the pressurised water reactor and secondary circuit to fully appreciate the passage route.

1.2 Pressurised Water Reactor

,A pressurised water reactor (PWR) is a type of nuclear reactor that is comprised of three water cycles. The primary circuit is a closed piped water loop which contains the reactor vessel, primary pump(s), steam generator(s) tubes and a pressuriser. Heat is generated by nuclear fuel in the reactor vessel and this heat is transferred to the reactor coolant water (in contact with the fuel) being pumped through the steam generator (SG) tubes. The water is prevented from boiling by the high pressure controlled by the pressuriser. The second closed water cycle includes the shell side of the SG which accepts the heat from the primary circuit. This heat generates the steam from the water in the secondary circuit which is transferred to spin turbines to produce electricity. The steam exhausting from the turbine is condensed by the cool environment provided by the third closed plant water cycle, the cooling water. See Figure 1.2 to view a diagram showing the 3 water cycles.
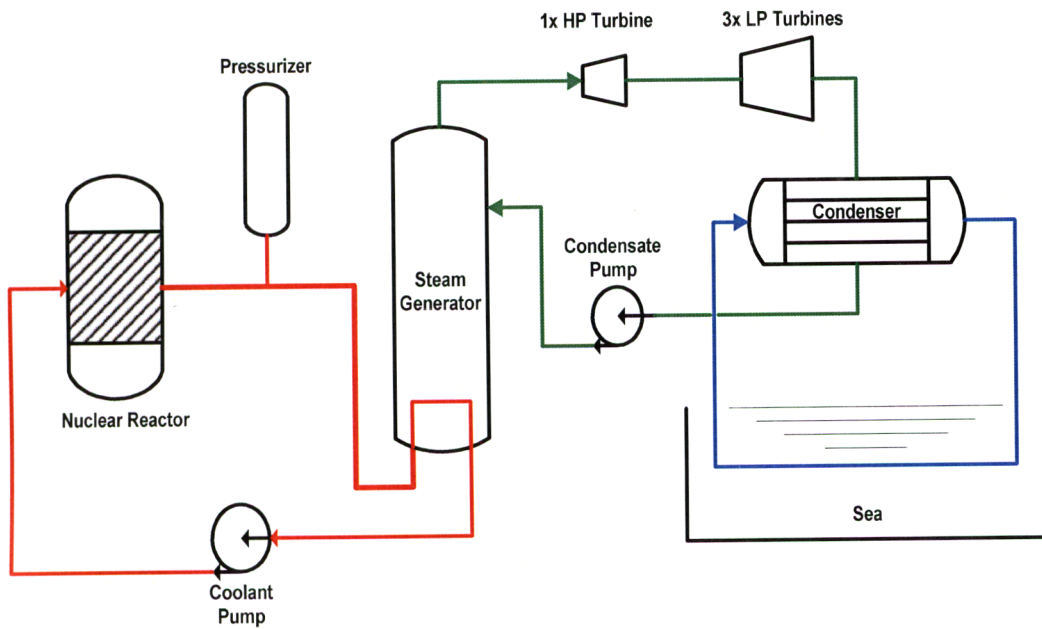
Figure 1.2: **Diagram showing the 3 water cycles**

1.3. Secondary Circuit

The secondary circuit is also referred to as the power plant steam / water cycle which consist of the condenser, condensate extraction pumps, low pressure heaters, Feed-water pumps, high pressure heaters, steam generator (shell side), steam lines, moisture separator reheaters followed by low and high pressure turbines from which the exhaust steam is condensed to water and collected back in the condenser. See Figure 1.3 to view diagram showing outline of the secondary water circuit.
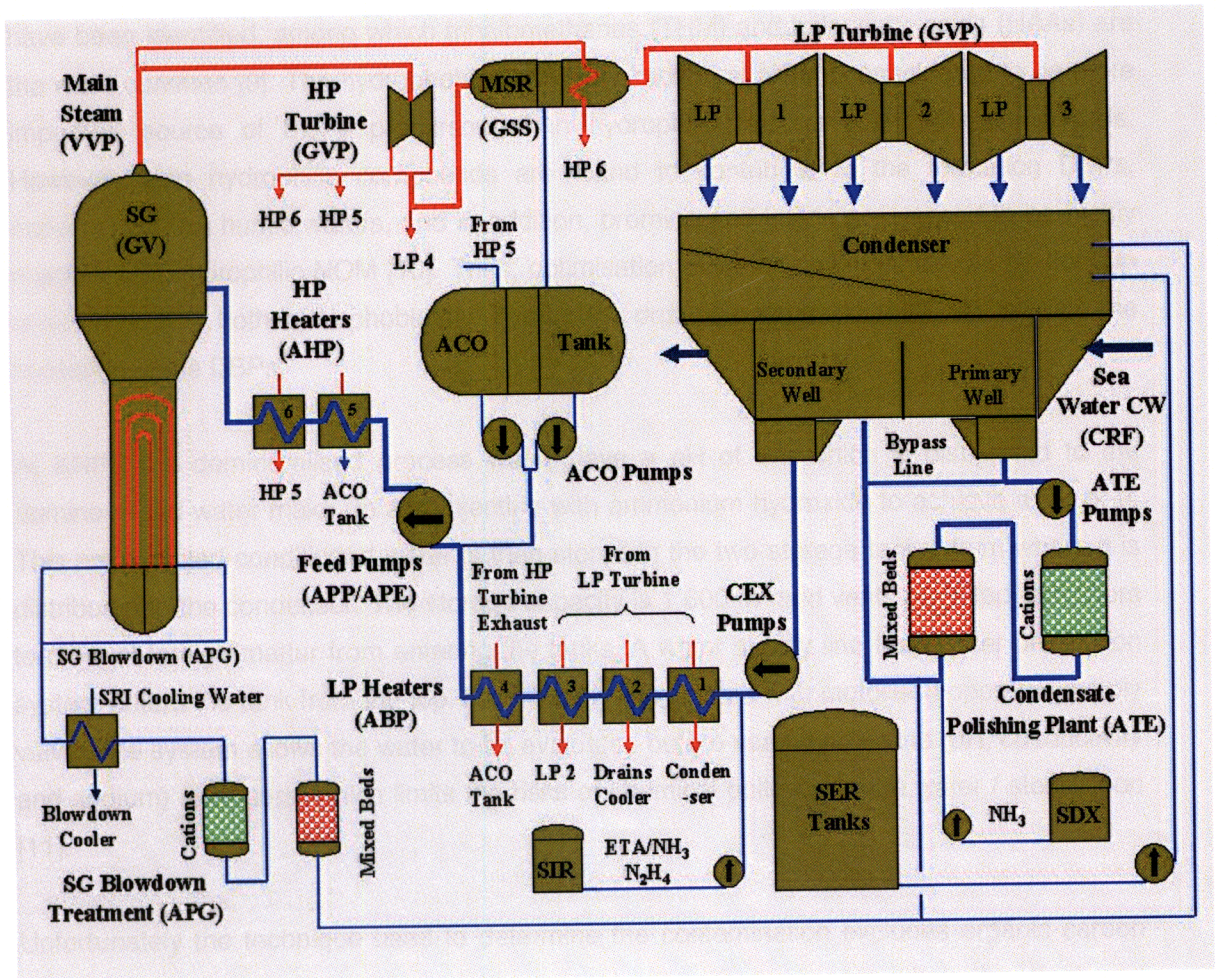
Figure 1.3: Diagram showing outline of the secondary water circuit

1.4 Passage of organic species through the make-up water

As it was discussed earlier that KNPS water obtained from Voelvlei Dam that contains natural organic matter (NOM). This water is the then chlorinated and treated with ion exchange to produce make-up water. However since this water contains NOM and NOM affects significantly on many aspect of water treatment, including the performance, application of water treatment chemicals and biological stability of water. NOM is responsible for the majority of the coagulant and disinfectant use in water treatment. It has tendencies to interfere with removal of other contaminants, it is responsible for fouling of membranes and it contributes to corrosion and acts as a substrate for bacterial growth in the distribution system [7].

Moreover NOM has been noted to be the major contributor of the disinfection by-products (DBP's) formation. DBP have become a focus of attention in water treatment, since they have been reported to have adverse health effects [8] – More than 600 compounds of DBPs

have been identified, among which trihalomethanes (THM) and haloacetic acids (HAAs) are the most common [9]. The hydrophobic and HMM fraction of NOM is considered to be more important source of DBPs precursors than hydrophilic fraction and LMM compounds. However, also hydrophilic compounds are found to contribute to the formation DBPs, especially in low humic waters, and in addition, bromine and iodine are noticed to be highly reactive with hydrophilic NOM [10]. Thus, optimisation of water treatment should be done in order to remove both hydrophobic and hydrophilic organic compound, than can mitigate the formation of the DBPs.

At KNPS the demineralised process water have a pH of 6.9 which is distributed to the demineralised water make up and injecting with ammonium hydroxide to achieve a pH of 9. This ammoniated conditioned water is then stored in the two storage tanks, from where it is distributed to the condenser. The storage capacity is 1 600 m^3 and vents are fitted with filters to prevent foreign matter from entering the tanks. A water supply line from water production system enters the tank from the top. Each supply line is fitted with motorised operated supply valve. The system allows the water to be evaluated before use by an online (pH, conductivity and sodium) analysers, which limits the risks of chemical pollution in the water / steam loop [11].

Unfortunately the technique used to determine the contamination excludes organic carbon determination because organic carbon was not seen as a concern when the plant was commissioned. This is therefore one of the passage routes of organic species as this water may contain levels of naturally organic matter.

1.5 Passage of organic species through the ion exchange resin

Depending on the manufacturing technique ion exchange resins have four different matrices [12]:

- Copolymers of styrene and divinylbenzene (DVB) are the matrix of most cation and anion resins used in water treatment.
- Copolymers of acrylic or methacrylic acids, esters, or nitrites with DVB are used to manufacture weak acid, weak base, and strong base resins.
- Epoxyamine condensates reacted with polyamines or ammonia produces weakly basic aliphatic anion resins.
- Phenol formaldehyde condensates are the matrix for strong acid cation and weak basic anion resins.

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Ion exchange resins used in water treatment plants are classified into four groups by chemical functionality:

- Strong acid cation.
- Weak acid cation.
- Strong base anions.
- Weak base anion.

Ion exchange resins can be a direct and indirect source of organics in pure water cycles. The resin inadvertently released from an ion exchange vessel is a source of organic and ionic impurities. Residual from manufacturing (chlorinated organics resin or chloride from the chloromethylation step in manufacturing anion resin), sulphonated products from cation resin, trimethylamine from anion resin, or demethyiamine or dimethylethanolamine from anion resin are potential sources of organics from ion exchange resins. The sulphonated leachables from cation resin can kinetically foul anion resin and degrade performance. As a result of that the leachable organic material from the resins can be an indirect source of organics [12].

1.6 Passage of organics species through pre-operational preservatives i.e. Activated Carbon

Make-up water is chlorinated to disinfect water by killing micro-organisms. Activated carbon is used to remove the residual free chlorine prior to ion exchange. Chlorination is dosed to raw water before filtration to decompose organics. Over a 100 different organic compounds have been identified in drinking waters, including ketones, halogenated compounds, ethers, benzene derivatives, nitro compounds, straight-chain hydrocarbons, and alcohols [13]. Pesticides and other chlorinated organics are a particular concern [14].

High concentrations of total trihalomethanes are present when raw water chlorination is practised [15]. When sufficient chlorine is added to create chlorine residual compounds, total trihalomethanes levels are related to the organic content of the water; higher levels are reported when precipitative softening is practised and the process is done at a high pH. 1,2-Dichloroethane and carbon tetrachloride are not present as a result of chlorination, whereas trihalomethanes, chloroform, bromodichloromethane, dibromodichloromethane and bromoform can be produced when water is chlorinated.

<u>Halogenation Reaction</u>

$$Cl_2 + CH_3CH_2CH_2CH_3 \xrightarrow{\quad Cl_2 \text{ @ } 300 \text{ °C} \quad} CH_3CH_2CH_2CH_2Cl + HCl \quad [16]$$
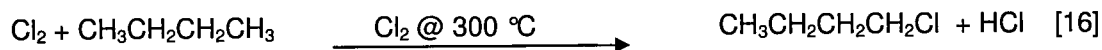
Compounds such as chloromethane can pass through an ion exchange resin bed and enter the steam cycle where it can decompose under thermo hydraulic condition to yield chloride ions [17]. Boiler tubes damage by the decomposition suspected chlorinated hydrocarbon has been reported [18]. In 1984 and 1985 chlorides in the steam cycle at Millston unit 2 was attributed to chlorinated organics in the make-up water, [19.20]. Chlorides can form acid chlorides in the crevice (when not balanced by strong cations) and are believed to be a major factor in denting (i.e. the growth of non-protective magnetite) and pitting. The presence of oxidants can promote the formation of acidic crevice conditions.

The activated carbon that is used to remove free chlorine can also be a possible source of chlorinated organics. The reaction of free chlorine with granular activated carbon to a level of 1 to 4 grams of chloride per gram of carbon produces a brown-black product and volatile organic compounds, including chloroform, trichloroethane, several chlorinated aromatics, and non-chlorinated aromatics [21]. The production of chlorinated organics is favoured at high pH. Chlorination will not produce significant levels of chlorinated organics on carbon until sufficient chlorine is accumulated. Another source of TOC from activated carbon is biological activity. Activated carbon beds can internally generate large amounts of bacteria which can contribute to TOC. Lignite – based carbon is a source of organics leached from slime producing fungal proliferation on carbon [22].

1.7 Koeberg Nuclear Power Station Water Supply from Municipality

Koeberg Nuclear Power Station (KNPS) is situated on the West Coast of the Western Cape Province of South Africa. Raw water to the station is pumped to the station from the Voëlvlei Dam near Sonkwasdrif in the Western Cape, which is the main supply of water of the City of Cape Town Municipality. At the dam the water is treated by flocculation, clarification, filtration and chlorination. At KNPS site the water is stored in two potable water unlined concrete reservoirs of 9 056 m^3 each. Although the potable water is already treated, it is re-chlorinated by sodium hypochlorite injection to prevent algae growth.

The potable water reservoirs supply water to the demineralisation plant which produces the purified process water for both the primary and secondary plant. The water is flocculated by addition of alum [$Al_2(SO_4)_3$] to remove suspended solids. The flocculated water is pumped through activated charcoal filters and the product is collected in the filtered water tank. The

filters are intended to remove the organic material, residual chlorine and suspended solids from the water. In practice the filters are effective in removing the flocculated suspended solids post alum dosing but do exhaust very quickly making them ineffective for organics removal.

Filtered water is pumped towards the demineralisation sets of vessels that consisting of a cation, anion and mixed bed resin vessels. The demineralised water from the outlet of the trains is collected in the demineralised water tanks. Demineralised water for the secondary plant is treated with ammonia to increase the pH to greater than 9. Untreated (non-ammoniated) 'pure' demineralised water is collected in a separate tank for supply to the primary plant. See Figure 1.4 to view the diagram showing the flow path from the municipality to Water Production Plant.
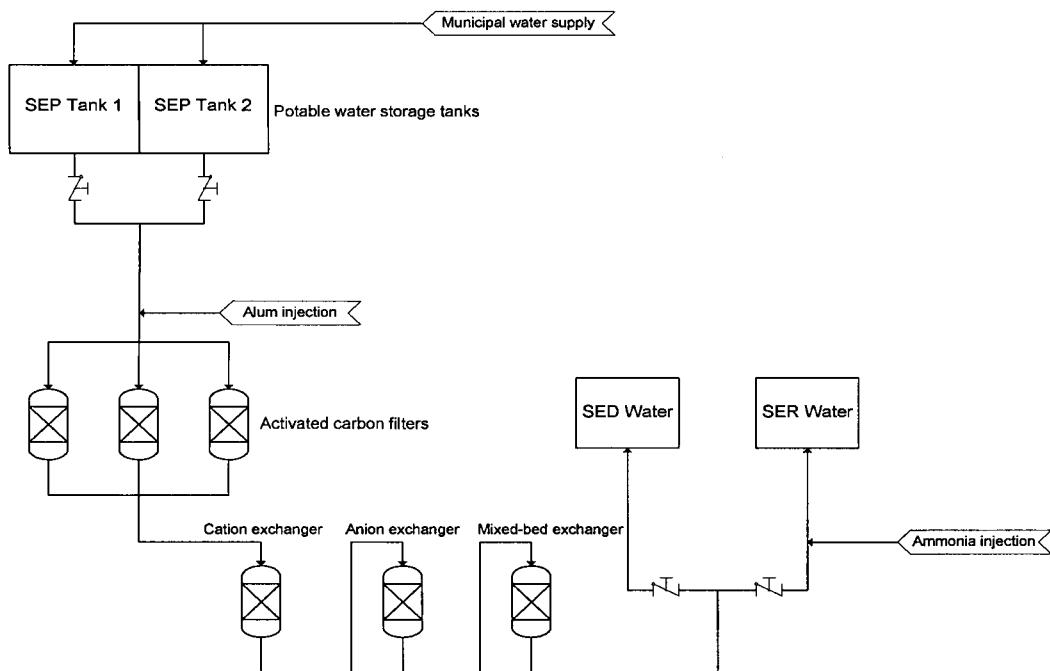
Figure 1.4: Diagram showing the flow path from the municipality water supply to Water Production Plant for KNPS

The presence of organic species in the secondary system at KNPS has initiated a need for the identification and determination of organic impurities. Excessive organic contaminants cause the resins to be fouled and this will cause the organochlorides and organosulphates impurities to pass through the ion exchange resin to the make-up water and this make up water is used to fill the condenser and finally steam generator. Organic impurities of very

high molecular weight > 10 000, are believed to be colloidal in nature and so could pass through resins beds to contaminate the final make up water [23].

At high temperature these organochlorides and organosulphates will break down and free chloride and sulphate will cause stress corrosion cracking in the Steam Generator. The chlorides and sulphates will also increase cation conductivity in the steam generators beyond technical operating specification and that can lead to the reactor being shut down and that will cost KNPS 1.5 million rands production loss per day. A KNPS reactor shut down can result in a loss of electric supply in the Western Cape which will cost the province and the country millions of rands. It is important to identify the organic species and to quantify the species so that a suitable process to minimise the organic species can be investigated, developed and implemented. The value of this project will be to improve the control of secondary chemistry at KNPS and also to reduce the amount of impurities that can enter the steam generator.

1.8 Historical evolution of secondary water chemistry

Historically, based on the fossil fired power station unit experience, most of the pressurised water reactors (PWR) units were using the coordinated phosphate treatment, since such a treatment is able to buffer contaminants entering the system and concentration in the steam generator (SG). The reason for this is that condenser tubes were historically made of copper alloy, for their high thermal conductivity, but these were not always leak tight. Phosphate was selected to buffer (neutralise) any acidity or alkalinity coming from contaminants, mainly cooling water in the condenser [24].

Besides this treatment, some plants were operating on all volatile treatment (AVT) with ammonia conditioning which was the case at the old French PWR of Chooz A, 300 MWe, in the 1960's, which had stainless steel tubing. Most of the PWRs up to 1974 were operating with phosphate treatment. The phosphate chemistry is a well-known chemistry, which is used in the fossil fired power plant to increase the pH value in the boiler water and to provide a chemical buffer to prevent pH excursions, which might be caused by chemical reactions and/or hydrolysis of the concentrated salt impurities at high operating temperatures. The pH increase by phosphate is based on its reaction with water, which produces sodium hydroxide.

$$Na_3PO_4 + H_2O \longrightarrow NaOH + Na_2HPO_4$$
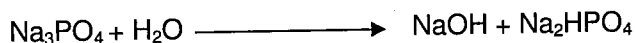
In the early 1970's, under phosphate treatment, alloy 600 MA started to suffer from corrosion. It has been first considered that locally, the chemistry was either too alkaline or too acidic respectively inducing stress corrosion cracking or wastage (thinning) of the steam generator tubing. Several Na/PO$_4$ ratios have been successively tried to avoid both type of corrosion but without success. In fact even both environments were able to coexist in different local parts of the steam generator and it became obvious that it was impossible to avoid corrosion of alloy 600 MA tubes, whatever the Na/PO$_4$ molar ratio was in the range of 2.0 to 2.6 [24].

It must be mentioned that even under phosphate treatment, some volatile reagent (hydrazine that thermally decompose to ammonia) is also added to get the desired pH in the entire secondary system, phosphate being added only to keep the expected buffered chemistry within the steam generator.

In 1974 Westinghouse decided to move to AVT i.e. without any solid additive that would not be volatile. Most of the pressurised water reactors with alloy 600 MA tubing effectively moved to AVT chemistry, with the exception of a few old units of limited power that did not have encountered major problems and did not want to take any unnecessarily risk and have the burden of changing the chemistry [24].

At the time of the phosphate treatment, utilities were used to operate with high impurity levels, much higher than what they are now, particularly for seawater cooled plants. This has been the cause for the "denting" phenomenon. The all volatile treatment without any buffering effect was unable to neutralise the acidity or alkalinity caused by cooling water ingresses or other pollutions, upon concentrate in the steam generator. This denting phenomenon induced extremely quick and severe degradation, requiring urgent steam generator replacement in several PWR units in the USA, particularly high for seawater cooled units [24].

What is Denting?

Denting is the process by which a corroding component deforms a SG tube due to the volumetric expansion that occurs during corrosion when the oxide occupies more volume than the metal from which it formed. Stresses and strains due to denting can aggravate Inter Granular Attack / Stress Corrosion Cracking (IGA/SCC) and can also cause Primary Water Stress Corrosion Cracking (PWSCC). Outer Diameter-Inter Granular Attack / Stress Corrosion Cracking (OD-IGA/SCC) at dents has mostly occurred with 600MA, and mostly at dents caused by corrosion of drilled hole carbon steel support plates [25].

Consequently, much more stringent specifications have been applied progressively in various countries having SG's of the Westinghouse and /or Combustible Engineering (CE) design with drilled circular holes in CS TSP. This together with boric acid treatment has been able to mitigate denting in remaining SG's in service and to avoid it in Japan. In some other countries with similar design, the improved chemistry allowed to avoid denting (France, Switzerland, and Sweden). Despite the application of such chemistry specifications, SCC appeared under AVT on the secondary side of alloy 600 MA SG tubing in many countries, starting in the early 1980's (Japan in 1981 for the first evidence of such cracking) [24].

Since the beginning of 1970s the PWR secondary side chemistry was modified significantly worldwide due to experienced SG problems. The reason for these SG degradation problems was the inadequate SG design and selected tubing material, as well as the applied secondary side chemistry. Based on the lessons learned the SG design and materials as well as secondary side chemistry were modified continuously in order to prevent or mitigate these SG problems.

In the late 1980's and early 1990's OD-IGA/SCC was still growing in many units where it had already started and was appearing in many others. Only a few units were remaining free of such corrosion at TSP or sludge pile on top of TS. Additional remedies in chemistry, besides lowering the specification limits of impurities that reached the lowest feasible values, have been decided for units with alloy 600 MA.

After the year 2000, when most of steam generators with alloy 600 MA were replaced or scheduled to be replaced with alloy 690 MA in the medium term, the main focus of chemistry evolution was related to flow accelerated corrosion, corrosion transport and decomposition within the SG's. This means that intervention were more to optimise the use of alkaline reagent that continuing to permanently decrease the level of impurities entering the SG's, that was already very low in most countries [24].

1.9 Feed-water system history specific to Koeberg Nuclear Power Station

Koeberg also benefited from earlier steam generator experience in having stainless steel broached-quatrefoil tube support plates which avoided the problems of denting. Though Koeberg is generally classified as a copper-free system, there are a few copper-containing components in the secondary circuit which have affected the treatment decisions taken over the years. See Figure 1.5 to view a diagram of the Schematic PWR recirculating steam generator cross section.
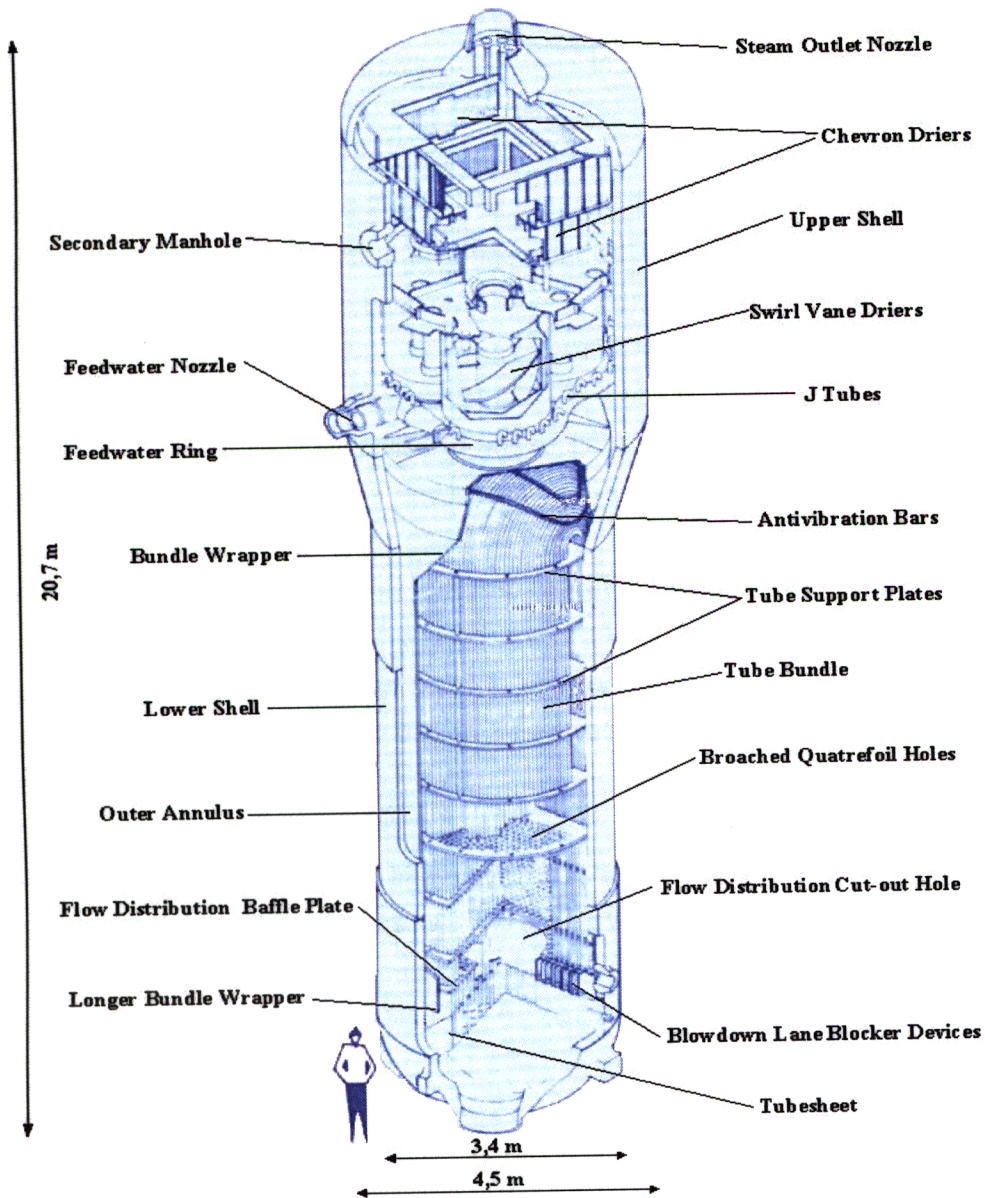
Figure 1.5: A diagram of a steam generator

Back in 1984 the original secondary circuit pH specification of the equipment manufacture's (OEM) was an operating pH range of between 8.8 and 9.2 and the system at Koeberg was thus commissioned at a pH 9.2. However, this was raised to pH 9.4 soon after start up. Originally condensate polishing was full flow but this was reduced to 1500 m^3/hr (40% of full flow) in 1986.

Condensate polishing is used at Koeberg Nuclear Power station to maintain the quality of the secondary circuit condensates at the level required for steam generators to operate satisfactory. The condensate polishing plant gives a very low degree of salinity (salt anions)

and a near to zero sodium content at the outlet. The performance of the plant is not affected by in-leakage of contaminants or polluting material into the condensate [26].

In the mid-80's, most Electricite de France (EdF) plants changed from ammonia to morpholine conditioning. Since Koeberg is a French-built plant and the EdF sister plant, it was considered at Koeberg but the Condensate Polishing Plant (CPP) resin regeneration frequency and cost would have been prohibitive if operation was to be maintained.

In 1989, the pH was raised further to pH 9.7 and it has been maintained at this level since then. At that time, condensate polishing was reduced to 1000 m^3/hr (27%). In early 1994 the CPP was placed in bypass mode, and it is now only used occasionally.

Pipe wall thickness measurements analysed by EdF using their CICERO code indicated that the increase to pH 9.7 had reduced the rate of flow-assisted corrosion (FAC) by approximately 50%. However, in order to reduce FAC to a level where most of the plant components would see out their design life, it was calculated that a further increase up to about pH 10 would be required.

The adoption of high all volatile treatment (AVT) was seriously considered for a number of years. The largest stumbling block was the difficulty of dispositioning the impact of such high levels of ammonia on the various copper-bearing components in the circuit. The most significant of these are:

- Condensate extraction pump impellers.
- Turbine gland steam condensers and
- Condenser air extractor condensers.

The final decision of the Koeberg Engineering Department was that comprehensive testing would first have to be completed on samples of these materials before they would give the go-ahead to raise the ammonia concentration - this would have resulted in both significant costs and a further lengthy delay.

This option has not been ruled out altogether. However, at that time Koeberg was concentrating on the testing with ethanolamine (ETA). Koeberg is currently using ETA for its feed water conditioning. The disadvantage of ETA is that it is an organic chemical which also contributes to the elevated cation conductivity (CC) in the steam generator [27].

1.10 Flow accelerated corrosion

Flow accelerated corrosion (FAC) also known as erosion-corrosion (EC) is a degradation mechanism that affects carbon steel (CS) piping carrying single phase, sub-cooled feed-water and steam lines carrying wet steam. The damage caused by FAC is higher than damage attributed to erosion or corrosion alone. CS feed-water piping corrodes during normal operation, forming a thin layer of iron oxide, mostly magnetite (Fe_3O_4), on the inside surface. This layer protects the underlying piping material from the corrosive environment, and in the absence of erosion, limits the corrosion rate. However, if stressors causing erosion are present, the layer of iron oxide will dissolve and the uncorroded metal surface will again be exposed to the corrosive environment, and piping corrosion will continue. Thus, the continuous process of oxide growth and dissolution leads to thinning of the pipe wall and ultimately to a catastrophic failure, when the pipe is subject to a pressure pulse of large magnitude [28].

FAC occurs under high flow rates, if the protective oxide layers on the surface of CS components and pipes cannot be maintained. The protective oxide layers are built on the CS surface by the reaction of iron ions, which are dissolved from the metal, with water at high temperatures. If these protective layers dissolve in an iron unsaturated fluid medium at the metal-fluid interface, or if iron ions released from the CS surfaces are immediately removed by a high flow, the protective layers cannot be built, and this results in the FAC degradation of CS components. Figure 1.6 presents a simple model describing the phenomena occurring during erosion-corrosion. The FAC mechanism, their stressors and parameters having influence on the development of FAC are well described in [A–B]. FAC will depend on the nature of the protective layer, which is dependent on the base material composition, the surrounding chemistry conditions and temperature. It has to be well understood that FAC is a two phase process: metal and water. In the case of steam flow, it can produce FAC following the above described mechanism only if a water film forms and flows on the metal surface (annular flow). The high steam velocities of typically 30 m/s 'push' the water film, increasing the velocity of the streaming water film on the metal surface. This is represented in Figure 1.7 although the water film has a lower velocity than steam, it results in higher than the usual linear velocities in pipes with single phase (liquid) flow. In the single phase-system a characteristic scalloped or orange skin shape surface appears whereas in two phase system a very thin oxide layer and the 'tiger striped' surface (Figure 1.8) are observed [29].
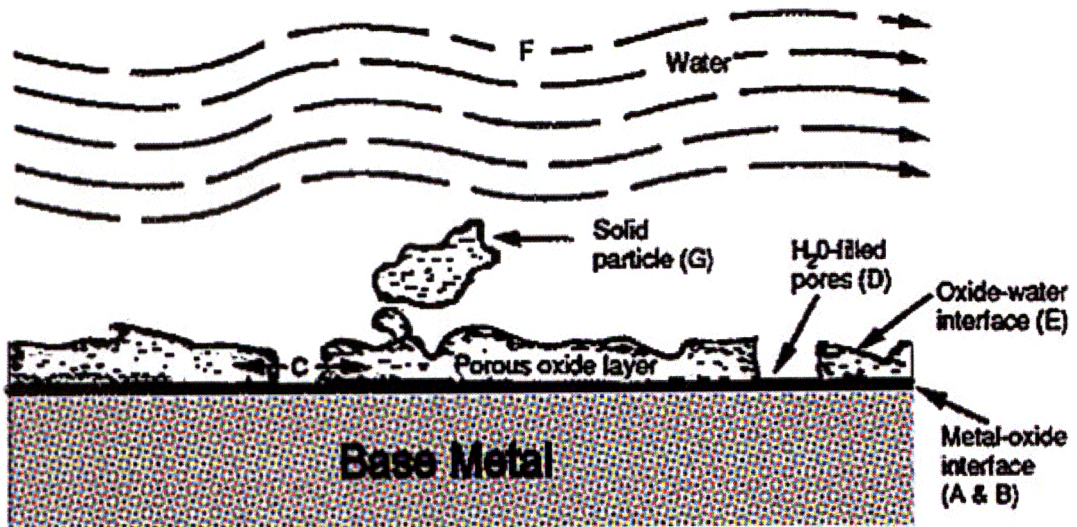
A. Iron hydroxides are generated: $Fe + 2H_2O \longrightarrow Fe(OH)_2 + H_2$

B. Magnetite is formed according to the Schikorr reaction:
$3Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2 + 2H_2O$

C. A fraction of the hydroxides formed in step B and hydrogen generated in steps A and B diffuse along pores in the oxide

D. Magnetite can dissolve in the pores

E. Magnetite dissolves at the oxide-water interface

F. Water flow removes the dissolved species by a convection mass transfer mechanism

G. Solid particles break off porous oxide layer by a mechanical erosion mechanism

Figure 1.6: Phenomena occurring during erosion-corrosion

SANCHEZ-CALDERA, L., Corrosion-Erosion in Steam Extraction Line of Power Stations, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge (1984).

Single-phase (water) flow   **Two-phase (water/steam) flow**
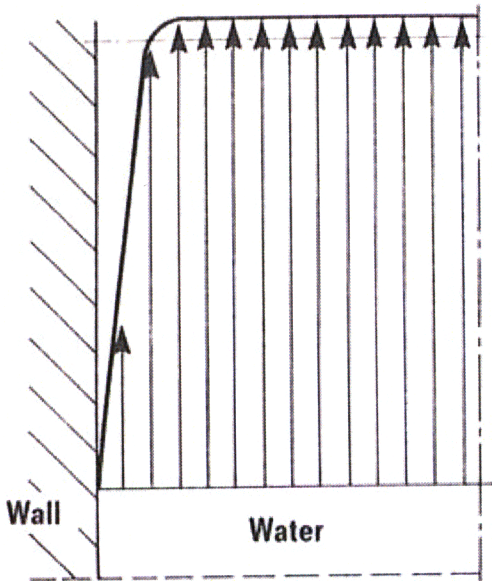
Reference velocity:
Mean velocity of the water
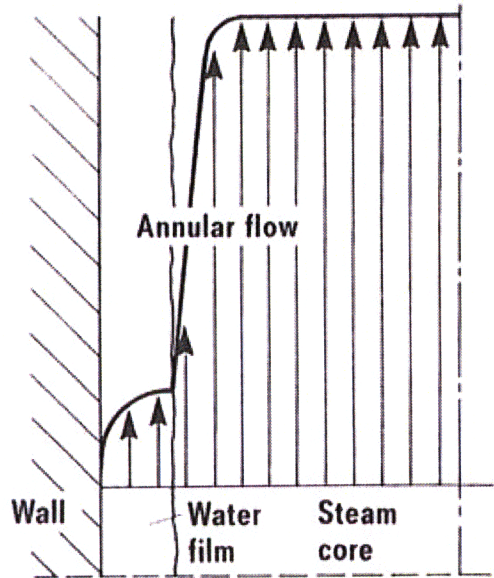
Reference velocity:
Mean velocity of the water film on
the component wall

Figure 1.7: Flow velocity profiles in single phase and two phases FAC [A]
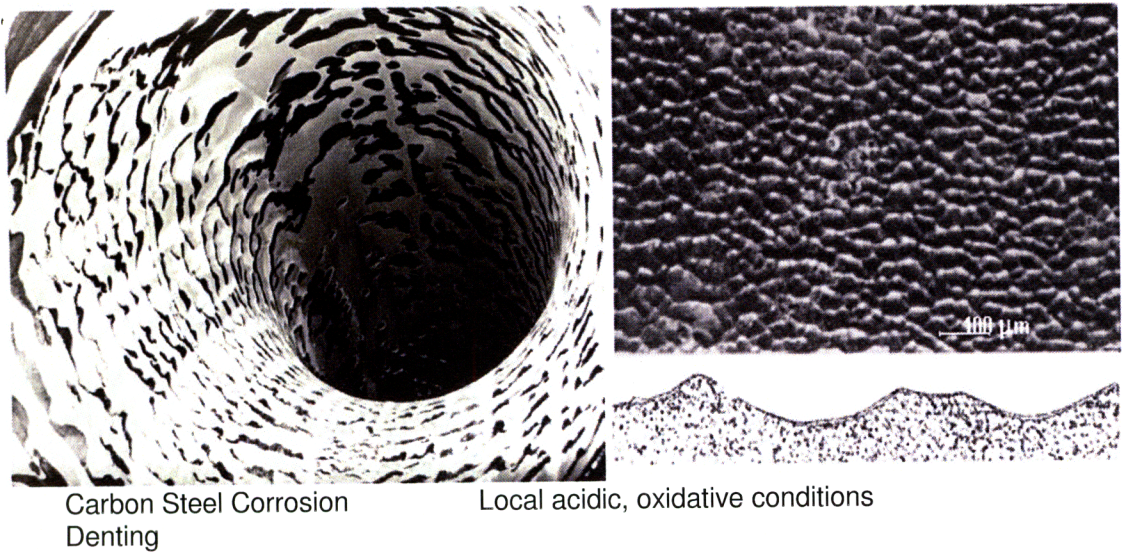
Carbon Steel Corrosion
Denting

Local acidic, oxidative conditions

Figure 1.8: Flow accelerated corrosion: pipe surface appearance [B]

CHAPTER TWO: LITERATURE SURVEY ON ORGANICS

In this chapter various papers are related to the research that had being conducted were read, summarised and conclusion are discussed and where similar work to Koeberg Nuclear Power Plant was observed that was highlighted on the concluding remark of each paper.

2.1 Survey on Organics

According to Rob Heijboer, Marga H. van Deelen-Bremer, Leo M. Butter and Andre G.L. Zeijseink from KEMA Power Generation & Sustainables.

It is well known that organic compound is cracked in the water steam cycle and affects the cation conductivity of the steam. KEMA and others demonstrated that the acid decomposition products like acetate and formate are enriched in the early condensate KEMA found strong indications that these organics played a role in a LP turbine blade failure. As a preventative measure future damages the Dutch Power Industry ordered KEMA to carry out research to assess the behaviour of organics in demineralisation plants based on ion exchange resins. On a survey that was done it appeared that not only the concentration of the organics (TOC) was different but also the composition.

The performance of the demineralisation plant is influenced by the quality of the raw water, not in the least by the composition of the TOC. The research revealed a seasonal influence on the TOC concentration and composition in the demineralised water after mixed bed. With the results they found it was easier to predict the possibility of operational disturbances and/or decreased make-up water quality.

They concluded that NOM/TOC concentration in raw water differs not only in concentration level but also in composition. Most of the NOM is removed in an IX resin demineralisation plant; however, the polysaccharide fraction is just partly removed and can contribute for about 50 % to the final TOC concentration in the produced demineralisation water. The PS-fraction is influenced by the season and hence the season will influence the final TOC concentration in the demineralisation water as well.

A PS model substance was removed by 30 % strong acid cation IX resin which is in a Ca^{2+} form. UV treatment after the anion filter in an IX resin demineralisation plant made it possible for 99% of the NOM/TOC to be removed in the feed water of the demineralisation plant.

This research by KEMA is relevant to KNPS and KNPS has also drafted a strategy on how to deal with water quality and the UV plant is one of the recommended suggestions to deal with organics at Koeberg. Koeberg has also observed the variation of TOC due to seasonal changes although this is not yet proven [30].

Rod Nashiem, Ram Davloor, Bill Harper, Kim Smith from Bruce Nuclear Power Station conducted a study in order to mitigate organically bound sulphate from water treatment plant and steam generator secondary side chemistry control at Bruce Nuclear Power Station.

The Bruce Nuclear Power Station is a source of more than 20 % of Ontario's electricity and it currently has six reactor units at the Bruce Nuclear Generating Station A (two units) and Station B (four units) stations located on Lake Huron. This paper discusses the challenges and operating experience gained in meeting WANO level 1 Chemistry Performance objectives for steam generator secondary side chemistry control, particularly with control of steam generator sulphate.

As a result of the problems experience a detail sampling and analysis program was conducted as part of this study and concluded that a major contributor to SG elevated sulphate in organically bound sulphate (OBS) in water treatment plant (WTP) effluent. The Bruce A and B water treatment plant (WTPs) consist of clarification with downstream sand and carbon filtration for lake water pre-treatment, which is followed by conventional Ion Exchange (IX) demineralisation. Samples taken from various locations in the process stream were analysed for a variety of parameters including both organic bound and inorganic forms of sulphate. The results were inconclusive with respect to finding the definitive source of OBS. This is primarily due to the condition that OBS in the samples, which are in relatively low levels, and is masked during chemical analysis by the considerably higher inorganic sulphate background. Additionally, it was also determined the on-line TOC level at different WTP locations did not always correlate well with OBS levels in the effluent, such that TOC could not be effectively used as a control parameter to improve OBS performance of the WTP operation.

Improvement efforts at both plants focused on a number of areas including optimisation of clarifier operation, replacement of IX resins, addition of downstream mobile polishing trailers, testing of new resins and absorbent, pilot-scale testing with a reverse osmosis (RO) rig, review of resin regeneration and backwashing practices, and operating procedure improvements. Both station reduced OBS levels from their respective water treatment plants. Bruce A made modification to the front end clarification process and replaced their old ion exchange (IX) resin. Bruce installed mobile trailers containing vessels filled with granular

activated carbon (GAC) and mixed bed resins (MB) for final polishing of the WTP effluent. They found significant reduction in the SG sulphate levels, resulting in the WANO Chemistry Performance Indicator (CPI) moving closer to the target value of 1.00. Steam generator chemistry improvement was most apparent in the hideout return studies, which displayed a dramatic reduction in sulphate levels, in addition to other constituents.

This work that was perform at Bruce is similar to what KNPS is doing which is to replace the IX resins. This project is almost complete because half of the resins have been replaced. KNPS is also facing similar challenges that Bruce Power Station has experienced with respect to WANO CPI which is currently at 1.04 at KNPS. It is anticipated that after the IX resin project is complete KNPS will be very close to the WANO CPI target value of 1.00. Just like at Bruce, KNPS has initiated a number of initiatives in order to deal with water quality of the Voëlvlei Dam and that includes monitoring TOC, replace GAC, replace IX, review the pre-treatment process and optimise the operating procedures [31].

Chemistry Perfomance Indicator (CPI)

The purpose of the chemistry performance indicator is to monitor operational chemistry control effectiveness. The indicator is based on concentrations of important impurities and corrosion products in selected plant systems by reactor and steam generator types and chemistry regimes, as appropriate The chemistry indicator combines several key chemistry parameters into a single indicator that can be used as an overview of the relative effectiveness of plant operational chemistry control.

The chemistry indicator compares the concentration of selected impurities and corrosion products to corresponding limiting values. Each parameter is divided by its limiting value, and the sum of these ratios is normalised to 1.0. For many plants, the limiting values reflect challenging targets. If an impurity concentration is equal to, or better than, the limiting value, the limiting value is used as the concentration. This prevents increased concentrations of one parameter from being masked by better performance in another. As a result, if a plant is at or below the limiting value for all parameters, its indicator value would be 1.0, the lowest chemistry indicator value attainable under the indicator definition. To ensure indicator stability, the limiting values will be periodically reviewed (every few years) to ensure they continue to represent challenging targets.

Gary Foutch and Allen Apblett reported on ion exchange resin fouling by organic amines in secondary systems at U.S. Nuclear Power Plants [32]. Their paper focuses on the research that was done by Oklahoma State University in August 2002, which investigated the resin degradation which is caused by ethanolamine.

Organic amines such as ETA added to power plant feed water to control iron concentrations have an impact on ion exchange resin performance. Several theories attempt to explain the cause. One such theory is that cation resin reacts with the amine, cleaving fragments, which then deposit on the anion exchange resin. The deposition blocks pores or permanently utilises exchange capacity on the anion resin, resulting in reduced exchange of impurities. Nuclear industry operators have recognized this phenomenon and are working with researchers to apply laboratory experience to improve plant performance. Ion exchange resins have been used for decades in nuclear power plants to help feed water purity requirements.

Much work has been done to try and understand the fouling mechanism that is apparently caused by the interaction of the resin with ETA. Some has been in the form of questionnaires and communication with various operators to understand conditions common to all those affected, some through cause and effect observations at the plants, some through process manipulation during plant operations, and some in the form of scientific research at various labs, including Oklahoma State University. Although it is believed that a general mechanism has been identified and conditions are known under which the fouling is more prevalent, there is still not a complete understanding of the condition or ways to prevent it.

Since not every plant experienced the fouling, differences could be examined between various plants. A survey was developed by EPRI and was distributed to various PWR's in the United States and Europe. It was extremely thorough and provided a significant amount of information that included the type of resin used, an overview of regeneration process, the condition under which the resin was operated, etc. The main observation that was apparent in plants that were experiencing fouling was that their condensate was operated at a high temperature. The significance of this was not known, but it appeared to hold true in all cases. Although the relationship between resins performance and condensate temperature is well understood, the relationship between high condensate temperature and degree of resin fouling caused by ETA was not understood.

More meetings were held regarding the resin fouling and its possible link to ETA, and plants collected data to help provide clues regarding the cause for fouling. Several plants collected data to help provide clues regarding cause for fouling. Several plants concentrated on

methods of removing the foulant to allow continued operation with ETA in the system, but there was not significant progress towards understanding the phenomenon. Test skid type research was conducted by nuclear plants in conjunction with several laboratories to compare the behaviour of resin in the presence of various amines. There was no formal research performed to attempt to understand the actual fouling mechanism until Oklahoma State University began a project in conjunction with EPRI.

Research concluded that there is a chemical reaction between ETA and the cation resin backbone, although the actual chemical reaction has not yet been confirmed. The use of macroporous resins may delay the effect of ETA, even though it should be expected that the reaction between resins and ETA will continue to take place. The reaction appears to involve the amine terminus of the pH control agent. There is synergism in the degradation of the anion resin that involves the cation resin. Both evidence of physical degradation as well as oxygen consumption demonstrated this. An alternate amine was suggested for future examination, N,N-dimethylaniline (NDEA).

Future work for Oklahoma State University

Although the industry knows more about the cause and effect relationship between resin and ETA, there have not been any significant breakthroughs in the past decade regarding methods to eliminate the problem. Making modifications to resins has helped lessen the effects or at least delay them from occurring, but the problem has not yet been resolved. For the plants that are affected by this phenomenon, it is costly and troubling. Minimising iron production from the secondary system is one of the highest priorities for plants and the choices of amines that are effective in this regard are limited. It will be difficult for plants to operate in this manner on a permanent basis, and the current situation needs to be viewed as a bridge to a better solution. Researchers and plants must continue to work together to find a solution. It is up to the plants that are most impacted by this to continue to bring attention to it so that it is not forgotten [32].

KNPS is also using ETA to control iron concentration. Plant chemist has also observed fouling at KNPS and as a result of that they are investigating the cause of the fouling together with Eskom microbiologist and recommendation to clean the pipe section that is fouled have been implemented. This work that is discussed at this paper is related to KNPS.

According to Guy W Hurtchinson (BNFL), Keith Garbett (Consultant) and Nigel J Drew (Nexia Solution Ltd) on paper titled: Concentration of organic carbon and THM in feed water of a Nuclear Power Plant, their work discusses the experiments that were performed at

United Kingdom Magnox coastal power station between September 1999 and September 2002. United Kingdom Magnox coastal power station operated for 25 years and organic fouling of the CPP resins, leading to impaired anion resin kinetics which was observed [33]

The station began to experience some on-load corrosion boiler tube leak by a source of halide. Sources of the organics material were investigated and THM were identified in the station 'Town's Water' supply. Seasonal variations, the change in concentration through the make-up water treatment plant and in the steam/water circuit were investigated. Approximately 4% of the TOC and 80% of the THM passed through the water treatment plant with some of the remaining THM breaking down in the once-through boiler, in this case releasing halide into the boiler. This requires palliative measures for boiler alkalisation and an upgrade to water treatment plant.

This station was using 2-amino-2-methylpropan-1-ol as the alkalising agent, until 1992 when this alkalising agent was replaced by 5-aminopentanol. Both amines produce small amount of acetate and formic acid as decomposition products during operation. The kinetics of resins in the CPP must also be monitored because of the effect from long–chain organic acids [33].

This work relates to KNPS in a sense that the THM have also been identified at KNPS and hence the identification and quantification of organics research have been conducted. However KNPS is using ETA and not 2-amino-2-methylpropan-1-ol like UK Magnox coastal power station.

Robert Svoboda, Frank Gabrielli, Herber Hehs, Hans gunter Seipp, Frank-Udo Leidich and Bruce Robert worked on organic Impurities and organic conditioning agents in the steam / water cycle [34].

They state that power plant is designed to run with pure water and steam and that for a simple cycle no other products would be required. If organics additives are used, the possible side effects have to be carefully monitored. Organic impurities in the steam / water cycle originate from the make-up water and, to a lesser degree as residues from erection and maintenance. None of these impurities will improve functionality in the steam / water cycle and what remain will be detrimental effects. Organic amines degrade to ammonia, carbon dioxide, and short-chain carboxylic acids. Organic oxygen scavengers degrade to carbon dioxide and organic acids. Organic dispersants and chelants degrade to organic acids.

With this, such product must be considered corrosive. Volatile low-chain carboxylic acids, like acetic acid, can reach the whole steam / water cycle. At lower temperatures, they are less

volatile, and will condensate together with water. The first condensate can have a high concentration of such impurities. Depending on the condensation of the conditioning agent, high concentration anionic impurities may lead to a low local pH. Only carbon dioxide seems to give negligible influence on the pH at the temperature of steam condensation. Depending on their distribution coefficient, acidic products may also stay to a certain degree in the boiler water and concentrate at the site of evaporation. If the boiler water does not have sufficient alkaline buffering, low-pH condition may also occur. Acidic degradation no matter if harmless or not, will show up increased cation conductivity. Such an increase in background is impairing the value of the cation conductivity monitoring, increase the risk of missing other chemistry incidents.

Another problem that was observed is the fouling that is caused by organic matter on the IX resins, mostly in the make-up water treatment plant, but also in condensate polishers. Organic matter may also form a precipitate, or together with particles like iron oxides agglomerate to an adhesive sludge. Such can impair heat transfer glog strainers and instrument lines and offer an environment for corrosion under the deposit.

From the manufacture point of view any organic matter in the steam water cycle brings the risk of detrimental side effects and should thus be avoided, unless organic matter is necessary, for example in certain process steam systems.

All this work relates to KNPS because some of the findings in this work have been experienced and are still being investigated by Plant Chemistry Section.

According to David M. Gray on his paper titled "Measurement of organics in power plant make-up water treatment"

Most efforts at producing pure water have focused on removing minerals, with processes that do not necessarily remove organic compounds. There is increasing awareness of the problems that organics can cause in the power plant cycle and this can drive changes in water treatment methods. A key to confirming and trouble-shooting organics removal processes is a reliable TOC (total organic carbon) measurement.

Organic contamination of pure power plant waters can cause a number of costly problems. It can foul resins in make-up and condensate deionizers and require more frequent resin cleaning and replacement. It can break down to organic acids that lower the pH of early condensate and cause turbine corrosion. It can deposit along with other contaminants into the heat exchange surfaces and significantly reduce efficiency. It can cause foaming in boiler

drums and increase carryover of other contaminants into the steam. Organics are a concern in plants where any of these problems occur. Measurement of TOC concentration is the first step in its reduction.

The major source of organics is make-up water. Surface waters have higher levels of naturally occurring organics than ground waters. But ground water sources are being depleted in many areas of the globe. As a result, there is greater reliance on surface water, reclaimed water and even municipal wastewater as the raw source for high purity make-up water for the water/steam cycle. A further complication is that surface water sources typically have significant seasonal variations in concentration and types of organics. A treatment system that can produce water with low organics during one season may be seriously challenged in another season.

A second source of organics can be from ion exchange resins in the treatment system. They are after all, organic polymers. Resin fines from physical breakdown can find their way into the steam cycle if they are not trapped. Chemical breakdown of resins even in their vessels can produce trace contaminants: predominately sulfonic acids from cation resins and amines from anion resins. In addition, traces of processing solvents may be released from new resins.

Conductivity is the common and economical measurement for detection of ionic contaminants usually minerals. Conductivity will detect organic acids and bases but it is insensitive to the majority of other organic contaminants. For this reason, TOC analysers oxidise organics to carbon dioxide that can be detected. In its ionic form, carbonic acid is readily detected by conductivity in pure waters. The increase in conductivity after oxidation gives a measure of the amount of carbonic acid produced. With proper correlation and calibration, it provides readout as ppb TOC.

While the need for TOC measurement has been increasingly recognised in the past two decades and instrumentation has been made available, the high cost and maintenance requirements of previous TOC analysis equipment have limited the use to a very few measurements. The introduction of a simple, low maintenance sensor used with multichannel multiparameter instrumentation makes TOC measurement more widely accessible [35].

KNPS has also started measuring TOC in the water production plant and also the source of organics is in the make-up water. KNPS specification procedures have been updated also to monitor the TOC on a regular basis. The work discussed compliments the finding that KNPS have observed.

In the study that was conducted by EPRI on Side-by-Side Comparison of Techniques for Analysing Organic Acids, Total Organic Carbon and Anions.

The objective of the study was to compare the organic acids sampling and analysis methods of Westinghouse and NWT Corporation. Sampling was performed at three sites, chosen to represent units with high, intermediate and low levels of organic contamination. To check the precision of each method, concurrent sampling was employed. To check the accuracy of each method, additions of standard organic solutions were made at one of the sites. Inorganic anions were also analysed at each site by each contractor. Theoretical values of cation conductivity were calculated from organic and inorganic analytical data and compared to values measured onsite at the time of sampling. TOC analyses were performed to evaluate different instruments and sampling techniques, as well as to provide additional information on the relationship between TOC and organic acids concentrations.

The method of weak acids is important for interpreting cation conductivity and understanding water chemistry as it pertains to material corrosion. The sampling methods used by Westinghouse and NWT for measuring trace levels of formic, acetic, propionic, carbonic and hydrofluoric acids in nuclear secondary cycles have been cross-tested and found to be accurate in the concentration range tested (2 to 160 ppb).

TOC is useful for estimating the bulk organic content of high-purity water and for trend analysis of organic contamination. Unexplainable discrepancies were found in the TOC levels determined by two instruments, the DC-80 and the OI 700. More will have to be known about the nature of neutral organics in nuclear plant secondary cycles before further verification of TOC techniques can be performed. Even when extreme care was taken, both NWT and Westinghouse were unable to reduce contamination during grab sampling to a point where it did not contribute significantly to the total organic content. As a result, on-line sampling is recommended when possible for performing TOC analyses.

It was concluded that neither of the organic acid sampling/analysis techniques used by the contractors can produce reliable results. TOC samples lose organic content with storage time and should be analysed no later than one week after they are taken, if at all possible, they should be stored in a refrigerated condition. State of the art techniques for TOC sampling and analysis can produce results varying by 20 to 50 ppb for levels in the range of 50 to 120 ppb, any proposed limits for TOC should be reviewed in that light. Results of anions analyses are quite sensitive to sampling and analytical techniques. Reasonable agreement between

calculated and measured values of cation conductivity suggests that both contractors had accurately determined all major anionic species [36].

The work that is discussed on this paper is also applicable to KNPS because cation conductivity is also measured at KNPS and it has been observed that is increases as the concentration of organic such as acetate, formate, oxalate and glycolate increases. All these organics contribute to total organic carbon.

On Friday, November 8, 1974, Russell E. Train, Administrator of the US environmental Protection Agency announced that he was ordering an immediate national survey to determine the concentration and potential effects of certain organic chemicals in drinking water. Part of the survey was to sample for trihalomethanes, carbon tetrachlorides, 1,2-dichromoethane. Because of the relevance of this work to KNPS, this work conducted on the survey will be discussed below.

For the survey six compounds were chosen for study, these compounds were known to be volatile, as a result of that a sampling procedure was chosen that would provide for minimum loss of the six compounds from the water to the atmosphere while the sample was in shipment or awaiting analysis by the purging technique. The container chosen were 50 ml "hypo-vial" sealed with Teflon-faced "Tuf-bond" discs, both available from Pierce Chemical Co.,Rockford, 111.

Before use, the glass vials were capped with aluminium foil and muffled at 400 °C for at least one hour to destroy or remove any organic matter interfering with analysis. With aluminium foil still in place, the bottles were packed (along with sufficient discs and aluminium seals to secure the discs in place, labels, and re-usable ice packs) in an insulated container and shipped to the appropriate regional office for sampling. Sufficient materials were provided for taking three raw and three finished – water samples. In the field, the vials were filled, bubble-free, to overflowing so that convex meniscus formed at the top. The excess water was displaced as the disc was carefully placed, Teflon side down, on the opening of the vial and crimped into place. A sample taken and sealed in this manner was completely headspace-free at the time of sampling. Usually a small bubble would form during shipping and storage, however. The sample that were collected from the 80 location from late January to end of april 1975, were labelled appropriately, repacked with frozen ice packs in the original insulated container, and returned via air mail to the water supply research laboratoty in Cincinnati. Upon receipt at the laboratory, the samples were refrigerated until analysed. Analytical method for chloroform, bromodichloromethane, bromoform, carbon tetrachloride, and 1.2-dichloroethane. The sample concentration procedure chosen for the initial step of

identification and measurement of the six volatile halogenated organics was used. In this procedure, the sample is purged with an inert gas that is passed, in series, through an adsorbed material that traps and concentrate the organic material of interest. The organics are then desorbed from the trapping material by heating under a gas chromatography (GC) column. Separation is then carried out with temperature programming [37].

As discussed earlier this work is relevant to KNPS, see appendix A to see KNPS procedure used to take trihalomethanes samples.

CHAPTER THREE: AN ORGANIC PROFILE OF KNPS SECONDARY PLANT

In this chapter, an organic profile at KNPS secondary plant, ion exchange, effect of total organic carbon on cation conductivity, conductivity and cation conductivity application in a power station, cation conductivity balance, chloride content of demineralized water and trihalomethane results will also be discussed.

3.1 An organic profile of KNPS secondary plant

Make-up water addition to the steam/water cycle at KNPS usually results in a corresponding increase of the chloride concentration in the SG blowdown system. During plant transients, when higher than normal make-up is required to the secondary plant, the concentration of chloride occasionally exceeds the limiting value for the WANO CPI. Irrespective of this, the demineralised water make-up supply tanks that are routinely analysed for chloride are within all recognised acceptable standards for secondary water make-up and therefore these tanks do not initially appear to be the source of chloride contamination.

Water treatment at the plant relies essentially on ion exchange which has been proven to be very effective in removing inorganic ionic species such as chloride. Organic compounds are less effectively removed by ion exchange and they pass through the treatment system and these organics reside undetected in the make-up water tanks. Historically, the elevated chloride concentration following high system make-up has been attributed to chlorinated organic compounds known as trihalomethanes being present in the make-up water tanks but no rigorous study has previously been undertaken.

It has been suspected that the majority of chloride in the secondary system originates from the organic impurities in the make-up, it was considered important to confirm this by compiling an organic profile of the secondary plant. The use of organic additives such as ethanolamine was also taken into account in the profile.

It is possible for organic material to enter the steam / water cycle of a power station in a number of ways. Make-up water, chemical additives and ion exchange resin leachates are the usual sources of organics entering the system during normal power operation. Other sources include cleaning agents, lubricants, bacteria and condenser leakage that can enter the steam / water cycle by contamination during outages or damaged plant during operation.

Although the steam / water cycle is a closed loop, water and steam is lost by imperfections in design and construction, material degradation and defective components. Normal operation includes interventions that occasionally require or result in a loss of steam and / or water from the secondary system. From several strategic positions on the secondary cycle on both the water and steam lines, continuous sample flows via the sampling system to the on-line analysers and grab sampling points. All of these operational losses of steam and water require the secondary system to be replenished. Make-up water is the source of natural organic matter (NOM) that enters the system during normal operation [38]. Water treatment that includes chlorination causes the formation of trihalomethanes (THM) and more specifically organochloride such as chloroform as a product from reaction of chlorine with NOM and microorganisms [39].

THM break down under the plant thermohydraulic conditions resulting in the increase of the chloride ion concentration. Chloride in contact with metal surfaces has a detrimental effect on the structural integrity for power plants. Inconel, a metal alloy consisting of nickel, chromium and iron, is used for the manufacturing of steam generator tubes of PWRs worldwide because of its physical properties. SG tubing is by far the most vital component of this type of nuclear power plant and Inconel is susceptible to chloride induced pitting corrosion. Chloride also causes stress corrosion cracking in austenitic stainless steels that constitute the balance of the plant systems [40]. For these reasons it is imperative that plant chemists must continue to strive to keep the chloride concentration as low as achievable.

Chemicals are added to the secondary circuit with the intent to establish the most favourable chemical conditions that will mitigate plant degradation by limiting corrosion mechanisms. It is usual to have additives that control pH and dissolved oxygen in the secondary system of a PWR. Historically inorganic additives such as trisodium phosphate and later ammonia have been used to control pH. Recent developments have established that organic amines (advanced amines) have superior properties and are often the preferred additive. Plants that use advanced amines, added to the organic loading, have consequences that are important to consider.

In power plant chemistry ion exchange (IX) resins are used to remove impurities from the process water. IX is extremely effective for inorganic ionic species but organic compounds are not as readily retained. These IX resins are organic polymers and under certain physical and chemical conditions break down results in leaching of organic material into the process water and increasing the organic load.

3.2 Ion exchange

Salt, by chemical reaction, is what is formed as a result of the reaction of acid and a base, such as hydrochloric acid reacting with sodium hydroxide to form salt and water.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$
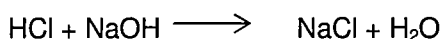
Sodium chloride (table salt) in its crystalline form when added to added to water dissolves and cannot be seen in the water. The dissolving process causes the sodium to dissociate from chloride and now the positively charged sodium ion is free to move in the water more independently from negative charged chloride ion than when they were in the crystalline solid state.

$$NaCl \longrightarrow Na^+ \text{ and } Cl^- \text{ (dissolved in water)}$$

The same would happen with other salts as they dissolve into water solution, becoming positive ions and negative ions.

Once the definition of ion is understood, the term ion exchange is rather simple, since it means that one ion in solution is exchanged or replaced by another. If both ions were in a water solution there would be no exchange, since they both would be free to move around in the water solution and nothing would be removed or replaced. It is only when one ion attached to an insoluble solid and the other is in solution that an exchange or replacement can be carried out. The fact should be pointed out that an ion exchange can only be carried out with ions of the same charge, that is, positive ions for positive ions, or negative ions for negative ions.

The earliest reported and verified studies on ion exchange took place in the mid-1850s. The work of Thompson and Way showed that when soil were treated with ammonium sulphate or ammonium carbonate, most of the ammonium ion (NH_4) was absorbed and calcium ion (Ca^{+2}) was released. This ion exchange reaction explains how ammonia fertilisation of soils is accomplished to allow plant growth. The aluminium silicates present in the soils were found to be solid, insoluble substance responsible for holding the ions exchange minerals or substance.

For the majority of application of ion exchange resin water treatment, it is necessary to know what ion and how much or what concentration of each presents [41].

For this work, water samples of the secondary cycle from KNPS have been analysed to gain better understanding of the overall effect of organic material on the system chemistry. During normal plant operation sources include NOM, chemical additives and IX resin leachates. This work focuses on the analysis and profiling of organic material entering the system during normal operation with more specific focus on THM because of its potential detrimental effect on the plant construction materials.

3.3 Effect of total organic carbon on cation conductivity

The most commonly used analytical technique to define the level of organics in water is total organic carbon (TOC). Analysis was performed using a Seivers 900 TOC analyser at certain strategic points in the water cycle to develop a profile which has never been previously done at Koeberg Nuclear Power Station. See Tables 3.1 to view the organic profile results.

System	Sample Discription	TOC in ppb	Acetate in ppb	Formate in ppb	Glycolate in ppb	Oxalate in ppb
SEP	Upstream of Charcoal filters - SEP Supply	2040	8.21	45.02	93.31	0.01
SDA 001 FI	Charcoal Filter - 001FI	933	14.95	0.85	102.12	655.49
SDA 002 FI	Charcoal Filter - 002FI	1110	17.33	1.07	112.89	716.81
SDA D/S chaorcoal	Downstream of Charcoal filters	1113	16.59	0.81	107.83	688.14
SDA 101 EX	Cation Exchange vessel	1130	1.25	0.62	125.59	462.18
SDA 102 EX	Anion Exchange vessel	38.6	0.11	0.38	1.72	0.01
SDA 103 EX	Mixed-bed Exchange vessel	43.2	0.13	0.46	0.35	0.03
SER 001 BA	Demineralised Water pH 9.5	44.5	0.19	0.56	0.35	0.13
1 CEX	Condenser Extraction system	1420	2.78	0.93	0.77	0.02
1 AHP	Feedwater heater drains recovery system	2231	5.98	3.55	1.51	0.12
1 VVP	Main steam system sample	2230	5.67	3.34	1.39	0.11
1 ACO	Drain Recovery System	4471	10.05	6.67	2.65	0.12
1 APG 001 GV	Steam Generator Blowdown System	5910	13.6	13.93	45.7	0.3
1 APG 002 GV	Steam Generator Blowdown System	5760	13.26	10.08	37.27	0.14
1 APG 003 GV	Steam Generator Blowdown System	5860	12.88	10.48	38.49	0.09

Table 3.1: Organic profile from the SEP system into the Steam Generator, 09 September 2011
The anion profile chromatograms are attached on Appendix G

3.4 Discussion and interpretation of the results in Table 3.1

A method to determine formate, acetate, glycolate and oxalate was developed using Ion Chromatography (IC). Once the method was developed the IC was calibrated, see appendix E, to view the calibration curve of the standards that were used to quantify and identify the organic species.

A method to determine formate, acetate, glycolate and oxalate was developed by procuring a different IC columns (Analytical Column AS-15, 2 x 250 mm, Guard Column AG-15, 2 x 50 mm and Concentrator Column AC – 15 4 x 50 mm) and these column enable separation of organic anions along with inorganic anions. The organic profile has shown that there is a relationship between total organic carbon (TOC) and other organic species such as acetate, formate, glycolate and oxalate.

The source of the total organic carbon in the upstream of the charcoal filters and downstream of the charcoal filters is natural organic matter from the dam.

Total organic carbon decreased by 54 % from upstream of charcoal filters – SEP supply to charcoal filters which implies 54 % of total organic carbon was removed by the charcoal filter, however, It was also observed that the acetate, glycolate and oxalate did not decrease as expected on the charcoal filters and also on the downstream of the charcoal filters which is an indication of gradual exhaustion of charcoal filters. The exhaustion of charcoal filters may require the filters to be replaced on regular basis.

It was also observed that the TOC value on the cation exchange vessel from downstream of the charcoal filter increased slightly which is an indication of the cation being exhausted and contaminated with organics species. This exhaustion will require the cation resin to be brine watched from time to time.

Total organic carbon value on the anion exchange vessel decreased by 97 % from the cation exchange vessel which indicate that the anion was removing majority of organics species. It was also observed that other organic species such glycolate and oxalate decreased by more than 99 % on the anion exchange vessel, this is expected for these species because the TOC comprise of various other organics i.e. THM, inorganic carbon, acetate, formate, glycolate and oxalate.

The ethanolamine (ETA) is added via chemical reagent injection system as a functional additive to increase the pH on the secondary circuit and as a result of that the TOC

increased when ETA was injected. The TOC is expected to increase when the ETA is added because ETA is an organic molecule.

As a result of ETA that was added to the secondary circuit it was observed that the TOC increased by 75.8 % from condenser to the steam generator whereas Acetate increased by 80 %, Formate by 93 %, Glycolate by 98 % and Oxalate by 93%. All of these organic species contribute to the cation conductivity in the steam generator. Previously organics species were not measure at Koeberg Nuclear Power Station. This was also the main reason for this project to be conducted so that all organics species that affects the cation conductivity are identified and quantified.

3.5 Conductivity and Cation Conductivity application in a Power Station

At Koeberg Nuclear Power Station a cation conductivity (CC) is used to determine water quality and as an indications of the amount of ionic impurities present in water. At KNPS cation conductivity is a measure of conductivity of the sample that is passing through a cation resin column in the H^+ form. This provides a good indication of condenser tube leaks. Condenser tube leak is the ingress of sea water that leaks into the condenser and eventually into the steam generator. The sea water contains high concentration of sodium, chlorides and sulphate and these species are harmful to the plant because they will cause stress corrosion cracking into the steam generator. It is therefore undesired for the power station to have condenser tube leak and hence the cation conductivity measurement is consider to be important.

The steam generator blowdown at KNPS is bound by operating technical specifications. In accordance with operating technical specifications out of specification cation conductivity results on the steam generator blowdown will require the unit to fall back to the limiting condition of operation (LCO) within a specified time. Failure to accomplish this would violate Koeberg's license to operate.

It is therefore important to report these analyses accurately. Although a cation conductivity analysis appears to be a simple, straightforward determination, complacency towards this measurement can easily result in inaccurate results, which could have detrimental effects on the long-term integrity of the plant. By quantifying CC, it is possible to highlight potential problem areas. This is an important aspect of Chemistry's programme of effective, pre-emptive chemistry control at KNPS and thus preventing out of specification conditions and promoting a healthier plant with an extended lifespan is encouraged.

<u>Conductivity (K_{25}):</u>

Conductivity is the conductance of a solution measured at 25°C between two electrodes, which are 1 cm^2 in area and 1 cm apart.   Conductance is proportional to the ionic

concentration of an aqueous solution; conductivity can be used to determine water purity. Each ion has its specific limiting ionic conductivity as represented in Table 3.1 [42].

In a direct current field the positive ions migrate toward the negative electrode, while the negatively charged ions migrate toward the positive electrode. Most inorganic acids (e.g. HCl), bases (e.g. Na_2CO_3) and salts (e.g. NaCl) are relatively good conductors. Conversely molecules of organic compounds such as sucrose and benzene that do not dissociate in aqueous solution, conduct a current very poorly, if at all.

Conductivity is a numeral expression of the ability of an aqueous solution to carry an electric current. This number is dependent on the total concentration of the ionised substances dissolved in the water and the temperature at which the measurement is made. The mobility of the various dissolved ions, their valences, and their concentrations affect conductivity [43].

Cations	$l_+^\circ\ 10^{-4}\ m^2\ S\ mol^{-1}$	Anion	$l_-^\circ\ 10^{-4}\ m^2\ S\ mol^{-1}$
H^+	349.8	OH^-	198.3
Na^+	50.1	F^-	55.4
K^+	73.5	Cl^-	76.3
Li^+	38.7	Br^-	78.1
NH_4^+	73.5	I^-	76.8
Ag^+	61.9	NO_3^-	71.5
Tl^+	74.7	ClO_3^-	64.6
$\frac{1}{2}Ca^{++}$	59.5	ClO_4^-	67.4
$\frac{1}{2}Sr^{++}$	59.5	BrO_3^-	55.7
$\frac{1}{2}Ba^{++}$	63.6	IO_3^-	40.5
$\frac{1}{2}Mg^{++}$	53.1	IO_4^-	54.6
$\frac{1}{2}Zn^{++}$	52.8	HCO_3^-	44.5
$\frac{1}{2}Pb^{++}$	69.5	$\frac{1}{2}CO_3^{--}$	69.3
$\frac{1}{2}Cu^{++}$	53.6	$\frac{1}{2}SO_4^{--}$	80.0
$\frac{1}{2}Co^{++}$	55.0	$HCOO^-$	54.6
$\frac{1}{2}Fe^{++}$	54.0	CH_3COO^-	40.9
$\frac{1}{2}Ni^{++}$	53.0	$\frac{1}{2}C_2O_4^{--}$	74.2

Table 3.2: Limiting Ionic Conductivities

<u>Cation Conductivity (CC)</u>:

The sample stream is passed through a column of cation exchange resin in the hydrogen form where the cations present in the sample are removed and replaced by an equivalent amount of hydrogen ions [44]. Dissolved salts originally in the sample e.g., NaCl are converted to their corresponding acids, e.g. HCl. When a NaCl solution is passed through the column, the Na^+ will exchange with the H^+ from the resin, since the metal ion (Na^+ in this example) has a greater affinity for the resin.
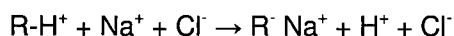
R-H^+ + Na^+ + Cl^- → R^- Na^+ + H^+ + Cl^-
[R – Resin Matrix]

The conductivity cell measures the conductivity due to HCl. The amount of HCl is equivalent to the amount of NaCl that was initially present. The purpose of this salt to acid conversion is that an acid has a much higher conductivity than the same concentration of the corresponding salt, and when measuring sample streams of high purity, this amplification of the conductivity enhances the ability to detect low levels of contamination. The reason that the acid, in all cases, will have a higher conductivity is because of the higher relative ionic conductance of the H^+ cation when compared to other cations (Table 3.2).

Accuracy and use of the CC balance at KNPS

The accuracy and use of the CC balance was tabled and discussed at the Chemistry Technical Review Committee Meeting, May 2010. From the Chemistry Technical Review Committee minutes, the issue was described as follows [45]:

"The '*cation conductivity CC vs. anion balance*' includes the calculation of the theoretical CC based on the anions present in the sample. At KNPS, it was developed for a 'pure' NH_3 regime in the secondary circuit, and therefore, does not account for ethanolamine (ETA) and its breakdown products formed under the conditions in the secondary circuit. Hence, in theory the $CC_{calculated}$ should always be less than the measured value, which is mostly the case, but the opposite is observed on occasion.

At Koeberg Nuclear Power Station it has also been observed that the discrepancy between the calculated and measured cation conductivity (CC) is not constant, but variable depending on a number of parameters on the plant. The following questions were raised:

- Should the discrepancy be constant?

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- What factors could influence the disagreement between the calculated and the measured CC value, and which of these could cause a variation over time?
- Is the calculation still of value?
- Should the rationale behind the variation in results, and the value of the calculation be documented?

The KNPS chemistry technical review committee requested that the rationale for the discrepancy to be documented and the usefulness of the calculation to be evaluated.

The following was an attempt to address the above described issue and to explain the underlying principles that result in the discrepancies observed between the manual and on-line cation conductivity measurement in the steam generator blowdown samples at KNPS.

3.6. Cation Conductivity Balance:

If the concentration of each anion in solution downstream of a cation ion exchange resin column (in the hydrogen form) is known, the cation conductivity can be calculated from the concentrations of each anion using the respective limiting ionic conductivities in Table 3.1 and the equivalent calculated H^+ concentration.

The equivalent conductance at infinite dilution is related to the ionic conductances as follows:

$$\Lambda\infty = \lambda^\circ_+ + \lambda^\circ_-$$

Where λ°_+ and λ°_- are equivalent ionic conductivities of the positive and negative ions.

The equivalent conductance of infinite dilution is related to the specific conductance and the concentration of electrolyte as follows:

$$\Lambda\infty = \frac{1000\ K}{C}$$

Where K is the specific conductance and C is the concentration mol/Kg.

The specific conductance for each anion can thus be calculated for each ion when this equation is adjusted to include the gram equivalent weight (formula mass divided by the ionic charge) of the relevant anion.

For example, the gram equivalent weight of Cl^- is 35.4 g/mol and SO_4^{2-} is 96.0 g/mol (divided by ionic charge = 48.0), as can be seen in the following equations. Multiply the factor by 1.00

x 10^{-6} to convert the gram equivalent weight in grams (g) to micrograms (μg). The same applies for all the factors.

$$K = \frac{\Lambda\infty \times C \times 10^6}{1000}$$

For Chloride:

$$K = \frac{(349.8 + 76.3) \times C \times 1.00 \times 10^6 \times 1.00 \times 10^{-6}}{1000 \times 35.4}$$

$$\therefore \quad K = 0.0120 \times C$$

For Sulphate:

$$K = \frac{(349.8 + 80.0) \times C \times 1.00 \times 10^6 \times 1.00 \times 10^{-6}}{1000 \times 48}$$

$$\therefore \quad K = 0.00895 \times C$$

For a solution containing 20 ppb chloride and 15 ppb sulphate, the calculated CC will be = (0.0120 x 20) + (0.00895 x 15) μS/cm

= 0,37 μS/cm.

The CC balance is the comparison between the measured CC value and the value calculated from the specific ionic conductivities of the ions present. It can serve as an integrity check for the measured value.

Ethanolamine effect on Cation Conductivity balance

Ethanolamine (ETA) secondary chemistry regime results in a higher measured CC than an ammonia regime. This is as a result of the relatively high organic acid concentration from the thermal hydrolysis and oxidative breakdown of ethanolamine.

Dauvois et al described the breakdown of ETA as follows [46]:

$OHCH_2CH_2NH_2$
Ethanolamine

NH_3 $\quad$ CH_3NH_2 $\quad$ $C_2H_5NH_2$ $\qquad\qquad$ $OHCH_2CH_2OH$
Ammonia $\quad$ Methanamine $\quad$ Ethanamine $\qquad$ Ethylene Glycol

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$\downarrow$ $\qquad$ $\downarrow$

CH$_3$CH$_2$OH $\qquad$ OHCH$_2$CO$_2$H

Ethanol $\qquad$ Glycolic Acid

$\downarrow$ $\qquad$ $\downarrow$

CH$_3$COOH $\qquad$ HO$_2$CCOOH

Acetic acid $\qquad$ Oxalic acid

$\qquad\qquad\qquad\qquad$ $\downarrow$

$\qquad\qquad\qquad\qquad$ HCOOH $\qquad$ + CO$_2$

$\qquad\qquad\qquad\qquad$ Formic acid
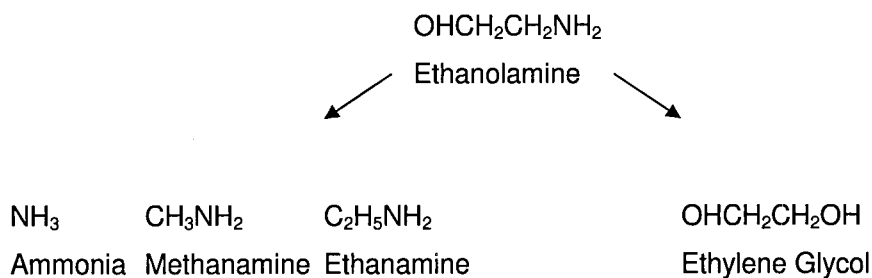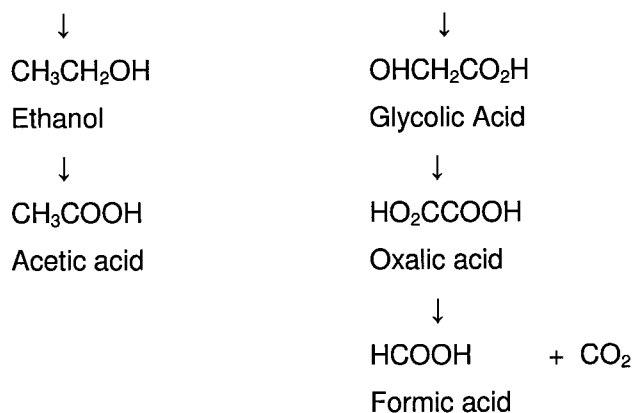
This means that the possible ion pairs in the secondary water treated by ETA can be predicted as follows:

C$_2$H$_5$ONH$_2$ + H$_2$0 $\qquad$ $\leftrightarrow$ $\qquad$ C$_2$H$_5$ONH$_3^+$ + OH$^-$

ETA $\qquad\qquad\qquad\qquad\qquad$ ETA cation

NH$_3$ + H$_2$0 $\qquad\qquad$ $\leftrightarrow$ $\qquad$ NH$_4^+$ + OH$^-$

Ammonia $\qquad\qquad\qquad\qquad$ Ammonium

CH$_3$NH$_2$ + H$_2$0 $\qquad\quad$ $\leftrightarrow$ $\qquad$ CH$_3$NH$_3^+$ + OH$^-$

Methanamine

C$_2$H$_5$NH$_2$ + H$_2$O $\qquad\quad$ $\leftrightarrow$ $\qquad$ C$_2$H$_5$NH$_3^+$ + OH$^-$

Ethanamine

OHCH$_2$COOH $\qquad\quad$ $\leftrightarrow$ $\qquad$ OHCH$_2$COO$^-$ + H$^+$

Glycolic acid $\qquad\qquad\qquad\quad$ Glycolate

HO$_2$CCOOH $\qquad\qquad$ $\leftrightarrow$ $\qquad$ HO$_2$CCOO$^-$ + H$^+$

Oxalic acid $\qquad\qquad\qquad\qquad$ Oxalate

CH$_3$COOH $\qquad\qquad$ $\leftrightarrow$ $\qquad$ CH$_3$COO$^-$ + H$^+$

Acetic acid $\qquad\qquad\qquad\qquad$ Acetate

HCOOH $\qquad\qquad\qquad$ $\leftrightarrow$ $\qquad$ HCOO$^-$ + H$^+$

Formic acid $\qquad\qquad\qquad\qquad$ Formate

$$CO_2 + H_2O \leftrightarrow CO_3^{2-} + 2H^+ \text{ (and } HCO_3^- + H^+\text{)}$$

Carbon dioxide   Carbonate (and bicarbonate)
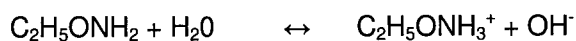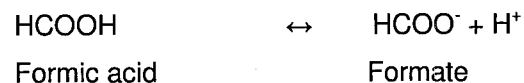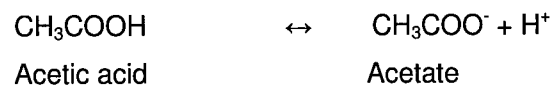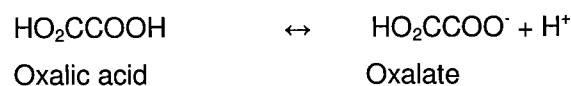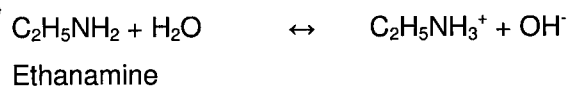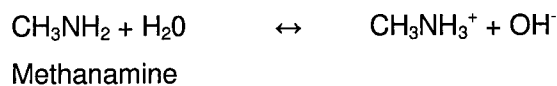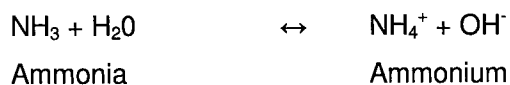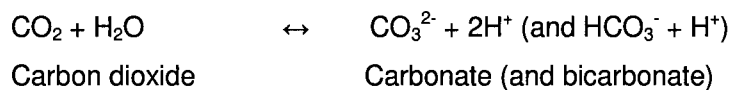
It is important now to note that there are abundantly more ionic species present in an ETA regime and since being less volatile than ammonia tends to concentrate in the steam generator blowdown. Most of the above indicated ion pairs are weak electrolytes thus low dissociation coefficients which is extremely sensitive to temperature change.

In the CC balance at Koeberg, the following 7 anions are analytically quantified by ion chromatography and calculated: fluoride, chloride, acetate, formate, nitrate, sulphate and phosphate. From the ionic species indicated in the breakdown of ETA, it is clear that there are anions such as glycolate, oxalate and carbonate that are always present and are not taken into account when calculated, but do contribute to the measured value causing a discrepancy between the two values.

Thus, the measured CC can be higher than the calculated CC when there are anions present that are not quantified and thus not included in the calculated value.

The chemistry strategy at KNPS is that the steam generator blowdown (APG) demineralisers are run into the ammonium / amine saturated form. The change out criteria is when the APG on-line cation conductivity specification value (0.5 µS/cm) is challenged. When a new resin charge is placed in service the APG CC is low at approximately 0.26 µS/cm and then increases steadily until approximately 0.46 µS/cm. The reason for the steady increase is due to the build-up of ETA breakdown products in APG as the resins approaches amine saturation point.

The result of this strategy is that the concentrations of the various ETA breakdown products fluctuate throughout the cycle according to the saturation condition of the APG demineralisers. The evidence for this is that the formate and acetate concentration follows the on-line CC trend.

As mentioned earlier, temperature has a fundamental effect on the dissociation of weak electrolyte ion pairs. The higher the temperature, the higher the dissociation and the higher the resultant measured CC. Also, as the concentration of weak electrolytes in solution increases, the significance of a temperature change on the measured CC becomes greater. The changing concentrations of the various organic ions cause apparent fluctuation because as these concentrations increase, the temperature influence on the measured CC also increases, and the opposite is also true.

If the temperature of the measured CC is higher than the temperature at which the sample is analysed for anions, it can result in a discrepancy between the measured and the calculated value. This magnitude of the discrepancy will appear to vary because of the fluctuation in the concentrations of the ETA break down products and also due to change in temperature. It has been noted that the on-line sample temperature is higher than 25°C (close to 30°C) and there is also considerable temperature variation between the individual SG sample points.

When considering the cation conductivity column operation, a discrepancy between the measured and calculated value may be caused by cation 'slippage'. In the perfect world, 100% of these cations are removed by the matrix and each (matrix and pollutant) cation is exchanged for an equivalent number of hydrogen ions. In reality, less than 100% exchange occurs and the performance of the CC column is dependent on a number of factors. These factors include flow rate, packing, resin quality, column dimensions and length of time in service. As described earlier, the breakdown of ETA results in a variety of ionic species, the cations dominated by amino-cations and the ammonium cation. A new / fresh CC column (H$^+$ form) may perform close to 100% if all the factors affecting the performance are optimised and well controlled. However, as the column stays in service it begins to saturate with amino-cations and ammonium cation and the performance deteriorates during the time in service. Sodium, a pollutant cation which is always present is moved forward on the column because the resin has have a higher selectivity for ammonium and amino-cation. From the beginning of a column run the sodium, ammonium and amino-cations elute from the column, but more significantly between the middle and saturation point.

The effect of the cation elution can result in a decreased measured CC because the ion pairs such as Na$^+$ anion$^-$, NH$_4^+$ anion$^-$ and amino-cation$^+$ Anion$^-$ are less conductive than the same ion pair (in the same concentration) in the acid (H$^+$) form.

Thus, the calculated CC may be higher than the measured CC if significant cation elution occurs.

The scenarios described above show that it is possible for the discrepancy between the calculated and measured cation conductivity to be variable depending on a number of parameters. The measured value is normally higher because not all the anions present in the sample are quantified and taken into account in the calculated value. When that cation conductivity column performance deteriorates it could result in the calculated cation conductivity may be being higher than the measured cation conductivity.

In fact, under normal plant conditions when the CC balance appears to be accurate, it is more likely to be as a result of the above opposing effects cancelling each other out than real accuracy. As a result of these scenarios discussed a need to develop a method to quantify for organics at koeberg Nuclear Power Station was realised. It is also anticipated that as a result of the organic method being developed a better understanding of the cation conductivity balance will be achieved.

3.7 Chloride Content of Demineralised Water

KNPS has two types of make-up water. 'Pure' demineralised water is for make-up to the primary circuit (SED). Make-up water for the secondary plant is demineralised water that has been treated with ammonium hydroxide solution to achieve a pH of > 9 (SER).

The specification for demineralised water at KNPS is described in the Station Chemistry Specification Documents. Chemical analysis for anions and cations is performed by IC. The specification requires the following anions to be determined on weekly routine basis: chloride, fluoride and sulphate. Each has a target value of less than 1.0 ppb and a limit value of 3.0 ppb maximum. These specifications are within all recognised acceptable standards for secondary make-up water [47].

The trends (Graph 3.1) from the Laboratory Information Management System (LIMS) indicate some recent trends for chloride. This demonstrates that the specifications are met for chloride in the secondary water make-up water tanks (9 SER 001 and 9 SER 002 BA). For a year (April 2011 to April 2012) of data chloride levels were generally less than 1 ppb. Only chloride is considered in this work but the specifications for the other relevant anions are met similarly. The two tanks are used alternately so only one tank will be supplying the plant at any given time.
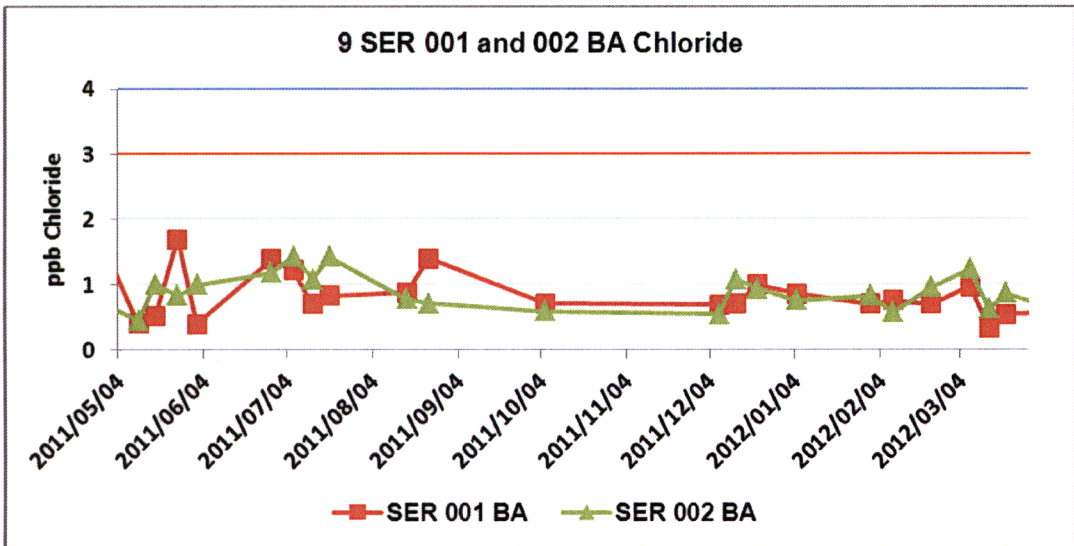
Graph 3.1: Secondary make-up water chloride analysis

UV radiation is used to break organic bonds. Demineralised water samples were treated with UV light at 254 nm to break down organic molecules. The intent of this is to release chloride ions into solution from the molecular structure through decomposition of the chlorinated organic compounds. In Table 3.3 are results from the secondary system make up water tanks SER 001 and SER 002 BA pre and post-UV treatment.

DATE	Pre – Chloride (ppb)	Post – Chloride (ppb)	× Increase
2011-05-11	0.41	111.0	271
2011-06-08	0.46	80.4	175
2011-07-06	1.22	756.0	620
2011-08-03	0.83	59.7	72
2011-09-28	0.78	89.0	114
2011-10-26	0.55	1014.6	1845
2011-11-23	0.83	865.3	1043
2011-12-21	1.00	82.7	83
2012-01-11	1.24	125.1	101
2012-02-15	0.87	218.0	251
2012-03-14	0.34	145.9	429
Average	0.78	322.50	414

Table 3.3: Pre- and Post-UV photocatalytic treatment chloride analysis of Secondary make-up water

These results confirm that there are organochloride molecules that are not removed by the water treatment and these end up in the make-up water tanks. This make-up water undergoes thermohydraulic breakdown in the feed train of the secondary plant and this results in elevated chloride levels which further concentrate in the steam generators.

On average the increase is approximately × 400 and high secondary make-up results in chemical excursions based on the chloride. The results also show that the extent of the increase varies considerably from month to month. The reason for this variation has not yet been established, however even the lowest increase observed (× 72) over a year of data is significant.

3.8 Trihalomethanes

THM are the product of reaction between halogens and organic material. The municipal raw water supplied to KNPS is sanitised by treatment with chlorine gas at the municipality treatment facility. This water is received at the power station and held in two raw water tanks (SEP 001 and 002 BA). These reservoirs are treated with sodium hypochlorite to inhibit microbial growth.

The results that follow are the average values obtained for five analyses sets performed during January 2012.

Sample Point	THM (ppb)
Raw water tanks (SEP001 & 002BA)	113.9
Filtered water tank (SDA001BA)	125.5
Demineralised water tank (SED001 BA)	36.1
Ammoniated demineralised water tank (SER001 & 002BA)	36.0

Table 3.4: THM analysis at various stages of water production

The following THM analysis was performed by the purge and trap gas chromatography – mass spectrometry method on the secondary make-up tank 9 SER 002 BA:

THM	Result in ppb
Chloroform (CHCl$_3$)	31.7
Bromodichloromethane (CHBrCl$_2$)	3.3
Dibromochloromethane (CHBr$_2$Cl)	1.0
Bromoform (CHBr$_3$)	< 1
Total	36

Table 3.5: THM compounds in secondary water make-up tank

3.9 Discussion of Results

The results in Table 3.3 indicate that THM is not removed by the charcoal filters. THM is not effectively removed by the demineralisation train and thus are found in the make-up water tanks (SER 001 and 002 BA).

The 36 ppb THM in SER 002 BA (Table 3.4) has the potential to generate a solution of approximately 30 ppb chloride based on decomposition of the THM compounds analysed. This is low when compared to the post-UV photocatalytic decomposition results obtained which generates a chloride concentration of 323 ppb (on average, see Table 3.2). This means that the secondary make-up water organic chloride is not limited to THM compounds, but contains other organochloride compounds that contribute even more significantly to the overall chloride inventory of the secondary plant.

CHAPTER FOUR: METHOD DEVELOPMENT AND QUANTIFICATION OF ORGANIC SPECIES

Chapter 4 will discuss the methods that were developed, procedures that were used and also instrumentation that were used to identify and quantify the organic species at Koeberg Nuclear Power Station. The sample preparation procedure for THM analysis is discussed in Appendix A, the sample preparation procedure for TOC analysis is discussed in Appendix B and also the procedure for anions analysis is discussed in Appendix C.

4.1 Table of content

- List of analytical methods that was used
- Principle operation of each method and instrument type and model
- Sample preparation, apparatus and reagents used
- Rationale behind methods used
- Sample points
- Table of results
- Results and discussion

4.2 List of analytical methods that were used

The following methods were used at KNPS to analyse the water samples:

- The GC-MS was used to analyse for THM in the Eskom Research Laboratory
- Total Organic Carbon (TOC) method
- Ion Chromatograph (IC)
- Liquid Chromatography – Organic Carbon Detection – Organic Nitrogen Detection was used by DOC-LABOR in Germany to analyse for DOC/HOC/CDOC/ In-organic Colloids and SUVA

4.3 Trihalogenated Method

Instrument type and model

Agilent Technologies 7890A GC and Agilent Technologies 5975C inert MSD with triple –Axis detector

Principle method: Gas Chromatography –Mass Spectroscopy (GC-MS)

Gas chromatography-mass spectroscopy (GC-MS) is one of the so-called hyphenated analytical techniques. As the name implies, it is actually two techniques that are combined to form a single method of analysing mixtures of chemicals. Gas chromatography separates the components of a mixture and mass spectroscopy characterises each of the components individually. By combining the two techniques both qualitative and quantitative analysis of sample can be carried out.

Principle of GC-MS

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Once the individual components of the sample are eluted through the GC column, these components enter the electron ionization (mass spec) detector. There, they are bombarded with a stream of electrons causing them to break apart into fragments. These fragments can be large or small pieces of the original molecules. The fragments are actually charged ions with a certain mass. The mass of the fragment divided by the charge is called the mass to charge ratio (M/Z). Since most fragments have a charge of +1, the M/Z usually represents the molecular weight of the fragment.

A group of 4 electromagnets called a quadrapole, focuses each of the fragments through a slit and into the detector. The quadropoles are programmed by the computer to direct only certain M/Z fragments through the slit. The rest bounce away. The computer has the quadrapoles cycle through different M/Z's one at a time until a range of M/Z's are covered. This occurs many times per second. Each cycle of ranges is referred to as a scan.

The computer records a graph for each scan. The x-axis represents the M/Z ratios. The y-axis represents the signal intensity (abundance) for each of the fragments detected during the scan. This graph is referred to as a mass spectrum. Each component has its own finger print mass spectrum. The GC-MS generally has a build in library that consists of a wide range of components together with its mass spectrum. When an analysis is carried out and a mass spectrum is obtained the component can be immediately identified because of the build in library [48].

4.4 Total Organic Carbon Method

Instrument type and model

SMM Instrument (Pty) Ltd and Sievers 900

Principle method

Organic compounds are oxidised to form carbon dioxide using UV radiation and a chemical oxidising agent (ammonium persulphate). Carbon dioxide is measured using a sensitive and selective membrane-based conductometric detection technique. For each TOC measurement, the concentration of inorganic carbon species (CO_2, HCO_3 and CO_3) is determined and after oxidation of the organic compounds, the total carbon (TC) content of the sample is measured. The concentration of the organic compounds is then calculated from the difference between the concentration of TC and total inorganic carbon (TIC), generally referred to simply as inorganic carbon (IC) [49].

$$TOC = TC - IC$$

4.5 Ion Chromatography

Instrument type and model

Dionex ICS – 3000 Reagent-Free Ion Chromatography (RFIC)

Principle Method

The objective of chromatography is to obtain separation between components of a mixture. In any chromatographic process, the components of a mixture are separated by using differences in the distribution of the sample components between 2 phases. One phase remains fixed in the system (the stationary phase), whereas the other (the mobile phase) moves through the system. The stationary phase is either a surface-active solid or a liquid held onto an inert solid support. The mobile phase can be a liquid or a gas. Separations occur because the stationary and mobile phases have different affinities for the sample components. The sample components therefore move at different rates along the stationary phase, which is either held in a column (column chromatography) or a self-supporting material like a piece of filter paper (planar chromatography). The mobile phase is called the carrier or eluent, since it carries the components along the stationary phase. The process by which the eluent causes a compound to move along the stationary phase is called elution (elution chromatography). The mobile phase that emerges from the stationary phase carrying the sample components is called the eluent. In instrumental chromatographic techniques, the separation takes place along a chromatographic column. A detector, located at the end of the column, provides an electrical signal indicating when a substance emerges from the eluent. The signal is plotted as a function of time. The result of a chromatographic separation is given in the form of a chromatogram. The time required to elute a component under a given set of conditions is known as the retention time of the component. It is measured from the time the sample is injected onto the column until the peak maximum of the eluant is detected.

The principle liquid chromatographic method used at Koeberg is ion chromatography, where the process taking place along the column is ion exchange. This process takes place between the mobile phase and the exchange groups that are covalently bonded to the stationary phase. It is a separation procedure in which ions of like charge are separated by elution from a column packed with a finely divided resin [50].

4.6 Ion Chromatography Main Components

Component	Function
Eluent	Carries the sample components through the system.
Isocratic pump (Anions and Cations IC models)	Uses gradient elution which improves separation efficiency.
Anion / Cation trap column	Remove contaminants from the eluent. The ICs have continuously regenerated trap columns (CRTCs).
Rheodyne valve export	Allows liquid streams to be switched.
Sample loop	Allows fixed volume of sample to be injected onto the analytical column.
Eluent Generators	Generates the eluent electrolytically.
Concentrator column (Low Level Anions and Cations)	Concentrates ions in the sample before injection onto the analytical column.
Guard Column	Prevents contaminants from entering the analytical column.
Analytical column	Separates the sample into its component ions.
Anion / Cation suppressor	Minimises the background conductivity of the eluent and enhances the sensitivity of the detector.
Detector	Detects the concentration of ions in the sample.
Computer	Stores calibration identifies and quantifies the ions.

Table 4.1 Main Components of ICS-3000

4.7 Liquid Chromatography – Organic Carbon Detection – Organic Nitrogen Detection

Material and Method

The purified mobile phase (a phosphate buffer exposed to UV-irradiation in an annular UV-reactor) is delivered with a high performance liquid chromatography pump at a flow rate of 1.1 mL/min to an autosampler and the chromatographic column (250mm x 20 mm, TSK HW 50S, 3000 theoretical plates). The chromatographic column is a weak cation exchange column on polymethacrylate basis. Prior to chromatographic separation, samples are made

particle-free by passing a 0.45 μm PES-filter. The first detector after chromatographic separation is non-destructive, fixed wavelength UV-detection (UVD 254 nm, type S-200) and thereafter the organic carbon detector. At the inlet of the organic carbon detector, the solution is acidified at a flow rate of 0.2 mL/min (gravity-driven) to convert carbonates to carbonic acid. The column is bypassed with a restricted flow (flow rate 0.1 mL/min, back pressure-driven) to obtain a dissolved organic carbon value at the dead volume time of each chromatographic run.

For nitrogen detection a side stream is diverted after ultra violet detector with a restricted flow rate 0.1 mL/min (back pressure-driven) for nitrogen analysis organic carbon detector and ultra violet detector calibration was based on potassium hydrogen phthalate. Its carbon mass was used to calibrate the organic carbon detector and its extinction coefficient at 254 nm was used to calibrate the ultra violet detector. The extinction coefficient was determined with a UV-spectrometer following the law of Lambert Beer. Organic nitrogen detector calibration was based on potassium nitrate. For data acquisition and data processing a customised software program was used (Chrom CALC, DOC-LABOR).

The diverted side stream after ultra violet detector enters a helical, fused silica capillary of about 4 m length and 1 mm inner diameter. The helix is fused into the electric discharge arc of a low pressure mercury lamp (80 cm length, 18 mm diameter) emitting at 185 nm and 254 nm. In this UV-reactor, organic carbon is converted to carbonic acid (which remains unstripped in the aqueous phase) while organically bound nitrogen (e.g. bound to humic substances or biopolymers) and inorganically bound nitrogen (ammonium, nitrite and urea) is converted to nitrate while primary nitrate remains unaltered. Nitrate absorbs strongly in the deep UV-range. This property was used to quantify nitrate in a UV-detector at 220 nm [51].

4.8 Rationale behind methods used

The sample condition on the plant changes from one day to another due to the pre-treatment activities that are applied in the sample. The samples should not be sampled and be kept for a long period before they are analysed due to the fact that some organic species (i.e. acetate, formate, glycolate and oxalate) are volatile in nature and if a sample are not analysed immediately the results will be inaccurate. The samples were taken on a quarterly basis since September 2010 to monitor the passage of organics from raw water into the feed trains systems. The analysis that was performed was THM, TOC, acetate, formate, glycolate and oxalate. The sample were also oxidised under the UV lamp and they were analysed for chlorides using ion chromatography.

4.9 Sample points

Koeberg Nuclear Power Station - Samples Points for Organic Research		
Sample on Label	**Sample Discription**	**Sample Point**
9 SEP	Upstream of Charcoal filters - SEP Supply	9 SDA 013 VE
9 SDA 001 FI	Charcoal Filter - 001FI	9 SDA 066 VE
9 SDA 002 FI	Charcoal Filter - 002FI	9 SDA 067 VE
9 SDA (C.Filter Down)	Downstream of Charcoal filters	9 SDA 047 VE
9 SDA 201 EX	Cation Exchange vessel	9 SDA 201 YZ
9 SDA 202 EX	Anion Exchange vessel	9 SDA 230 YZ
9 SDA 203 EX	Mixed-bed Exchange vessel	9 SDA 260 YZ
2 CEX	Condenser Extraction system sample	SIT 017 VL
2 ACO	Feedwater heater drains recovery system sample	SIT 039 VL
2 AHP	HP Feedwater heating system sample	SIT 067 VL
2 VVP	Main steam system sample	SIT 095 VL

Table 4.2: Sample points located in the demineralise plant

Table of Results

Sample ID	Sample Date	THM in ppb	TOC in ppb	Chloride in ppb	Post Chloride in ppb
9 SEP	2010-09-27	123	2490	752	11850
9 SDA 001 FI	2010-09-27	238	1440	628	11739
9 SDA 002 FI	2010-09-27	230	1400	626	11741
1 SDA (C.Filter downstream)	2010-09-27	122	1480	623	11735
9 SDA 201 EX	2010-09-27	40	1400	663	11784
9 SDA 202 EX	2010-09-27	110	60	12	76
9 SDA 203 EX	2010-09-27	109	50	1.6	96
9 SER 002 Ba	2010-09-27	100	60	2.81	283

Table 4.3: TOC, Chlorides (Pre and Post UV treatment analysed at KNPS) and THM results analysed at Eskom Lab in JHB

Table of Results

Sample ID	Sample Date	THM in ppb	TOC in ppm	DOC in ppb
9 SEP	2011-12-07	113.91	0.98	980
9 SDA 001 FI	2011-12-07	140.37	1.22	1050
9 SDA 002 FI	2011-12-07	116.09	1.20	1120
1 SDA (C.Filter downstream)	2011-12-07	125.49	1.20	1070
9 SDA 201 EX	2011-12-07	112.47	1.16	1200
9 SDA 202 EX	2011-12-07	84.74	0.38	340
9 SDA 203 EX	2011-12-07	42.10	0.12	90
9 SER 001 Ba	2011-12-07	35.92	0.10	80

Table 4.4: THM, TOC and DOC results

Graph of TOC and THM
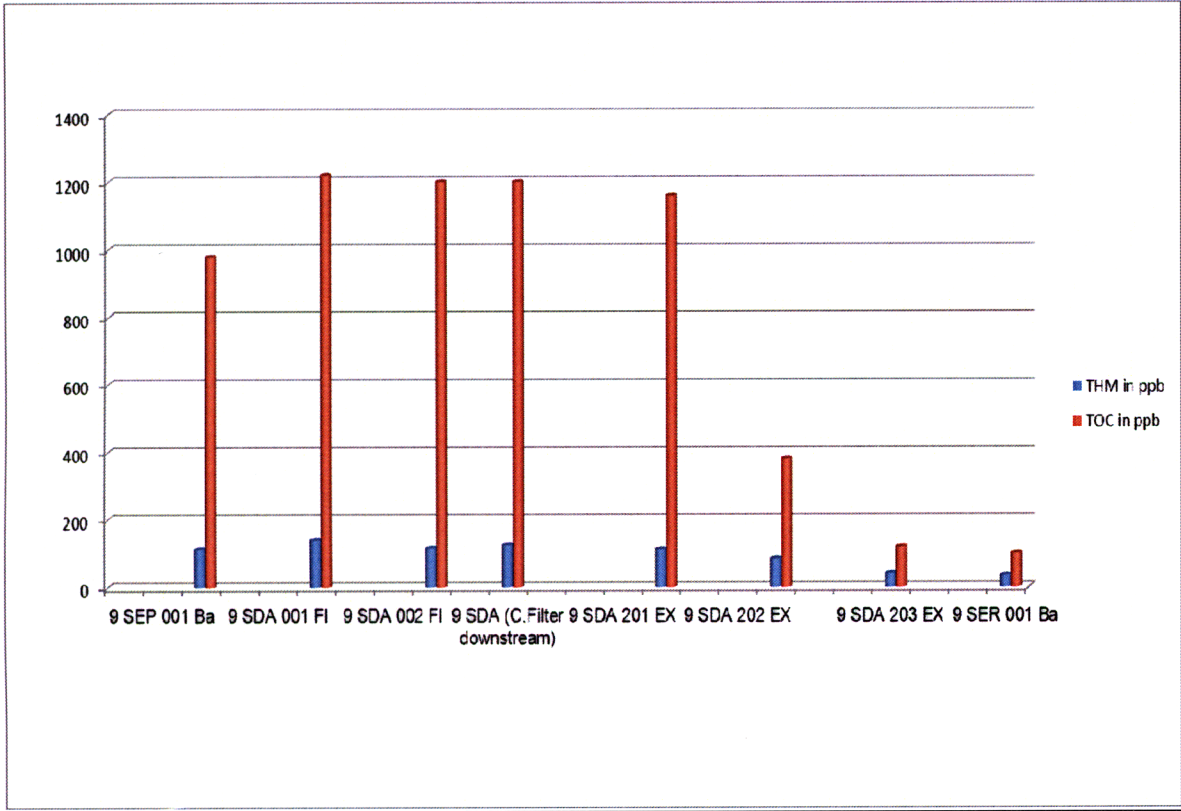
Graph 4.1: THM results versus TOC on the sample taken on 07/12/ 2011

Table of Results

Sample ID	Sample Date	DOC in ppb C	HOC in ppb C	CDOC in ppb C
9 SEP	2012-02-23	1148	150	998
9 SDA 001 FI	2012-02-23	978	34	945
9 SDA 002 FI	2012-02-23	1004	48	956
9 SDA (C.Filter downstream)	2012-02-23	938	68	869
9 SDA 201 EX	2012-02-23	1057	155	902
9 SDA 202 EX	2012-02-23	53	15	38
9 SDA 203 EX	2012-02-23	42	6	38
9 SER 001 Ba	2012-02-23	44	6	38

Table 4.5: DOC - LABOR (DOC, HOC and CDOC) results

Table of Results

Sample ID	Bio polymers in ppb C	HS in ppb C	BB in ppb C	LMW N in ppb C	LMW A in ppb C	SUVA in L/(mg.m)
9 SEP	16	422	314	247	n.q	2.97
9 SDA 001 FI	20	392	294	238	n.q	2.96
9 SDA 002 FI	22	401	301	231	n.q	3.26
1 SDA (C.Filter downstream)	11	3.82	285	192	n.q	3.14
9 SDA 201 EX	n.q	414	268	213	7	2.99
9 SDA 202 EX	6	n.q	5	26	n.q	22.39
9 SDA 203 EX	8	n.q	5	22	n.q	27.25
9 SER 001 Ba	5	n.q	4	28	2	29.62

Table 4.6: DOC - LABOR (Biopolymers, Humic Substance, Building block, LMW Neutrals, LMW Acids and SUVA sample taken 2012-02-23) results

4.10 Results and discussion

In Table 4.3 the results for THM, TOC, Chlorides and Post Chlorides (the sample were oxidised and analysed for chlorides) are displayed. The reason for these analyses was to investigate and determine if there is any relationship between TOC, THM, Chlorides and Post Oxidation Chlorides. Chlorides are known to be a cause of stress corrosion cracking (SCC) that can take place in the steam generator and therefore it is important to determine its concentration and its origin so that it can be mitigated. The Post Oxidation Chloride is the chloride that is attached to the organic molecule in a form of trihalomethane and it can only be determined by oxidising the sample and analyse for chloride using ion chromatography.

Some of the THM can be removed by water production GAC filters (9 SDA 001 Fl and 9 SDA 002 Fl). However, in these experiments the THM result were higher after the water pass through the filters (9 SDA 001 Fl and 9 SDA 002 Fl) which is an indication of filters being exhausted with organic fouling. The common filter outlet has however removed some of the THM.

The THM results increased from common filter outlet after the water passes SDA 102 EX (anion resin) and this is an indication of anions resin being fouled with organics.

As a result of these findings KNPS initiated a project to change charcoal filters on a regular basis and also apply a brine solution on the anions resins to clean the organic fouled resins. The TOC analyser was also purchased as a result of this project so that the TOC concentrations can be monitored on a regular basis. KNPS chemistry surveillance procedure was updated to reflect the recommended frequency to monitor TOC upstream and downstream of the charcoal filters. With all these mitigation it is expected that the chlorides reduces such that steam generators are not at risk of stress corrosion cracking.

Table 4.4 shows the results of the samples that were taken on the 07 December 2011, from the KNPS water production plant following a flow as described in Figure 1.4. Graph 4.1 shows a relationship between the total organic carbon (TOC) and the trihalomethanes (THM). It should be noted that the TOC increases with THM which implies that the two parameters are directly proportional to each other. This would also imply that if you decrease the amount of total organics that enters the SEP you with also decrease the amount of THM and therefore decrease the amount of chlorides that will go through the steam generator. It was also observed that substantial amount of organics was removed by both anions resins (SDA 102 EX) and mixed bed resins (SDA 103 EX). The anion resins will be fouled by these organics over a period of time and therefore it is important from time to time to clean the

anion resins so that the organic fouling is reduced. The work that was done here demonstrates the importance of identifying and quantifying the organics material at the KNPS water production plant.

In table 4.5 and table 4.6 samples were sent to DOC-LOBOR for natural organic matter characterisation. Size - exclusion chromatography coupled to three detectors (organic carbon, organic nitrogen and UV-absorption), was applied to subdivide the pool of organics matter in a natural water sample into six major sub-fractions which could be assigned to specific classes of compounds: biopolymers, Humic-Substances, Building Blocks, Low Molecular-weight Acid, Low Molecular-weight nuetrals and Hydrophobic Organic Carbon.

The results also revealed that there was no presence of biopolymer which is an indication of absence of polysaccharide. Polysaccharide is considered to be a dominant material of biopolymer. The absence of these organic species is a good indication of KNPS treated water.

From these analyses it was concluded that KNPS water does not need an extensive pre-treatment. It was also observed that the charcoal filter had no impact on the dissolved organic carbon (DOC). It was also observed that the cation resins had no impact on the DOC and strong acid cation was fouled which was not expected.

On the make-up water there were no indication of oxidation product of DOC and only 2 ppb of organic acid were found. DOC-LOBOR report concluded that neither water treatment plant nor water steam cycle have any problems as far as organics are concerned.

CHAPTER FIVE: RESULTS, RECOMMENDATIONS AND CONCLUSION

This chapter will mainly deal with the conclusion and the recommendations derived from the results obtained during experimental.

5.1 Conclusion

It can be concluded from this research that the identification and quantification of organic species at KNPS is important. The results that were obtained have shown a relationship between TOC, THM, acetate, glycolate, formate and oxalate. It is also important that these parameters be measured on a regular frequency so that organic fouling of the anion resin can be monitored and the corrective actions could be employed. As a result of this project KNPS purchased the TOC analyser to monitor total organic carbon in the make - up water

system. KNPS purchased an IC column that enable KNPS to monitor organic acid anion and inorganic anions as shown in Appendix E and Appendix F. The KNPS surveillance procedure was updated to reflect that TOC must be monitored in a particular frequency.

An organic profile of the water production plant has been established, an organic profile of the secondary water / steam cycle has been establish, the effect of organics on CC balance was discussed. Analytical methods have been developed for total organic carbon and organic acids. It has been proven that organochlorides are responsible for elevated chloride levels in the SG's. Although THMs contribute significantly, it is other (possibly larger) organochloride compounds that are even more significant.

This research project has also initiated various projects at KNPS. One of the projects was the anion resin routine clean-up where the organic that fouls the anion resins are cleaned by being soaked in a solution that contain 5 % sodium chloride and 2 % sodium hydroxide and this process is also known as a "brine washed". Procedures were compiled and they are currently being utilised by Koeberg Chemistry Staff.

One of the projects that was initiated was to replace the anion resins in the water production plant and that cost KNPS more than 3 million rands. The resin at KNPS was not replaced for more than 15 years and this was one of the sources of contamination on the water production plant.

This project has also initiated a strategy on how KNPS should deal with the poor water quality and those recommendations were communicated to Engineering group so that modification can be initiated. The motivations were as follows:

- Chlorine Injection System: Change dosing from hypochlorite to chlorine dioxide. The rationale for this is that with ClO_2, the disinfection by-products (DCBs) are greatly reduced when compared to HOCl. i.e. Organochloride reduction.

- Protect the charcoal filters by sand filtration after flocculation. Rationale: if the insoluble matter is removed prior to entering the granular activated carbon (GAC), the GAC will be much more effective in holding organic material.

- Treat filtered water with UV at 254nm prior to demineralisation. Rationale: the DCBs will be broken down releasing associated inorganic species such as chloride and sulphate into solution from the organic molecules. These 'free' inorganic ions will now be removed by the demineralisation train.

- Degas SER (and SED) water. Rationale: Besides removing O_2 (good reason on its own), the organic contaminants of concern are volatile and can be removed by degassing.

- "Breathers" on water storage tanks. Rationale: Protects the water from sea-air contamination.

- Replace the GAC on an optimised frequency based on total organic carbon (TOC) concentration u/s vs d/s strategy. This is in progress and the rationale should be clear.

- Use coconut based GAC which is widely used for removal of chlorinated hydrocarbons.

Finally as a result of this project a paper was written and presented in Germany in May 2012. This paper was also published in the Power Plant Chemistry Vol. 14 (2012) No. 7, p 424 [52].

Appendix A

Sample Preparation Procedure for THM

- 100 ml Pyrex amber glass Schott bottles were used to take the samples.
- Bottles were cleaned with lab detergent and rinsed with demineralised water and dried at 150°C in an oven, then cooled and sealed before use.
- Samples were collected in duplicate.
- Ascorbic acid was added to all samples that contain residual chlorine before they were sampled.
- Bottles were filled to just overflow and the ascorbic acid was not flushed.
- There were no air bubbles in the bottle when sealed.
- 5 drops of 1:1 HCl were added to each 100 ml bottle and the bottles were sealed and shaken.
- HCl and ascorbic acid were not mixed prior to adding sample.
- The samples were chill to <4°C after sampling and stored at 4°C before they were analysed.

Appendix B

Sample Preparation Procedure for TOC

- 250 ml Pyrex amber glass Schott bottles were used to collect the samples.
- The sample bottles were washed with a detergent and rinsed at least three times with tap water to thoroughly remove the detergent.
- The bottles (and not the caps) were rinsed with 100 ml of 10% HNO_3 followed by three ultra-pure water rinses. Rinsing the caps with 10% HNO_3 could damage them if they are not resistant to oxidation as this is a strong acid.
- The bottles were dried without the caps in an oven at temperatures between 275 and 325°C for four hours.
- The bottles were cooled at room temperature.
- The bottles were ready for sampling.

TOC Working Procedure

- Switch on the analyser using the main power switch. The analyser should power up and display the start-up screen.
- Select the main button to display the main screen.
- Flushing the reagent syringes
- If the analyser has not been used for over 48 hours, the decomposition of persulfate can produce oxygen bubbles in the syringe pump and the reagent addition lines.
- To prevent the bubbles from entering the sample stream and interfering in the TOC measurement, a reagent flush is used to remove the bubbles and fill the syringe with fresh reagent.
- A reagent flush is also recommended after running samples with a high result (above 2 ppm).

To initiate a syringe flush, follow these steps:

- Press the Menu button.
- Select the Maintenance tab.
- Press the Consumables tab
- Press the Flush button.
- Select the Both button.
- Ensure the sipper tube is placed into Milli-Q water and press the Flush button.
- When the flush is complete press the OK button.
- Before starting any analyses, check the analyser's consumables status.
- The Main screen an overview graphic that indicates the relative life status of the analyser's consumables.
- Status indicators on the main screen change colour as the need for replacement nears.
- To display more detailed information about the consumables status, follow these steps:
- Press the Menu button.
- Select the Maintenance tab.
- Press the Consumables tab.
- The status of each of the consumables is displayed, with an estimated remaining life and their expiration date.
- If new consumables need to be installed, inform the Instrument Technician.

Measurement

Before starting normal analyser operation, confirm that the mode settings match your configuration needs.

- Press the Menu button.
- Select the Setup tab.
- Select Grab to measure TOC directly from a sample flask or vial port.
- Press the Main button to exit and save your settings.
- Select the correct configuration by setting Reagent Flow Rates.
- Press the Menu tab.
- Select the Setup tab.
- Press the Configure Mode button to set the flow rates.
- Select the Reagent Manual tab.
- For MilliQ water, ensure the Reagent button is set to Manual.
- Press the Oxidiser button and use the keyboard to enter a value.
- Press the Enter button to save the value or press Cancel to retain the current settings
- without making any changes.
- For known samples below 1 ppm, ensure the Reagent button is set to Manual.

Appendix C

Sample Preparation Procedure for IC

The culture flasks were rinsed with deionized water for three times.
They were filled with deionized water and soak overnight.
The water was discarded and filled with deionized water.
This water was analysed to make sure that it was clean of impurities.
The samples were collected using these clean culture flasks.

Ion Chromatography working Procedure

- Start up
- Switch on the pc.
- Double click on the *Chromeleon* icon on the desktop.
- In the browser window, select the sequence to be run.
- Open the workspace window.
- Copy the sequence to the *Old Sequences* folder.

- Rename the sequence to the current date.
- Check the levels of the eluent bottles fill if required.
- Open the priming valve of the eluent pump.
- Click on the *PRIME* tab in the workspace.
- Click on *OK* in the pop-up message window.
- The pump will prime for a set time.
- When the priming stops, check for air bubbles in the eluent line.
- If no bubbles are observed in the eluent line, close the priming valve.
- Click on the relevant *START UP* tab in the workspace (*KWC-AC-ANA-092*
- *Rev 0)*
- Disconnect the AXP pump by selecting *Control* in the top menu.
- Select *Command* in the drop down menu.
- Expand the *AXP_Pump* tree.
- Select *Disconnect* and click *Execute.*
- Disconnect the outlet line of the AXP pump.
- Connect a syringe with a Luer adaptor to the outlet of the AXP pump.
- Press *Prime* on the AXP pump and draw a vacuum with the syringe.
- Stop priming when liquid flow is observed, and no air bubbles are visible in the pump inlet line.
- Connect the outlet line of the AXP pump.
- Select *Command* in the drop down menu.
- Expand the *AXP_Pump* tree.
- Select *Connect* and click *Execute.*
- Click the *SmartStartup Wizard* icon in the workspace to start the equilibration programme.
- Select the method equilibration to be run.
- Click *Next.*
- Ensure that the *Equilibrate* tab is ticked for all the components.
- Click *Next.*
- Click *Finish.*
- Click *No* in the pop-up message window.
- Click *Start* in the *Batch* window.
- When the equilibration is completed, a message is displayed informing the
- operator that the equilibration was successful.
- Click *Ok.*

Sample Run

- Open the browser window.
- Enter the samples to be run in the sequence.
- In the sample sequence, set the sample status of the samples to be run as
- Single.
- Open the workspace window.
- Place the sample tube in the sample.
- Load the sample using a syringe connected to the sample port on the IC.
- When the syringe is filled, click on the *Batch Start/Stop* icon.
- Ensure that the correct sequence is selected in the *Batch* window.
- Click on the *Ready Check* tab.
- Click *Ok* in the *Check Results* window.
- Click on the *Start* tab in the *Batch* window.
- Click *Ok* in the pop-up message window.

Standardisation

A multi-point standardisation must be performed in the following instances:

- Once a month.
- When a new eluent cartridge was installed.
- When a component was changed.
- When the QC indicates that a standardisation is required.
- Prepare standards as per standard working instruction AC-IC-SI.
- Ensure that the standard name entered in the sequence is the same as in the amount table. If these names are not the same, there will be no amount associated with the standard in the sequence.
- Standardise the instrument by starting with the lowest standard first.
- Once the all standards have been run, check that the %RSD for all ions is below 5%.
- If not, the standards the relevant standards must be re-run.
- Once the instrument has been standardised, print out the calibration batch report for all the standards and file in the standardisation file.
- The calibration batch report can be printed by double clicking on the relevant quantification programme in the browser window.
- Click on the printer layout icon and select the calibration batch report page.
- Click on the print icon to print the report.

- The amount table must also be printed out and filed with the standardisation.
- To print the amount table, double click on the relevant quantification programme in the browser window.
- Ensure that the QNT Editor is selected, if not click on the QNT editor icon.
- Go to File, click on Print QNT Method.
- Ensure that only amount table is selected and deselect the other parameters by unchecking the tick box for each parameter.
- Click Ok and the amount table and retention times for the relevant ions will be printed.
- Shut Down.
- Click on the Shutdown tab.

Appendix D

These are the THM results that were sent for analysis to Eskom laboratory in Johannesburg. The sample was taken from the water production plant so that the organic species can be identified and be quantified.

⊗ Eskom

CERTIFICATE OF ANALYSIS

To: Mr Lance Davis
Koeberg Power Station
Private Bag X10
Kernkrag
7440
Tel.: (021) 550-5588

REPORT NUMBER:	WL2010-010064
SAMPLED ON:	
SUBMITTED ON:	04 October 2010
REPORTED ON:	17 February 2011

ELEVEN WATER SAMPLES FOR TRIHALOMETANE DETERMINATION

SAMPLE RECEIPT AND HANDLING
Eleven water samples were received in 250ml glass Schott bottles. On receipt, the samples were transferred to a refrigerator where they were kept until subcontracted to CSIR for analysis.

ANALYTICAL METHODS
Trihalomethanes were determined using the CSIR's purge and trap GC-MS method, GC-050.This is a SANAS accredited method.

RESULTS
Trihalomethane results are given in Appendix 1.

Cody Makhuba
SNR TECHNICIAN/LAB SUPERVISOR
Water Chemistry Laboratory

Appendix 1.THM results

Report reference no.:WL2010-010064

Sample		2271739-9SEP	2271740-9SDA 001F1
Chloroform	ppb as CHCl₃	100	200
Bromodichloromethane	ppb as CHBrCl₂	18	32
Dichlorobromomethane	ppb as CHBr₂Cl	5	6
Bromoform	ppb as CHBr₃	<1	<1
Total trihalomethanes		123	238

Sample		2271741-9 SDA 002F1	2271742-9 SDA(C.Filter down)
Chloroform	ppb as CHCl₃	3	100
Bromodichloromethane	ppb as CHBrCl₂	<1	18
Dichlorobromomethane	ppb as CHBr₂Cl	<1	4
Bromoform	ppb as CHBr₃	<1	<1
Total trihalomethanes		3	122

Sample		2271743-9 SDA 201 EX	2271744-9 SDA 202 EX
Chloroform	ppb as CHCl₃	30	98
Bromodichloromethane	ppb as CHBrCl₂	8	10
Dichlorobromomethane	ppb as CHBr₂Cl	2	2
Bromoform	ppb as CHBr₃	<1	<1
Total trihalomethanes		40	110

Sample		2271745-9 SDA 203 EX	2271746-2 CEX
Chloroform	ppb as CHCl₃	100	<1
Bromodichloromethane	ppb as CHBrCl₂	8	<1
Dichlorobromomethane	ppb as CHBr₂Cl	1	<1
Bromoform	ppb as CHBr₃	<1	<1
Total trihalomethanes		109	0

Sample		2271747-2 ACO	2271748-2 AHP
Chloroform	ppb as CHCl₃	<1	<1
Bromodichloromethane	ppb as CHBrCl₂	<1	<1
Dichlorobromomethane	ppb as CHBr₂Cl	<1	<1
Bromoform	ppb as CHBr₃	<1	<1
Total trihalomethanes		0	0

Sample		2271749-2 VVP
Chloroform	ppb as CHCl₃	<1
Bromodichloromethane	ppb as CHBrCl₂	<1
Dichlorobromomethane	ppb as CHBr₂Cl	<1
Bromoform	ppb as CHBr₃	<1
Total trihalomethanes		0

- 2 -

Comments:

Some of the results are outside Eskom Standard for Portable Water (GGS 0517 Rev. 2) of less than 100 ppb of THM.

Appendix E

These are the calibration curve for all the standards that were used to quantify and Identify the results that were obtained using the Ion Chromatography.

Calibration Batch Report

Sequence:	MBS Project 2011-09-10		Inj. Vol.:		
Program:	ICS 2100 STD3 84		Operator:	HOTLAB	
Inj Date/Time:	11/09/11.16.21		Run Time:	30.00	
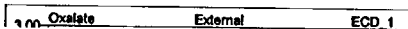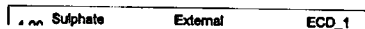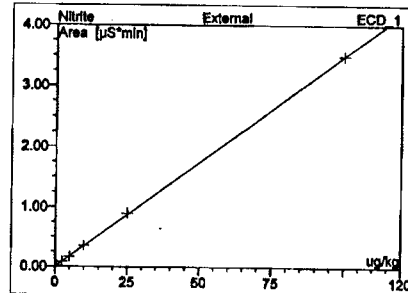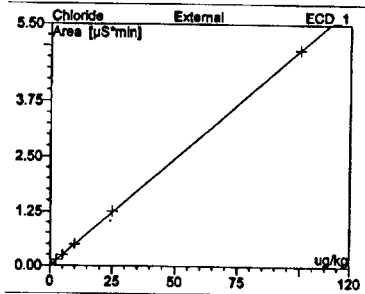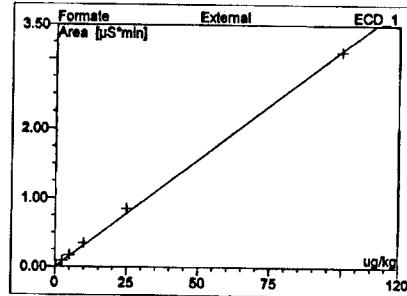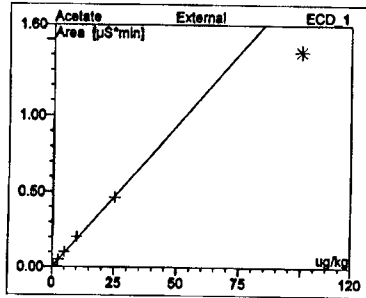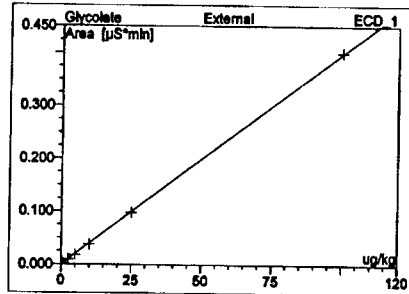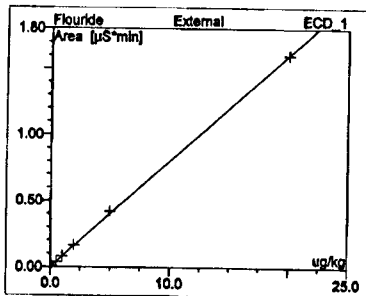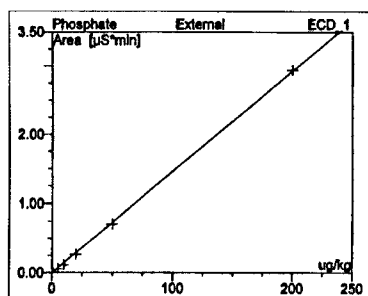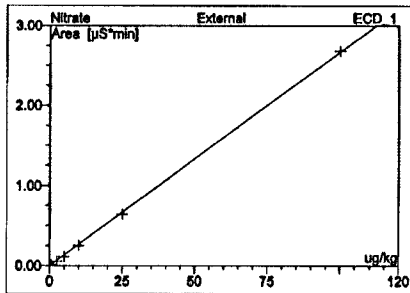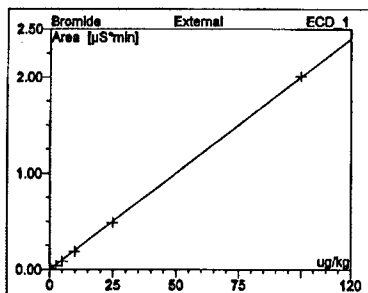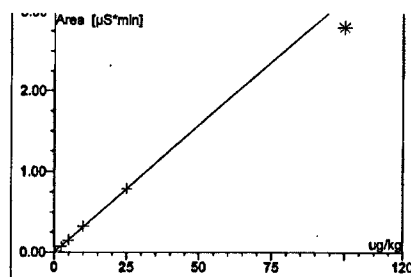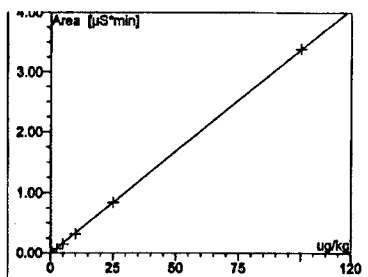
No	Ret. Time min	Peak Name	Cal.Type	Points	Rel. Std. Dev. %	Corr.Co. (C1)
1	5.22	Flouride	ALin	7	2.424	0.0602
2	6.18	Glycolate	ALin	7	2.462	0.0040
3	6.72	Acetate	ALin	6	5.336	0.0166
4	7.36	Formate	ALin	7	5.065	0.0313
5	11.67	Chloride	ALin	7	1.155	0.0492
6	13.20	Nitrite	ALin	7	1.679	0.0349
7	16.29	Sulphate	ALin	7	2.126	0.0338
8	16.74	Oxalate	ALin	6	2.529	0.0316
9	17.60	Bromide	ALin	7	3.208	0.0200
10	18.73	Nitrate	ALin	7	3.355	0.0267
11	19.55	Phosphate	ALin	7	4.132	0.0146

ANION_report/Calibration(Batch)

Appendix F

These are the anion results standards that were used during calibration of the Ion Chromatography. The report below shows the standard from standard 0 to standard 6.

Sample Name:	Std 0		Inj. Vol:	1.0
Sample Type:	standard		Dilution Factor:	1.0000
Program:	ICS 2100 STD0 $1		Comment:	
Inj. Date/Time:	09/09/11 15:17		Run Time:	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/Kg
1	5.23	Flouride	BMB*	0.000	0.000	0.00
2	6.18	Glycolate	BMB*	0.000	0.000	0.00
3	6.71	Acetate	BMB*	0.000	0.000	0.00
4	7.37	Formate	BMB*	0.004	0.022	0.12
5	11.68	Chloride	BMB*	0.005	0.037	0.10
6	13.23	Nitrite	BMB*	0.000	0.002	0.00
7	16.30	Sulphate	BMB*	0.000	0.003	0.01
8	16.79	Oxalate	BMB*	0.000	0.000	0.00
9	17.60	Bromide	BMB*	0.000	0.001	0.00
10	18.69	Nitrate	BMB*	0.000	0.000	0.00
11	19.54	Phosphate	BMB*	0.000	0.000	0.00
		TOTAL:		0.01	0.07	0.24
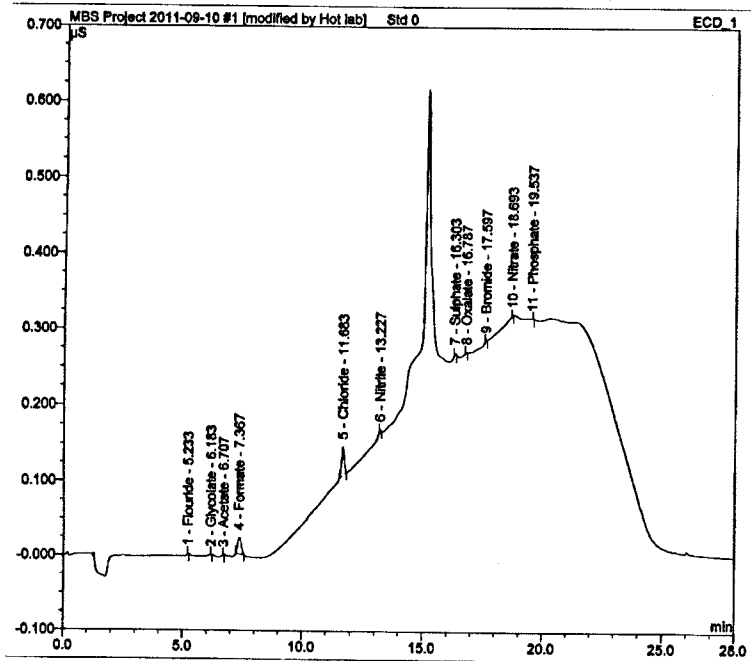
MBS Project 2011-09-10 #1 [modified by Hot lab]   Std 0   ECD_1

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Sample Name:	Std 1			Inj. Vol.:	10
Sample Type:	standard			Dilution Factor:	1.0000
Program:	ICS 2100 STD1 81			Comment:	
Inj. Date/Time:	09/09/11 15:47			Run Time:	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.23	Flouride	BMB	0.008	0.050	0.09
2	6.19	Glycolate	BMB	0.002	0.010	0.48
3	6.73	Acetate	BM	0.009	0.038	0.46
4	7.36	Formate	MB	0.019	0.086	0.60
5	11.68	Chloride	BMB*	0.033	0.215	0.68
6	13.21	Nitrite	BMB*	0.016	0.095	0.46
7	16.30	Sulphate	BM	0.015	0.097	0.43
8	16.75	Oxalate	MB	0.014	0.088	0.46
9	17.62	Bromide	BMB*	0.009	0.039	0.43
10	18.76	Nitrate	BMB*	0.011	0.042	0.41
11	19.56	Phosphate	BMB*	0.007	0.031	0.47
		TOTAL:		0.14	0.79	4.97

MBS Project 2011-09-10 #2 [modified by Hot lab]   Std 1   ECD_1
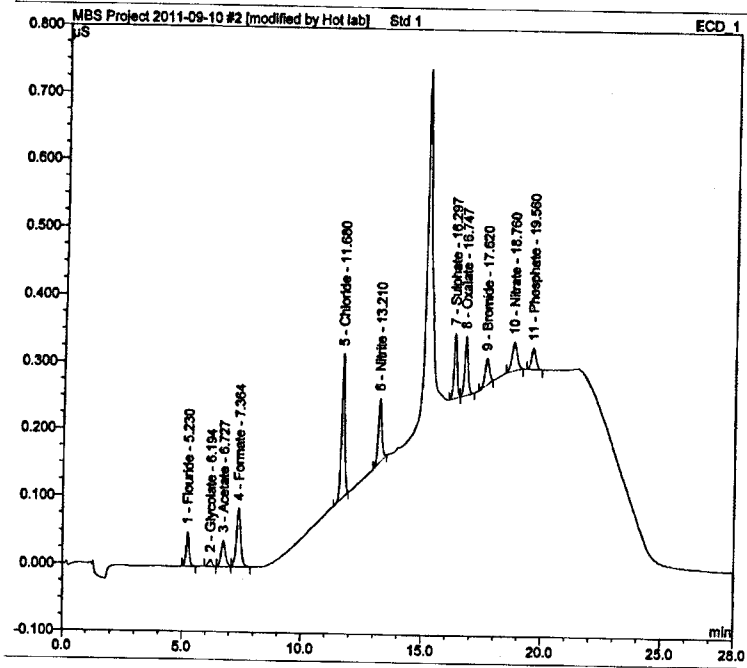
Sample Name	Std 3			Inj. Vol.	1.0
Sample Type:	standard			Dilution Factor	1.0000
Program	ICS 2100 STD2.B3			Comment:	
Inj. Date/Time:	09/09/11 16:17			Run Time:	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.22	Flouride	BM	0.038	0.255	0.47
2	6.19	Glycolate	M *	0.009	0.045	2.21
3	6.73	Acetate	M *	0.049	0.216	2.60
4	7.36	Formate	MB	0.085	0.366	2.73
5	11.66	Chloride	BMB	0.129	0.801	2.61
6	13.21	Nitrite	BMB	0.081	0.461	2.32
7	16.30	Sulphate	BM *A	0.070	0.474	2.06
8	16.75	Oxalate	MB*	0.072	0.460	2.29
9	17.61	Bromide	BMB*	0.039	0.177	1.95
10	18.75	Nitrate	BMB*	0.052	0.203	1.93
11	19.56	Phosphate	BMB*	0.048	0.221	3.27
		TOTAL:		0.67	3.70	24.45

MBS Project 2011-09-10 #3 [modified by Hot lab, 1 peak manually assigned]   ECD_1

Sample Name	Std 3				In. Vol:	1.0
Sample Type:	standard				Dilution Factor:	1.0000
Program:	ICS 2100 STD3 S4				Comment:	
Inj. Date/Time:	09/09/11 16:44				Run Time:	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.22	Flouride	BM	0.076	0.524	0.97
2	6.18	Glycolate	M	0.017	0.089	4.33
3	6.72	Acetate	M	0.099	0.429	5.26
4	7.36	Formate	MB	0.169	0.762	5.41
5	11.67	Chloride	BM	0.241	1.553	4.90
6	13.20	Nitrite	MB	0.161	0.937	4.61
7	16.29	Sulphate	BM *^	0.146	0.998	4.31
8	16.74	Oxalate	MB*	0.149	0.949	4.71
9	17.60	Bromide	BMB*	0.081	0.365	4.06
10	18.73	Nitrate	BM *	0.110	0.429	4.11
11	19.55	Phosphate	MB*	0.112	0.505	7.64
		TOTAL:		1.36	7.54	50.29

MBS Project 2011-09-10 #4 [modified by Hot lab, 1 peak manually assigned]   ECD_1

74
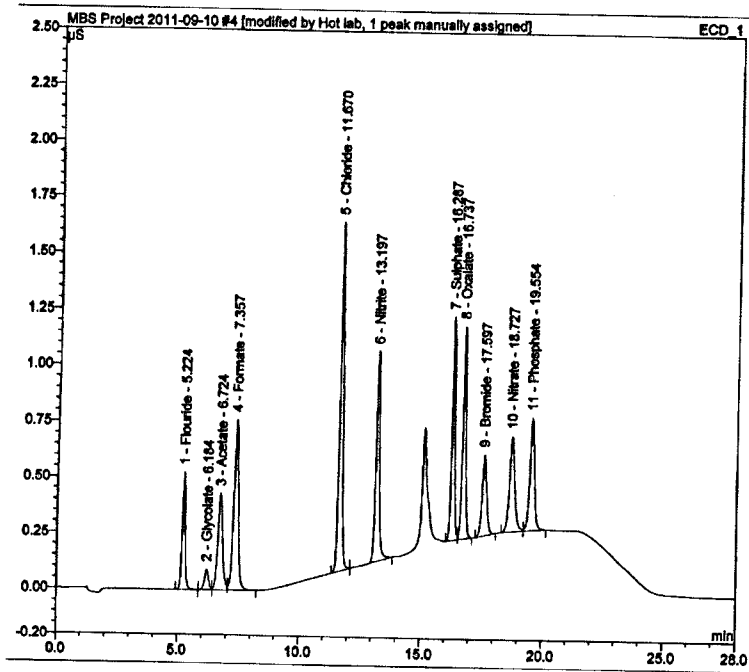
Sample Name:	Std 4		Inj. Vol:	1.0
Sample Type:	standard		Dilution Factor:	1.0000
Program:	ICS 2100 STD4 95		Comment:	
Inj. Date/Time:	09/09/11 17:18		Run Time:	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.23	Flouride	BM	0.163	1.081	2.03
2	6.19	Glycolate	M	0.037	0.191	9.26
3	6.73	Acetate	M	0.202	0.841	10.74
4	7.36	Formate	MB	0.348	1.536	11.13
5	11.67	Chloride	BMB	0.493	3.142	10.02
6	13.20	Nitrite	BMB	0.347	1.969	9.93
7	16.30	Sulphate	BM	0.316	2.159	9.36
8	16.75	Oxalate	M	0.321	2.008	10.17
9	17.60	Bromide	M	0.186	0.805	9.31
10	18.72	Nitrate	M	0.251	0.954	9.40
11	19.55	Phosphate	MB	0.265	1.175	18.08
		TOTAL:		2.93	15.86	109.43

75
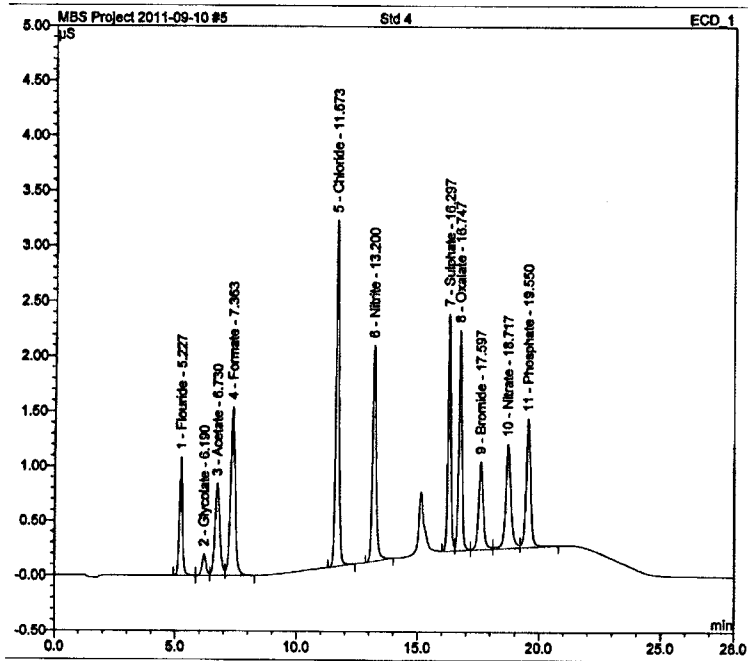
Sample Name:	Std 5			Inj Vol:	1.0
Sample Type:	standard			Dilution Factor:	1.0000
Program:	ICS 2100 STD# 56			Comment	
Inj Date/Time:	09/09/11 17:48			Run Time	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount mg/ltr
1	5.23	Flouride	BM	0.420	2.751	5.23
2	6.19	Glycolate	M	0.097	0.499	24.43
3	6.74	Acetate	M	0.464	1.834	24.64
4	7.37	Formate	MB	0.851	3.652	27.18
5	11.68	Chloride	BMB	1.255	7.917	25.51
6	13.20	Nitrite	BMB	0.897	4.953	25.70
7	16.30	Sulphate	BM	0.842	5.688	24.93
8	16.75	Oxalate	M	0.790	4.826	25.01
9	17.59	Bromide	MB	0.483	2.166	24.17
10	18.69	Nitrate	bM	0.641	2.558	23.96
11	19.55	Phosphate	MB	0.707	3.232	48.25
		TOTAL:		7.45	40.08	279.02

ANION_report/Integration

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)
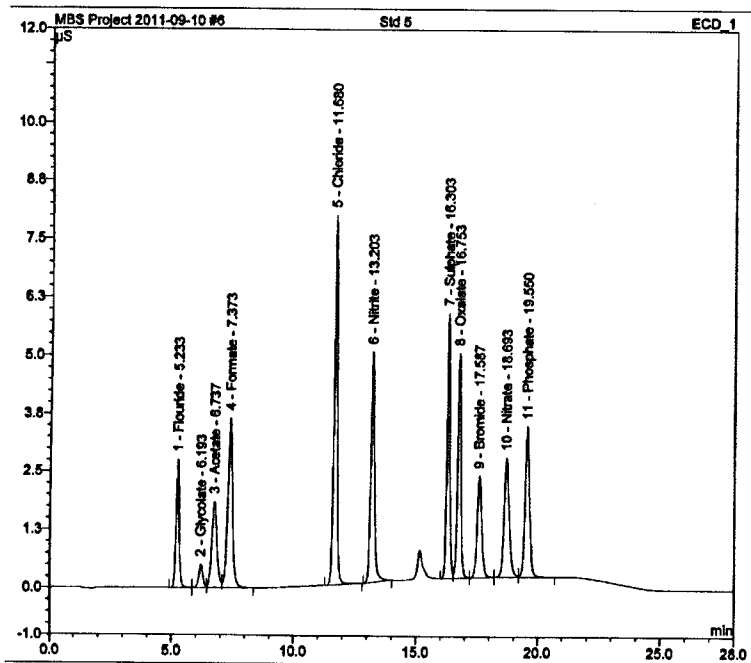
Sample Name:	Std 6			Inj. Vol:	1.0	
Sample Type:	standard			Dilution Factor:	1.0000	
Program:	ICS 2100 STD6 87			Comment		
Inj. Date/Time:	09/09/11 13:13			Run Time	26.00	

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.26	Flouride	BM	1.599	10.068	19.94
2	6.21	Glycolate	M	0.400	1.970	100.26
3	6.76	Acetate	M	1.420	5.102	75.36
4	7.40	Formate	MB	3.105	12.431	99.32
5	11.65	Chloride	BMB	4.913	30.300	99.87
6	13.16	Nitrite	BMB	3.486	17.463	99.86
7	16.25	Sulphate	BM *	3.383	22.393	100.13
8	16.70	Oxalate	MB*	2.800	16.129	88.62
9	17.50	Bromide	BM *	2.007	8.615	100.34
10	18.56	Nitrate	M *	2.683	9.894	100.38
11	19.44	Phosphate	MB*	2.942	12.654	200.79
		TOTAL:		28.74	147.04	1084.86

77
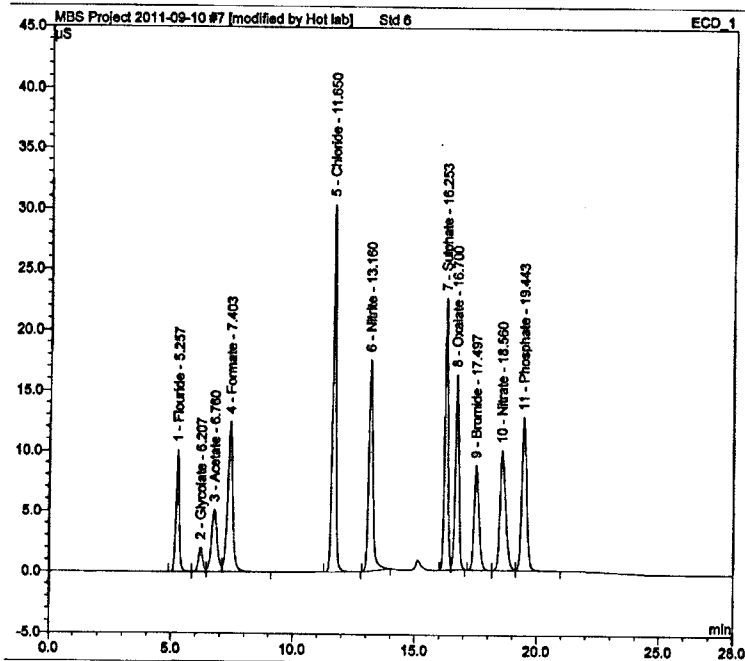
Appendix G

These are the anion results that were obtained using Ion Chromatography. The sample that were analysed were from the water production plant, feed-trains and steam generators.

Sample Name:	9 SEP			Inj. Vol:		1.0
Sample Type:	unknown			Dilution Factor:		200.0000
Program:	ICS 2100 control R1			Comment:		
Inj. Date/Time:	09/09/11 18:49			Run Time:		28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.23	Flouride	BMB	0.019	0.131	46.61
2	6.01	Glycolate	BMB*	0.002	0.005	93.31
3	6.72	Acetate	BMB*	0.001	0.003	8.21
4	7.36	Formate	BMB	0.007	0.032	45.02
5	11.64	Chloride	BMB*	5.072	31.246	20620.31
6	13.20	Nitrite	BMB*	0.006	0.036	33.72
8	16.27	Sulphate	BMB*	2.791	18.232	16468.56
9	17.61	Bromide	BMB*	0.003	0.013	25.09
10	18.73	Nitrate	BMB*	0.064	0.257	475.75
11	19.51	Phosphate	BMB*	0.000	0.003	5.85
		TOTAL:		7.97	49.96	37824.43
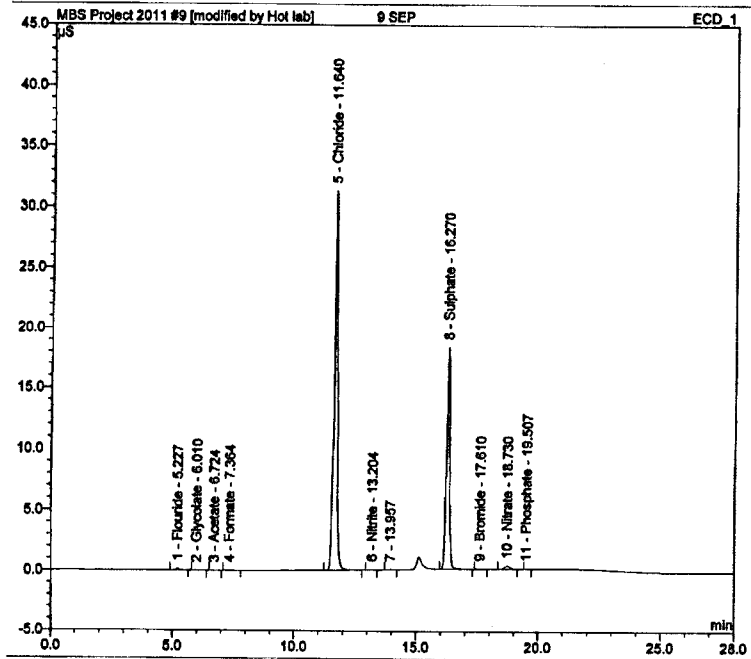
MBS Project 2011 #9 [modified by Hot lab]   9 SEP   ECD_1

Sample Name:	I SDA 001 R1			Inj. Vol.:	1.0	
Sample Type:	unknown			Dilution Factor:	1.0000	
Program:	ICS 2100 sample R2			Comment:		
Inj. Date/Time:	09/09/11 19:19			Run Time:	28.00	

No.	Time min.	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.45	Flouride	BM *	0.229	1.484	2.85
3	6.36	Glycolate	M *^	0.407	1.067	102.12
4	7.42	Acetate	M *^	0.262	0.046	14.95
5	7.63	Formate	MB*	0.026	0.102	0.85
6	11.25	Chloride	BMB*^	629.226	2575.160	12791.04
7	13.26	Nitrite	Rd*	0.023	0.158	0.67
9	16.79	Sulphate	BMB*	0.114	0.633	3.46
10	17.51	Oxalate	BMB*	13.687	35.703	655.49
			TOTAL:	643.99	2614.35	13571.43
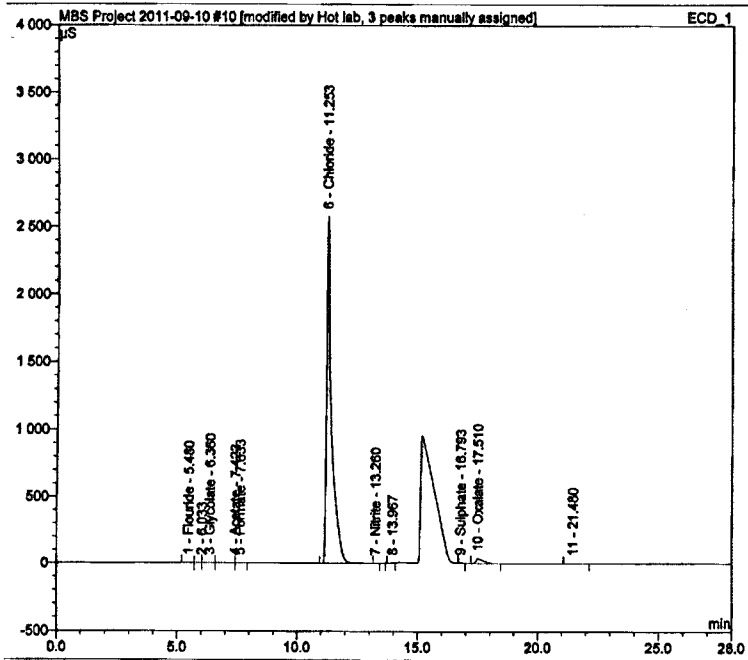
MBS Project 2011-09-10 #10 [modified by Hot lab, 3 peaks manually assigned]   ECD_1

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Sample Name:	8 SDA 002 Fl		In Vol.	1.0
Sample Type:	unknown		Dilution Factor:	1.0000
Program:	ICS 2100 sample R3		Comment	
Inj. Date/Time:	09/09/11 19:53		Run Time	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount ug/kg
1	5.45	Flouride	BM *	0.235	1.487	2.93
3	6.36	Glycolate	M *^	0.450	1.176	112.89
4	7.42	Acetate	M *^	0.327	0.071	17.33
5	7.63	Formate	MB*	0.033	0.120	1.07
7	11.26	Chloride	BM ^	633.939	2588.906	12886.85
8	13.26	Nitrite	MB	0.130	0.517	3.74
9	16.69	Sulphate	BMB	0.106	0.000	3.23
10	17.51	Oxalate	BMB	14.968	38.363	716.81
		TOTAL:		650.19	2630.64	13744.83

MBS Project 2011-09-10 #11 [modified by Hot lab, 3 peaks manually assigned]   ECD_1

Sample Name:	S BDA D/8 CF
Sample Type:	unknown
Program:	ICS 2100 sample R4
Inj. Date/Time:	09/09/11 20:27

Inj. Vol.:	1.0
Dilution Factor:	1.0000
Comment:	
Run Time:	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.44	Flouride	BM *	0.247	1.553	3.08
3	6.32	Glycolate	M *	0.430	1.107	107.83
4	7.40	Acetate	M *^	0.313	0.062	16.59
5	7.56	Formate	MB*	0.025	0.096	0.81
6	11.24	Chloride	BMB*^	630.551	2574.387	12817.98
7	13.25	Nitrite	BMB*	0.022	0.142	0.63
8	16.67	Sulphate	BMB	0.110	0.000	3.33
9	17.51	Oxalate	BMB	14.369	36.846	688.14
		TOTAL:		646.07	2614.19	13638.40

MBS Project 2011-09-10 #12 [modified by Hot lab, 2 peaks manually assigned]   ECD_1
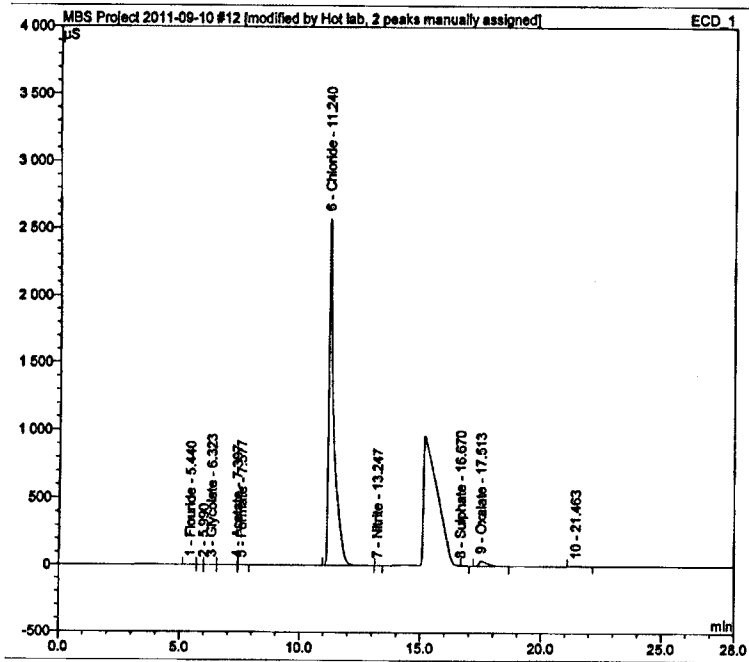
Sample Name:	9 SDA 101 EX			Inj Vol:	1.0
Sample Type:	unknown			Dilution Factor:	1.0000
Program:	ICS 2100 sample R5			Comment:	
Inj. Date/Time:	09/09/11 21:01			Run Time:	26.00

No.	Time min.	Peak Name	Type	Area µS*min	Height µS	Amount µg/Kg
1	5.40	Flouride	BMB*	0.316	2.094	3.93
2	6.28	Glycolate	BMB*	0.501	0.877	125.59
3	6.49	Acetate	Rd*^	0.024	0.002	1.25
4	7.55	Formate	BMB*	0.019	0.095	0.62
5	11.22	Chloride	BMB*^	624.598	2541.856	12696.96
6	13.24	Nitrite	BMB*	0.010	0.071	0.30
7	16.64	Sulphate	BMB	0.123	0.676	3.64
8	17.53	Oxalate	BMB	14.603	37.812	462.18
		TOTAL:		640.19	2583.48	13294.48
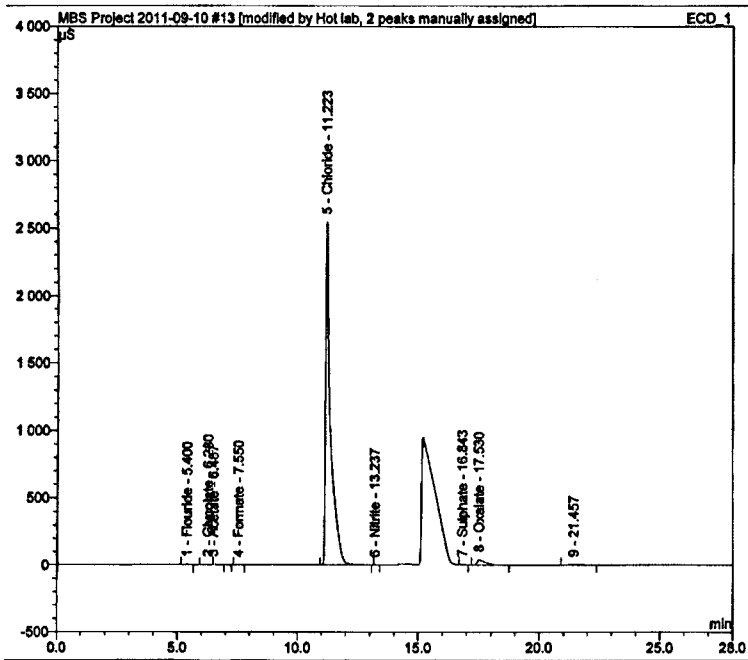
MBS Project 2011-09-10 #13 [modified by Hot lab, 2 peaks manually assigned]   ECD_1

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Sample Name:	# SDA 102 EX			In. Vol.	110	
Sample Type:	unknown			Dilution Factor:	1.0000	
Program:	ICS 2100 sample R6			Comment:		
Inj. Date/Time:	09/09/11 21:36			Run Time:	25.00	

| No. | Time | Peak Name | Type | Area | Height | Amount |
	min			µS*min	µS	ug/kg
1	5.25	Flouride	BM *	0.066	0.436	0.82
2	6.02	Glycolate	M *	0.007	0.023	1.72
3	6.74	Acetate	M ^^	0.002	0.009	0.11
5	7.38	Formate	MB*	0.012	0.054	0.36
6	11.64	Chloride	BMB*	5.692	34.907	115.70
7	13.21	Nitrite	BMB*	0.011	0.065	0.31
8	16.26	Sulphate	BMB*	3.906	25.266	115.67
9	18.71	Nitrate	BMB*	0.076	0.310	2.83
		TOTAL:		9.77	61.07	237.55
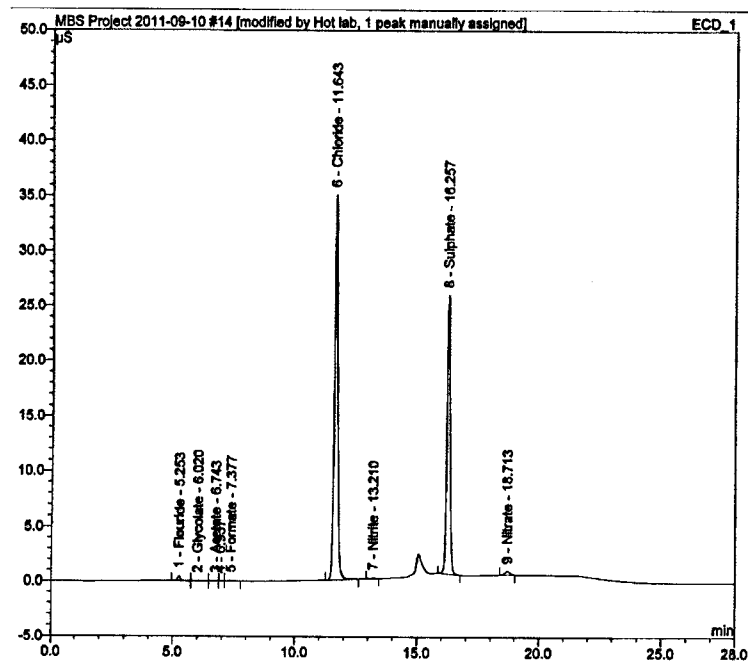
ANION_report/Integration

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Sample Name:	S SDA 103 EX			Inj. Vol.	1.0	
Sample Type:	unknown			Dilution Factor:	1.0000	
Program:	ICS 2100 sample R7			Comment:		
Inj. Date/Time:	09/09/11 22:09			Run Time:	26.00	

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.25	Flouride	BM *	0.101	0.671	1.26
2	6.18	Glycolate	M *	0.001	0.004	0.35
3	6.74	Acetate	M *	0.002	0.009	0.13
4	7.38	Formate	MB*	0.014	0.065	0.46
5	11.66	Chloride	BMB*	0.076	0.488	1.54
6	13.21	Nitrite	BMB*	0.007	0.040	0.19
7	16.29	Sulphate	BMB*	0.082	0.499	2.44
8	16.71	Oxalate	BMB*	0.001	0.005	0.03
9	17.60	Bromide	BMB*	0.001	0.006	0.04
10	18.74	Nitrate	BMB*	0.007	0.028	0.28
		TOTAL:		0.29	1.81	6.71
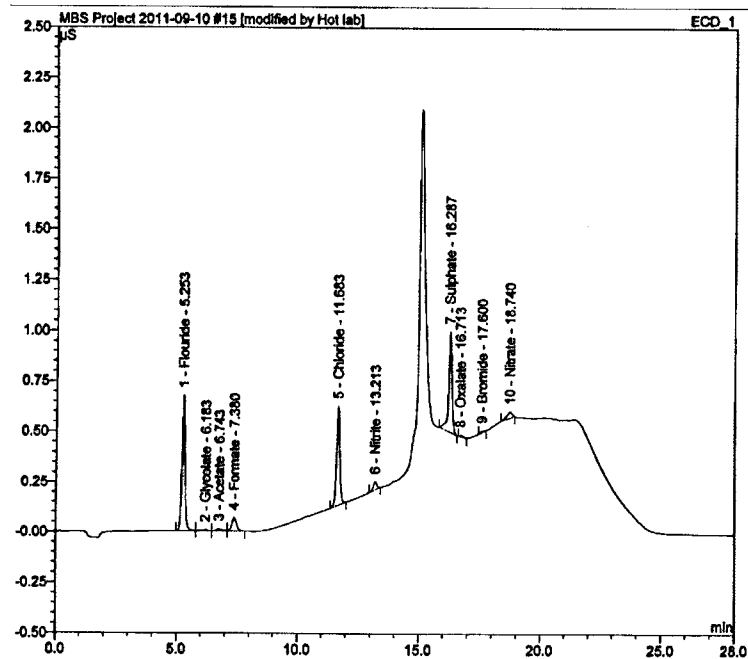
ANION_report/Integration

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)

Sample Name:	9 BBR 001 EA		In. Vol:	1.0
Sample Type:	unknown		Dilution Factor:	1.0000
Program:	ICS 2100 sample R2		Comment:	2011-09-09
Inj. Date/Time:	10/09/11 14:37		Run Time:	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.25	Flouride	BMB	0.003	0.018	0.03
2	6.01	Glycolate	BMB*	0.001	0.004	0.35
3	6.75	Acetate	BM *	0.004	0.013	0.19
4	7.38	Formate	MB*	0.018	0.079	0.56
5	11.66	Chloride	BMB*	1.962	12.360	39.88
6	13.20	Nitrite	BMB*	0.010	0.057	0.28
7	16.27	Sulphate	BMB	0.019	0.137	0.57
8	16.72	Oxalate	BMB	0.004	0.026	0.13
9	17.57	Bromide	BMB	0.002	0.009	0.09
10	18.70	Nitrate	BM	0.029	0.093	1.09
12	19.54	Phosphate	MB	0.006	0.024	0.41
		TOTAL:		2.06	12.82	43.59

MBS Project 2011-09-10 #10 [modified by Hot lab]   ECD_1
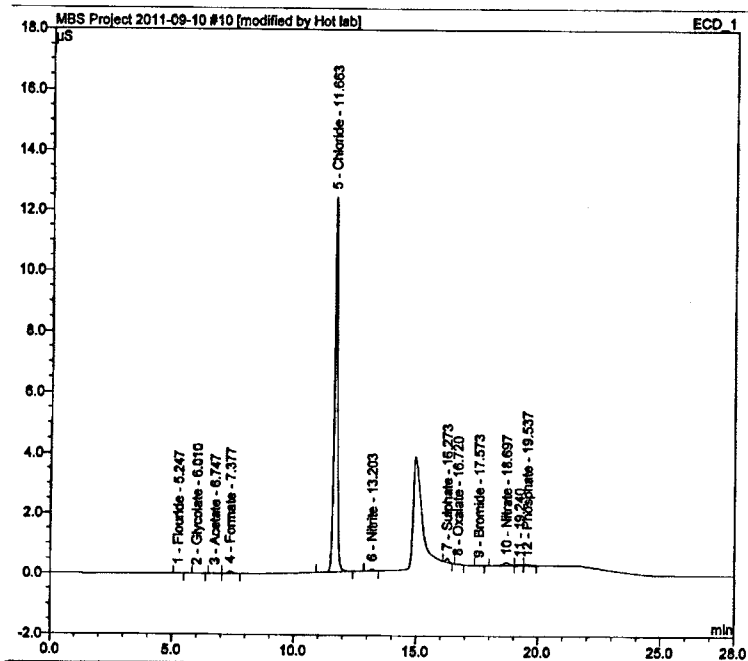
Sample Name:	1-CEX			In. Vol.:	1.5	
Sample Type	unknown			Dilution Factor:	1.0000	
Program:	ICS 2100 sample R8			Comment:		
Inj. Date/Time:	09/09/11 22:43			Run Time:	28.00	

No.	Time min.	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.25	Flouride	BM	0.060	0.404	0.75
2	6.20	Glycolate	M	0.003	0.012	0.87
3	6.75	Acetate	M	0.042	0.167	2.22
4	7.38	Formate	MB	0.027	0.109	0.85
5	11.68	Chloride	BMB	0.050	0.319	1.03
6	13.21	Nitrite	BMB	0.007	0.032	0.20
7	16.28	Sulphate	BMB	0.026	0.174	0.76
8	16.56	Oxalate	BMB*	0.001	0.000	0.03
9	17.61	Bromide	BMB*	0.001	0.005	0.04
10	18.73	Nitrate	BMB*	0.015	0.057	0.56
		TOTAL:		0.23	1.28	7.30

MBS Project 2011-09-10 #16 [modified by Hot lab]   ECD_1

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)
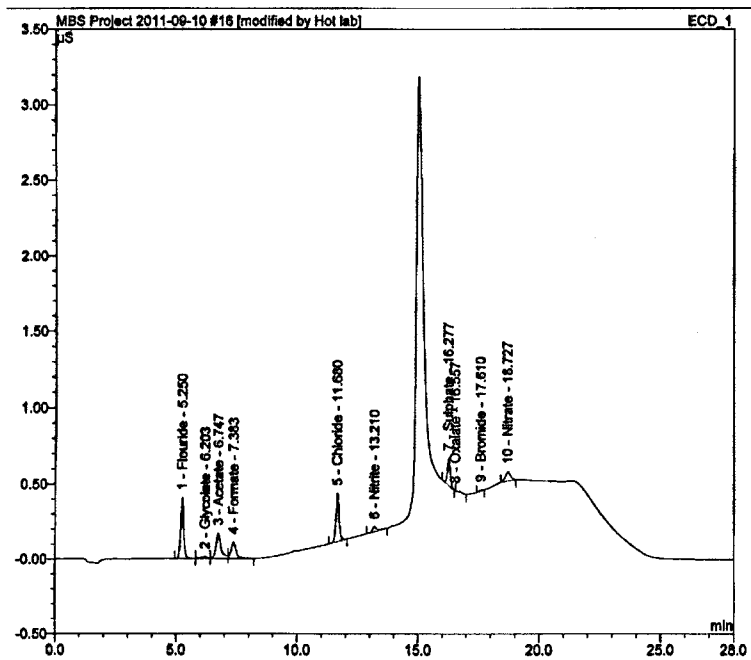
Sample Name:	1 AHP	Inj. Vol.:	1.6
Sample Type:	unknown	Dilution Factor:	1.0000
Program:	ICS 2100 sample R9	Comment:	
Inj. Date/Time:	09/09/11 23:17	Run Time:	26.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.25	Flouride	BMB	0.043	0.287	0.53
2	6.21	Glycolate	BM	0.007	0.035	1.82
3	6.75	Acetate	M	0.122	0.477	6.49
4	7.41	Formate	MB	0.142	0.624	4.54
6	11.68	Chloride	BMB	0.114	0.733	2.32
7	13.21	Nitrite	BMB	0.017	0.065	0.48
8	16.28	Sulphate	BMB	0.025	0.171	0.75
9	16.73	Oxalate	BMB	0.004	0.028	0.14
10	17.60	Bromide	BMB*	0.001	0.005	0.04
11	18.72	Nitrate	BMB*	0.032	0.131	1.21
		TOTAL:		0.51	2.56	18.32
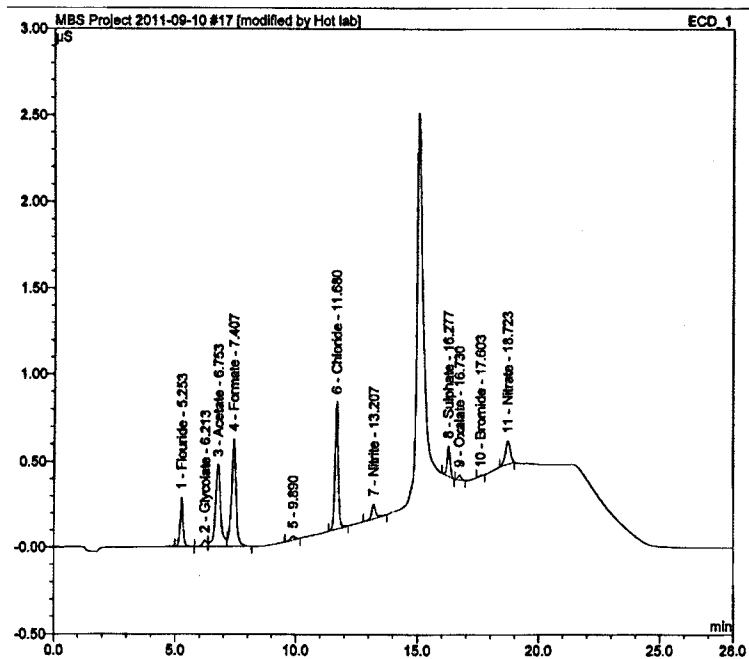
MBS Project 2011-09-10 #17 [modified by Hot lab]   ECD_1

Sample Name:	1-A50		Inj. Vol.:	1.0
Sample Type:	unknown		Dilution Factor:	1.0000
Program:	ICS 2100 sample R10		Comment:	
Inj. Date/Time:	09/09/11 21:51		Run Time:	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.25	Flouride	BMB	0.045	0.305	0.57
2	6.22	Glycolate	BM	0.012	0.059	2.93
3	6.77	Acetate	M	0.281	1.051	14.93
4	7.46	Formate	MB	0.182	0.772	5.81
6	11.69	Chloride	BMB	0.035	0.222	0.71
7	13.21	Nitrite	BMB	0.018	0.089	0.51
8	16.27	Sulphate	BMB	0.008	0.059	0.25
9	16.73	Oxalate	BMB	0.004	0.027	0.14
10	17.55	Bromide	BMB*	0.001	0.004	0.03
11	18.72	Nitrate	BMB*	0.036	0.150	1.34
		TOTAL:		0.62	2.74	27.20

MBS Project 2011-09-10 #18 [modified by Hot lab] ECD_1

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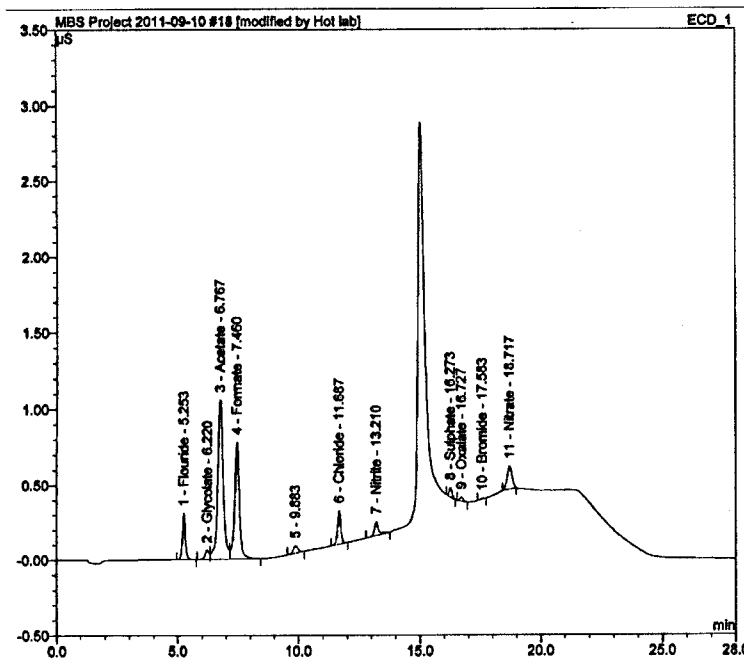
Sample Name:	1 VVP		Inj. Vol.	1.0	
Sample Type:	unknown		Dilution Factor:	1.0000	
Program:	ICS 2100 sample R11		Comment:		
Inj. Date/Time:	10/09/11 00:26		Run Time	28.00	

No.	Time min	Peak Name	Type	Area µS·min	Height µS	Amount µg/kg
1	5.25	Flouride	BMB	0.021	0.142	0.26
2	6.21	Glycolate	BM	0.007	0.034	1.74
3	6.75	Acetate	M	0.125	0.506	6.63
4	7.41	Formate	MB	0.133	0.585	4.25
6	11.67	Chloride	BMB	0.027	0.172	0.56
7	13.20	Nitrite	BMB	0.014	0.072	0.40
8	16.26	Sulphate	BMB	0.006	0.040	0.17
9	16.72	Oxalate	BMB	0.004	0.025	0.13
10	17.58	Bromide	BMB*	0.001	0.004	0.03
11	18.72	Nitrate	BMB*	0.013	0.056	0.50
		TOTAL:		0.35	1.64	14.66

MBS Project 2011-09-10 #19 [modified by Hot lab]   ECD_1

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)

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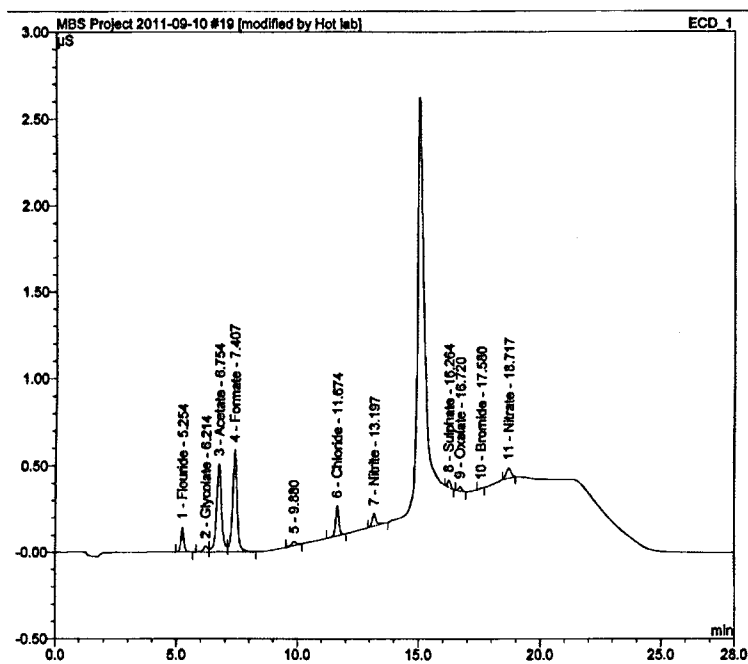
Sample Name:	1 APG 001 GV		Inj. Vol.:	1.0
Sample Type:	unknown		Dilution Factor:	1.0000
Program:	ICS 2100 sample R12		Comment:	
Inj. Date/Time:	10/09/11 01:00		Run Time:	28.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.26	Flouride	BMB	0.093	0.618	1.16
2	6.23	Glycolate	BM	0.182	0.855	45.70
3	6.78	Acetate	M	0.256	0.908	13.60
4	7.63	Formate	MB	0.436	1.427	13.93
6	11.69	Chloride	BMB	0.090	0.568	1.83
7	13.21	Nitrite	BMB	0.019	0.100	0.54
8	16.28	Sulphate	BMB	0.020	0.138	0.60
9	16.73	Oxalate	BMB	0.010	0.061	0.30
10	17.60	Bromide	BMB*	0.003	0.016	0.15
12	18.73	Nitrate	M *	0.026	0.093	0.96
13	19.23	Phosphate	MB*	0.007	0.026	0.46
		TOTAL:		1.14	4.81	79.23
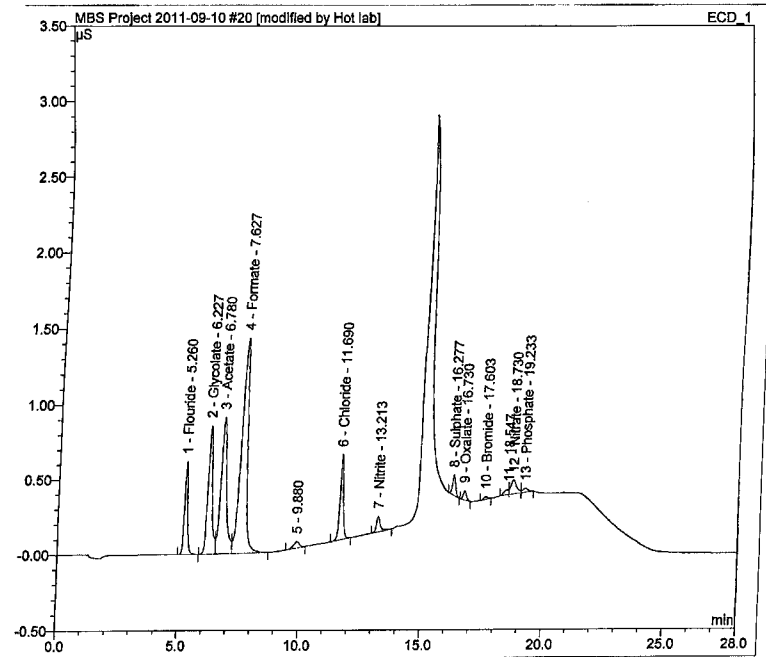
MBS Project 2011-09-10 #20 [modified by Hot lab]   ECD_1

Sample Name:	1 ASG 002 GV			Inj. Vol:	1.6	
Sample Type:	unknown			Dilution Factor	1.0000	
Program:	ICS 2100 sample R13			Comment		
Inj. Date/Time:	10/09/11 01:34			Run Time	28.00	

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.26	Flouride	BMB	0.085	0.567	1.06
2	6.23	Glycolate	BM	0.149	0.694	37.27
3	6.78	Acetate	M	0.250	0.884	13.26
4	7.62	Formate	MB	0.315	1.047	10.08
6	11.69	Chloride	BMB	0.065	0.405	1.32
7	13.22	Nitrite	BMB	0.013	0.065	0.38
8	16.29	Sulphate	BMB	0.013	0.090	0.38
9	16.74	Oxalate	BMB	0.004	0.029	0.14
10	17.61	Bromide	BMB*	0.002	0.012	0.12
12	18.75	Nitrate	M *	0.012	0.033	0.46
13	19.23	Phosphate	MB*	0.008	0.026	0.53
		TOTAL:		0.92	3.85	64.99

ANION_report/Integration

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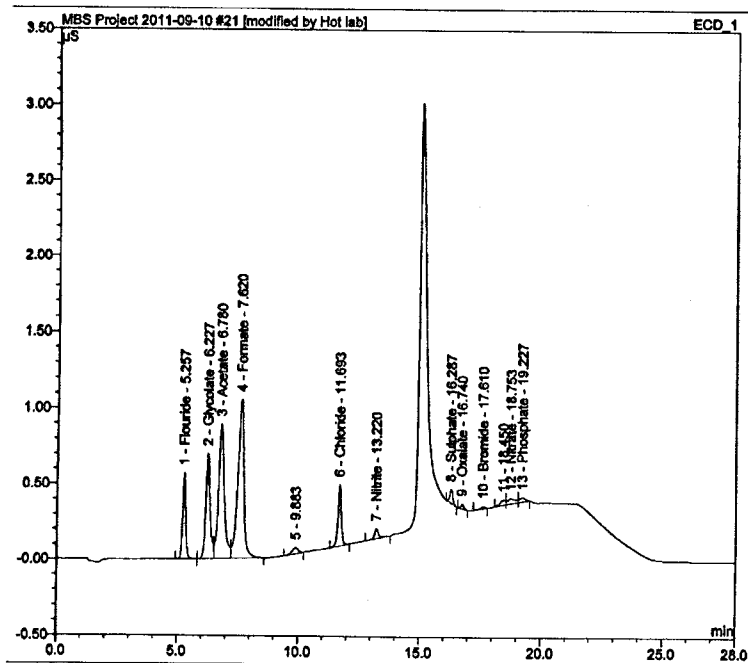
Sample Name:	1 APG 003 GV			Inj. Vol.	1.0	
Sample Type:	Unknown			Dilution Factor	1.0000	
Program:	ICS 2100 sample R14			Comment		
Inj. Date/Time:	10/09/11 02:08			Run Time	28.00	

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount µg/kg
1	5.26	Flouride	BMB	0.082	0.549	1.03
2	6.23	Glycolate	BM	0.154	0.692	38.49
3	6.78	Acetate	M	0.243	0.858	12.88
4	7.61	Formate	MB	0.328	1.052	10.46
6	11.69	Chloride	BMB	0.073	0.456	1.48
7	13.21	Nitrite	BMB	0.010	0.053	0.30
8	16.25	Sulphate	BMB	0.012	0.063	0.35
9	16.57	Oxalate	BMB	0.003	0.000	0.09
10	17.55	Bromide	BMB	0.003	0.012	0.13
		TOTAL:		0.91	3.75	65.20

MBS Project 2011-09-10 #22 [modified by Hot lab]   ECD_1

1 - Flouride - 5.257
2 - Glycolate - 6.227
3 - Acetate - 6.777
4 - Formate - 7.607
5 - 9.880
6 - Chloride - 11.687
7 - Nitrite - 13.210
8 - Sulphate - 16.253
9 - Oxalate - 16.570
10 - Bromide - 17.550

ANION_report/Integration
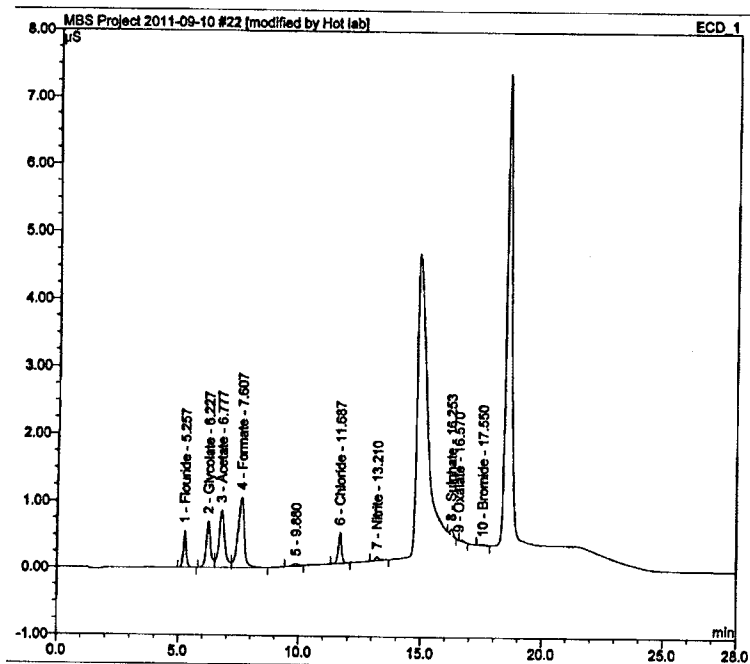
Appendix H

These are the results that were sent to Germany for organic characterisation. The sample was taken on the water production plant at KNPS.

DOC-LABOR DR. HUBER **WWW.DOC-LABOR.DE**

DOC characterisation of Koeberg Nuclear Power Station waters REV1

Your proj.-ID/ our proj.-ID:	/ Eskom_7a (A2753a)
Project Partner/ contact:	Mandisi Stwayi /
# and type of samples:	8 (water)
Measuring conditions:	column: 51001 / 031 flows: 1.5 / Ø / Ø buffer: STD

Sampling date:	2012-Feb-	STD ☒	MC ☐	
Incoming date:	2012-Feb-23	report:	Y ☒	N ☐
Measuring date:	2012-Feb-23-24	data processing:	Dipl.-Ing. A. Balz	
Date of Report:	2012-Mar-20 21: REV1	report:	Dr. S. Huber	

Technical note: LC-OCD stands for "Liquid Chromatography – Organic Carbon Detection". Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV-absorbance at 254 nm (UVD) and organic bound nitrogen (OND). All concentration values refer to mass of organic bound carbon (OC). As a „rule-of-thumb" compound mass is about twice (for acids threefold) the value of OC. Chromatograms are processed on the basis of area integration using the program ChromCALC. In many samples the acid fraction contains low-molecular mass humic acids which are subtracted by ChromRES on the basis of SAC/OC ratio for HS. Thus, despite the visible presence of an acid peak there may no LMW acids be present.

SUMMARIC PARAMETERS:

DOC (Dissolved OC): Determined in the column bypass after in-line 0.45 µm filtration.

HOC (Hydrophobic OC): Difference DOC minus CDOC, thus all OC retained on the column is defined as „hydrophobic". This could be natural hydrocarbons or sparingly soluble "humins" of the humic substances family.

INORGANIC COLLOIDS (respond only in UV-Chromatograms): Negatively charged inorganic polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si are detected by UV light-scattering (Raleigh-effect).

CDOC (Chromatographic DOC): This is the OC value obtained by area integration of the total chromatogram. Chromatographic subfractions of CDOC are:

ROM = Refractory Organic Matter

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Results

Table 1

Project: Eskom_7a	DOC Dissolved ppb-C %DOC	HOC* Hydrophob ppb-C %DOC	CDOC Hydrophil. ppb-C %DOC	BIO-polymers ppb-C %DOC	DON (Norg) ppb-N	N/C µg/µg	% Proteins in BIOpol.** % BIOpol.	Humic Subst. (HS) ppb-C %DOC	DON (Norg) ppb-N	N/C µg/µg	Aromaticity (SUVA-HS) L/(mg*m)	Mol-Weight (Mn) g/mol	Position in HS diagram –	Building Blocks ppb-C %DOC	LMW Neutrals ppb-C %DOC	LMW Acids ppb-C %DOC	Inorg. Colloid. SAC (m⁻¹)	SUVA (SAC/DOC) L/(mg*m)
9SDA 201EX	1057 100%	155 14.8%	902 85.4%	n.q.	n.q.	–	–	414 39.1%	7	0,02	2,12	479	A	268 25.4%	213 20.2%	7 0.8%	n.q.	2,99
9SDA 001FI	978 100%	34	945 96.6%	20 2.1%	n.q.	–	–	392 40.1%	11	0,03	1,79	461	B	294 30.0%	238 24.3%	n.q.	0,04	2,96
9SDA 002FI	1004 100%	48 4.7%	956 95.2%	22 2.2%	n.q.	–	–	461 45.9%	9	0,02	1,92	462	C	391 39.0%	231 23.0%	n.q.	0,05	3,25
9SDA (C-Filter Down)	938 100%	68 7.3%	869 92.7%	11 1.1%	n.q.	–	–	382 40.5%	8	0,02	1,83	461	D	285 30.0%	192 20.0%	n.q.	0,03	3,14
9SEP	1148 100%	150 13.1%	998 86.9%	16 1.4%	n.q.	–	–	422 36.8%	9	0,02	2,04	458	E	314 27.0%	247 21.5%	n.q.	0,01	2,97
9SDA 202EX	53 100%	15 27.6%	38 72.2%	6 11.9%	n.q.	–	–	n.q.	n.q.	–	–	–	–	5	26	n.q.	0,03	22,39
9SDA 203EX	42 100%	6 14.2%	36 85.8%	8 19.7%	n.q.	–	–	n.q.	n.q.	–	–	–	–	5	22	n.q.	0,03	27,25
9SER 002BA	44 100%	6 12.9%	38 87.1%	6 0.9%	n.q.	–	–	n.q.	n.q.	–	–	–	–	4	26	2	0,02	29,62

LMW = low-molecular weight
DON = Dissolved organic nitrogen
n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)
n.m. = not measured

*:Grey colour in HOC: Significance unclear
**:under the presumption that all org. N in the BIOpolymer fraction originates from proteins

Discussion

Pre-treatment

Town water used for demineralisation is of excellent quality:

1. DOC is around 1 ppm only.
2. Water has undergone a very efficient flocculation step.
3. biopolymers are practically not present, thus raw water is presumably a ground water.
4. There are no indications of biologically available organic matter.

Such waters do not require extensive pre-treatment. After mechanical cleaning (removal of particles) and (if necessary) destruction of free chlorine (e.g. with carbon filters) such water may directly be sent to SAC filter.

Therefore it is not surprising that charcoal filters have no impact on DOC, except destruction of chlorine (if present).

Demineralisation

The cation filter has no impact on DOC and this is very good. Fouling of SAC filter is not to be expected.

Due to excellent raw water composition, waters after SBA and MB are well below 100 ppb.

Water from storage tank

Sample 9SER 002BA contains ammonium. There are almost no indications for oxidation products of DOC, only 2 ppb of organic acids are found.

Conclusions.

An excellent system with very good data in respect to DOC.

Neither Water Treatment Plant nor Water Steam Cycle should have any problems as far as organics are concerned.
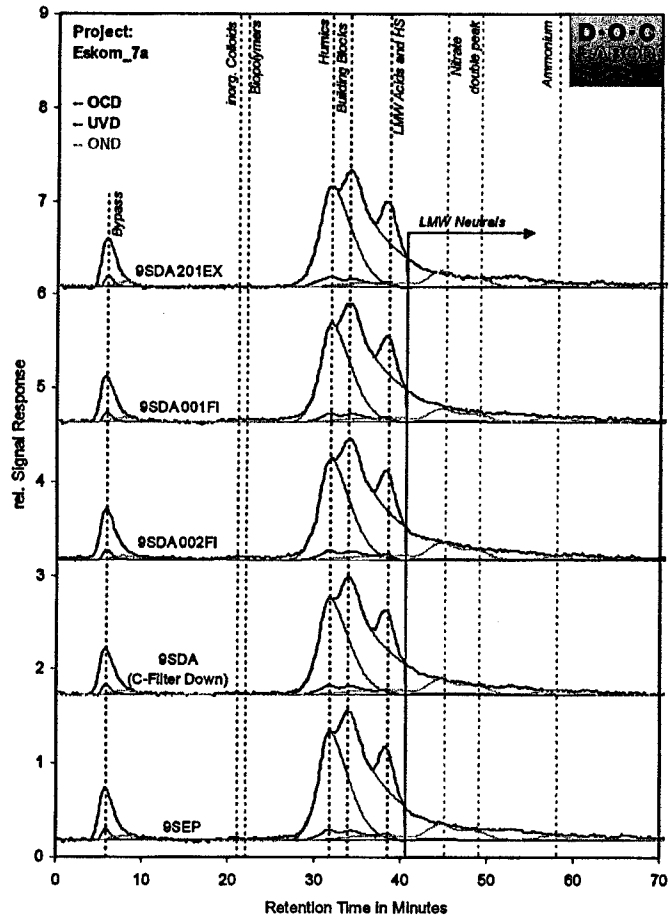
End of Report
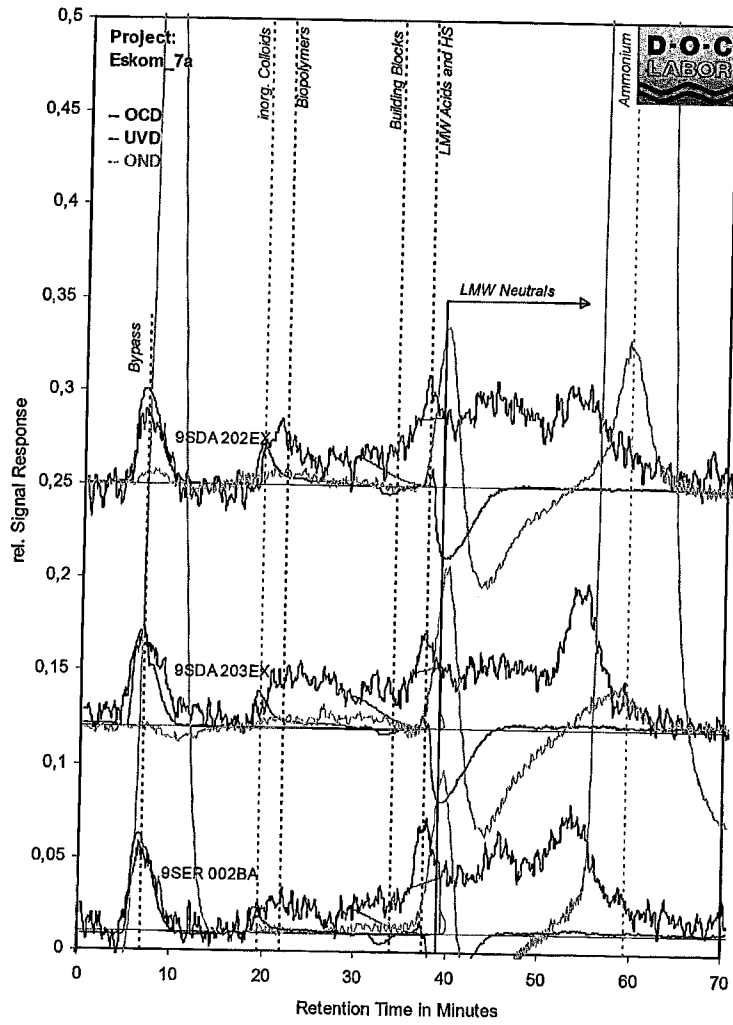
3

95

Fig. 1a: LC-OCD chromatograms
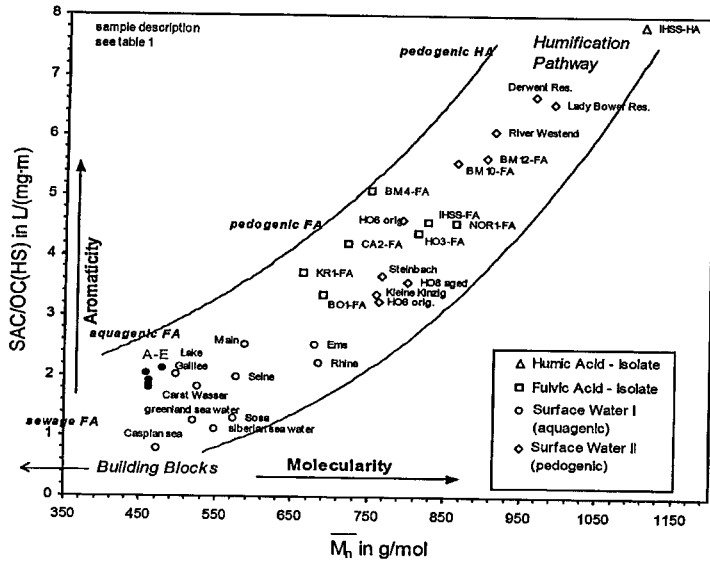
Fig. 1b: LC-OCD chromatograms

Fig. 2: Humic substances diagram

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