

DECLARATION

I declare that this dissertation is my own un-aided work that has not been submitted to any university or tertiary institution. It is submitted for the Degree Magister Technologiae to the Department of Chemistry, Vaal University of Technology, Vanderbijlpark.

Signature

Date:

DEDICATION

I dedicate this to all the people who believe that the “Root of education are bitter, but the fruits are sweet”. Get education, be empowered and make a difference in life.

ACKNOWLEDGEMENTS

I would like to thank Professor EB Naidoo, Mr G Gericke and Mrs J Reeves for the support that they have given me throughout my studies.

My colleagues, Dipuo Chaha, Happiness Mojela, Lebo Pooe, Tebogo Tseka, Setsweke Phala, Arnot and Kriel Power Stations staff. I would like to say, without you, this would have been not possible.

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My beautiful family: Kesa, Keamogetse and Kewaone for being patient and spending some of your time without me due to my studies.

ABSTRACT

Natural organic matter if not removed from water used for electricity generation has dire consequences that affect the long term plant health. The main problem is that organic matter at higher temperature and pressure disintegrate into smaller organic acids and carbon dioxide. This causes the cycle water and steam to be acidic and this can result in corrosion of the plant.

The raw water from the Komati (Arnot power station) and Usutu (Kriel power station) scheme were analysed to determine the organic profile and seasonal variation. There was a noticeable variation in the quality of the water with an increase in DOC during rainy season. The water was found to be containing hydrophobic as well as hydrophilic molecules that could be quantified with a liquid chromatography organic detector (LC-OCD).

Current water treatment processes employed at the two stations, Arnot and Kriel, has demonstrated the capability of removing organics to just over 50 percent at the pre-treatment section. The water treatment plant includes demineralisation plant that was able to produce water that met Eskom's target specifications of less than 250 ppb DOC values.

Qualitative and quantitative analysis of the steam-condensate water was done by use of an ion chromatography method. The determined organic anions were found to be acetates, formates and lactates.

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DESCRIPTION OF ACRONYMS

ACC	Acid cation conductivity
Blr	Boiler
CEP	Condensate extraction pump
CPP	Condensate polisher plant
DBP	Disinfection by-product
DCC	Degassed cation conductivity
DOC	Dissolved organic acid
DVB	Divinyl-benzene
FTIR	Fourier transformer infrared
GC-MS	Gas chromatography mass spectroscopy
HAA	Halo acetic acid
HOC	Hydrophobic organic acid
HPSEC	High performance size exclusion chromatography
IC	Ion chromatography
KHP	potassium hydrogen phthalate
LC-OCD	Liquid chromatography organic carbon detector
LMWOA	Low molecular weight organic acid
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
OCD	Organic carbon detector
OEM	Original equipment manufacturer

OND	Organic nitrogen detector
QC	Quality control
RO	Reverse osmosis
SUP	superheated
SUVA	Specific ultraviolet absorption
THM	Trihalo methane
TOC	Total organic carbon
UF	Ultra-filtration
UHP	Ultra-high purity
UVD	Ultra-violet detector

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Thermal electricity generation requires a power plant (boiler, turbine and generator), heat source (coal) and water. Poor quality water can result in boiler tube leaks (due to corrosion) and deposition in critical parts of the plant [1]. These problems (corrosion and deposition) result in the efficiency of the electricity generating plant being compromised if not controlled and minimised.

It is therefore a requirement that ultra pure water be used for electricity generation, because it contains only trace amount of dissolved solids and salts [2]. Water treatment processes are used to treat and purify raw water to produce ultra pure water with conductivity of 0.060 $\mu\text{S}/\text{cm}$ (standard specification for Eskom's power plants).

It is the responsibility of a chemist in a power plant to ensure that the cycle water used for power generation is free from contaminants that cause corrosion and deposits in various parts of the plant. The other responsibility is to ensure that the pH of the water (ultra-pure) is raised to the required pH and conductivity that inhibits corrosion.

Ammonium hydroxide and sodium hydroxide are generally used to increase the pH from approximately 6.8 (the pH of demineralised water) to above pH of 9 in some power plants [3]. Dosing with these bases, besides increasing the pH, is also to increase the conductivity of the boiler-steam/water [4]. It is however important to still maintain and monitor the overall chemistry to within the specified control limits.

1.1.1 Organics in raw water

Raw water supplied from dams, contains dissolved solids, liquids (oils), gases, micro organisms, algae and suspended matter [5]. This suspended matter comprises of colloidal matter, inorganic suspended matter and organic matter.

Organic matter (Natural Organic Matter/NOM) is largely made up of large complex molecules e.g. humic, fulvic and tannic acids, polysaccharides, free/lower molecular weight organic acids and low molecular weight neutral compounds. All these complex molecules are collectively referred to as Total Organic Carbon (TOC). These components originate from decaying microbiological, vegetable and animal matter and also include man-made substances such as pesticides and herbicides.

High concentrations of TOC in cycle water used for electricity generation can result in the following problems [1,2,3]:

- Fouling of condensate polisher resins, requiring more frequent resin regeneration and replacement due to impaired kinetic performance
- Break down (of TOC) to low molecular weight organic acids that lower the pH of early condensate that has a possibility of causing turbine corrosion
- Deposition of organic carbons along with other contaminants (present in the water) onto heat exchange surfaces that can significantly reduce heat exchange efficiency, and
- Corrosion as well as foaming in boiler drums, and that result in an increase in carryover of other contaminants into the steam.

Organic matter in water occurs as insoluble, soluble and colloidal constituents. Clarification in the water treatment plant assists in the removal of insoluble organic matter. Removal of soluble and colloidal matter is done mainly by using flocculation and coagulation in water treatment processes [5]. Further removal of organic matter is carried out at the demineralisation water plant by ion exchange processes.

1.1.2 Contaminants in cycle water used for electricity generation

The other contaminants (besides TOC) that are of major concern in the cycle water are chlorides, sulphates, silica and sodium. The sources of these contaminants are mainly the in-leakage of cooling water through the condenser tubes and slippage from water treatment processes.

1.1.3 Measurements of contaminants in cycle water

Acid cation conductivity (ACC, sometimes referred to as KHI, an abbreviation for Konductivity of Hydronium Ion) is normally used as a tool to measure the level of contaminants in the cycle water of a power plant (refer to illustration in figure 1.1).

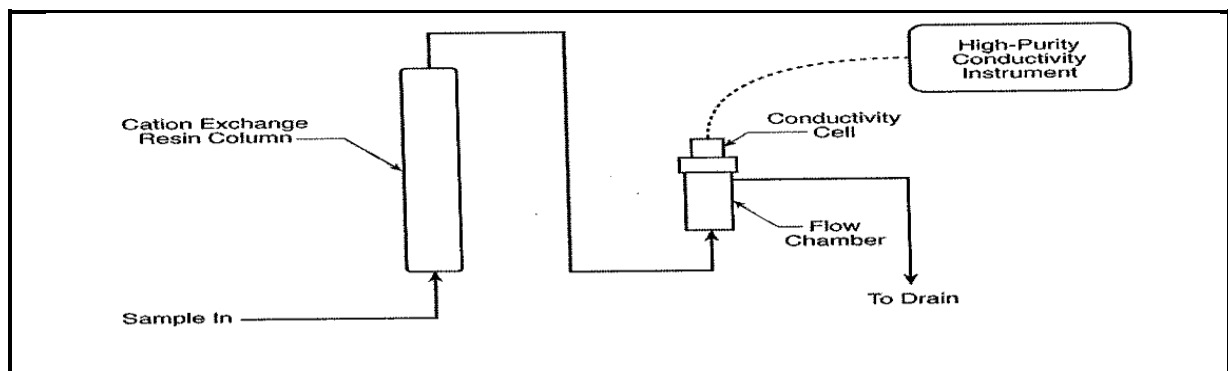


Figure 1.1: Typical cation conductivity flow diagram [6]

The water sample that contains cations (ammonium, traces of iron, copper and sodium) and anions (chlorides, sulphates, carbonates and nitrates) is passed through a cation exchanger resin (Cation Exchanger Resin Column). The resin in the column is styrene polymer copolymerised with divinylbenzene (DVB) with H^+ ions attached to the polymer [7]. The purpose of this resin column is to remove all the cations present in the sample and replace them with H^+ cations.

The reaction or exchanger mechanism is as follows;



Figure 1.2 depicts an example of the cation exchange process. The cation used in the example is a calcium ion.

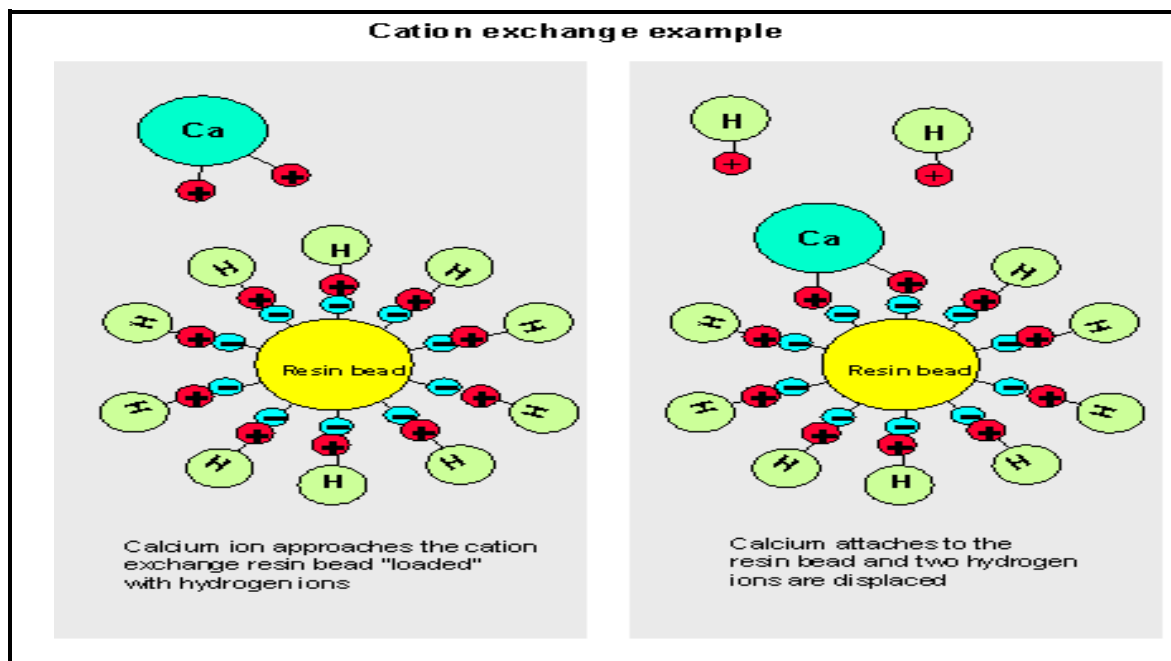


Figure 1.2: Cation exchange mechanism [7]

The conductivity measurement at the conductivity cell (at the outlet of the cation exchanger resin column) is envisaged to be $0.055 \mu\text{S/cm}$. The presence of anions (Cl^- , SO_4^{2-} and CO_3^{2-}) after exchange of cations in the resin column, however, results

in elevated conductivity due to the formation of mineral acids (HCl, H₂SO₄ and H₂CO₃).

Chlorides and sulphates concentrations are measured by ion chromatography and their concentrations are correlated with the acid conductivities obtained. In most cases, it is observed that the concentrations of the two anions (Cl⁻ and SO₄²⁻) do not account for the higher than expected ACC values obtained. It was found that in most cases, the masking species were the dissolved gases (mainly carbon dioxide) that were present in the cycle water. Carbon dioxide, when dissolved in water at low pH's form carbonic acid which results in high conductivity [6].

1.1.4 The measurement of dissolved gases in cycle water

Technological developments resulted in instrument suppliers providing instruments that are able to remove dissolved gases from ultra-pure water. This makes it possible for the conductivity of ultra-pure water free from carbonic acid to be determined [8]. The conductivity obtained after removal of dissolved gases is referred to as degassed cation conductivity (DCC).

DCC is obtained by passing the sample through a cation resin column to remove ammonia and other cations that are dissolved in the water. The conductivity is then measured and the water sample is passed through a reboiler unit that removes the dissolved gases. Figure 1.3 illustrates the principle of degas conductivity.

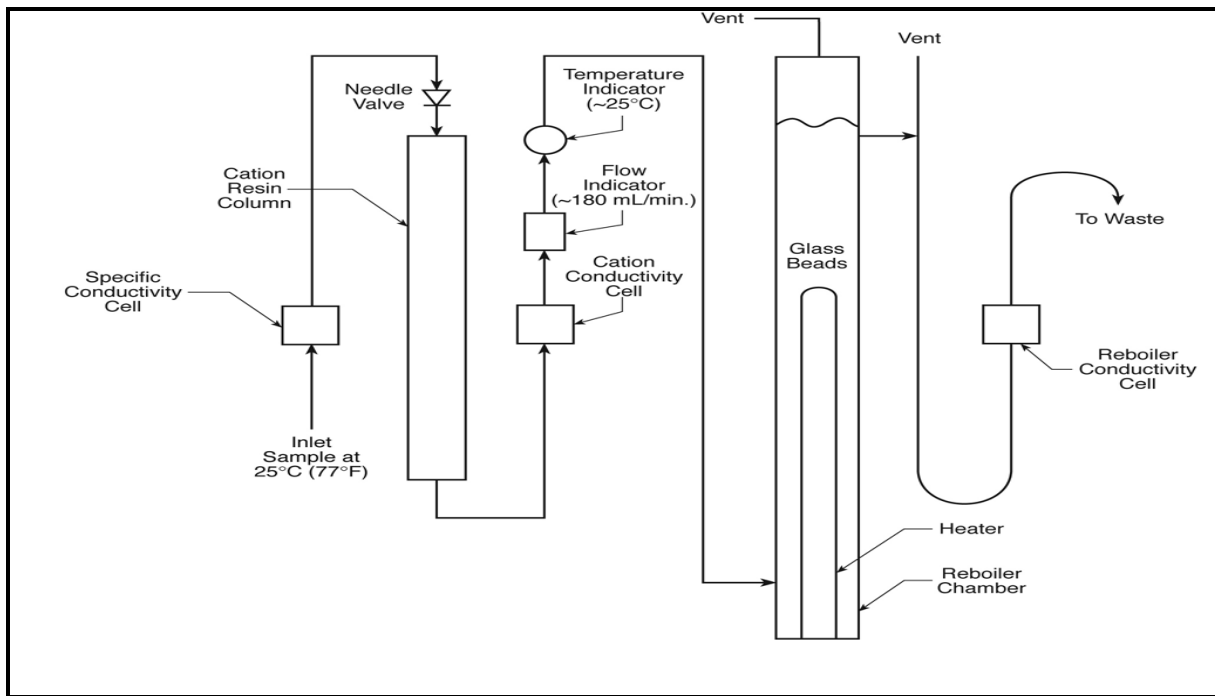


Figure 1.3: Principle of degas conductivity determination [8]

The conductivity after degassing the sample is determined at the reboiler conductivity cell and correlated with the measured anions (chlorides and sulphates).

Theoretical conductivity determined by the correlation of the ultra-pure water conductivity, conductivity that is due to anions (analysed by IC) and degas cation conductivity is always found to be less than the actual cation conductivity measured. Equation 1 shows the calculation for the measured cation conductivity.

$$\text{Measured cation conductivity} = K_{25\text{Cl}/\text{SO}_4}^2 + K_{\text{H}_2\text{O}} + K_{?} \dots \dots \dots \text{.Equation 1.1}$$

Where, $K_{25\text{Cl}/\text{SO}_4}^2$ is the conductivity contribution due to chlorides and sulphates at 25°C

$K_{\text{H}_2\text{O}}$ is the conductivity contribution due to dissociation of water at 25 °C and

$K_{?}$ is the conductivity due to unknown specie (subject of the study)

These suggest that there are other species that contribute to the conductivity of the cycle water. One of the aims of this research as described in Section 2 of this thesis, is to determine the source of this un-accounted conductivity ($K_?$).

The suspect species were determined by using chromatographic methods of analysis. Ion chromatography (IC) is an established method that can be used to determine trace amounts of anions in solution [9].

1.2 PROBLEM STATEMENT

The quality of water used for electricity generation is crucial hence it is monitored and controlled at specified chemistry target values. Poor quality water can result in boiler tube leaks (due to corrosion) and deposition of suspended/dissolved particles in critical parts of the plant. Raw water, when received from dams, contains dissolved solids, liquids, gases, micro organisms, algae and suspended matter [5]. This suspended matter comprises of colloidal matter, inorganic suspended matter and organic matter.

Organic matter is largely made up of large complex molecules e.g. humic, fulvic and tannic acids together with polysaccharides, free organic acids and low molecular mass neutral compounds. All these complex molecules are collectively referred to as Total Organic Carbon (TOC). This TOC break down (at high temperature and pressure) to form carbon dioxide and low molecular weight organic acids that lower the pH of early condensate that causes turbine corrosion [1,2].

1.3 OBJECTIVE OF THE STUDY

- 1.3.1 To determine the organic profile of the raw water from the Komati (Arnot Power Station) and Usutu (Kriel Power Station) water scheme
- 1.3.2 To identify different types of organic acids found in the main steam of the power plant
- 1.3.3 To diagnose the impact of the organic acids on plant operation
- 1.3.4 To analyse for the concentration of organic acids found in main cycle water
- 1.3.5 To set specifications for the maximum concentrations of organic acids allowed in cycle water of a power plant.

1.4 VALUE OF THE STUDY

This research is undertaken to assist in the reduction of the chemistry induced failures (corrosion and boiler tube leaks).

The study will also ensure that Eskom stays within the Original Equipment Manufacturer (OEM) guidelines. Transgressions of OEM's guidelines have negative financial implications on insurance claims.

This study will also facilitate a better understanding of the influence of various low molecular weight organic acids on the acid cation conductivity in a cycle water of a power plant.

1.5 SCOPE OF THE STUDY

Chapter 1: This chapter gives a brief overview of the requirements for water purity quality required for electricity generation. It also outlines the possible contaminants present in ultra-pure water, their sources and removal (water treatment processes), and also how these contaminants are measured. The emphasis of this study is based on the contaminants resulting from Natural Organic Matter (NOM) and the impact in power generation process.

Chapter 2: Literature survey on Natural Organic Matter in raw water. Properties, characterisation methods, removal in water treatment processes of NOM in water will also be discussed in this chapter. Finally the possible thermal degradation by-products will be introduced, with the intention of laying the foundation for the experimental methods for the study of this thesis.

Chapter 3: Analytical equipment (both on-line and laboratory) and materials used as well as sampling points and locations will be discussed in this chapter.

Chapter 4: Results and discussion of the experiments will be reported in this chapter.

Chapter 5: Conclusions from the interpreted results and recommendations will be discussed in this chapter.

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CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Raw water from natural streams, dams and rivers contain as part of its constituents, natural inorganic compounds (mainly salts) and organic matter. These natural inorganic salts occur in abundance on the earth's crust and they include sodium, potassium, silicates, chlorides, sulphates and phosphates, to mention but a few [1].

Natural organic matter (NOM) includes various life forms, decaying plant vegetation (tree branches and dead tree logs) present in flowing streams. The constituents of this natural organic matter dissolves in water and results in short and long complex chains of organic matter being introduced [2]. In severe cases this might result in a light discolouring (yellow to brown) of the water.

Industrial waste products such as, agricultural fertilisers, herbicides and insecticide may be dissolved into the river waters [3]. Many if not all water systems suffer from an opaqueness generally known as turbidity which is as a result of the fine particles of clay and sand suspended in it. All these properties of water pose a challenge in water treatment processes [4].

It is relatively easier to remove inorganic matter than it is to remove NOM in raw water. The water treatment processes can remove up-to 80% of NOM from raw water, depending on the nature of the organics present in the water [5]. A discussion on the nature of organics and its removal is discussed in the next sections of this Chapter.

2.2 NATURAL ORGANIC MATTER

NOM has been found to be a mixture of organic compounds that occur in both ground and surface waters. Removal of NOM from water can be challenging because of its conversion to disinfection by-products (DBPs) when chlorine is added for disinfection during water treatment processes. The resulting DBPs from these water treatment processes are tri-halomethanes (THMs) and haloacetic acids (HAAs) [6].

Components of NOM are found to be hydrophobic and hydrophilic in nature. The largest fraction is generally hydrophobic, which makes up the dissolved organic carbon (DOC). Figure 2.1 depicts the classification of NOM in raw water (surface water).

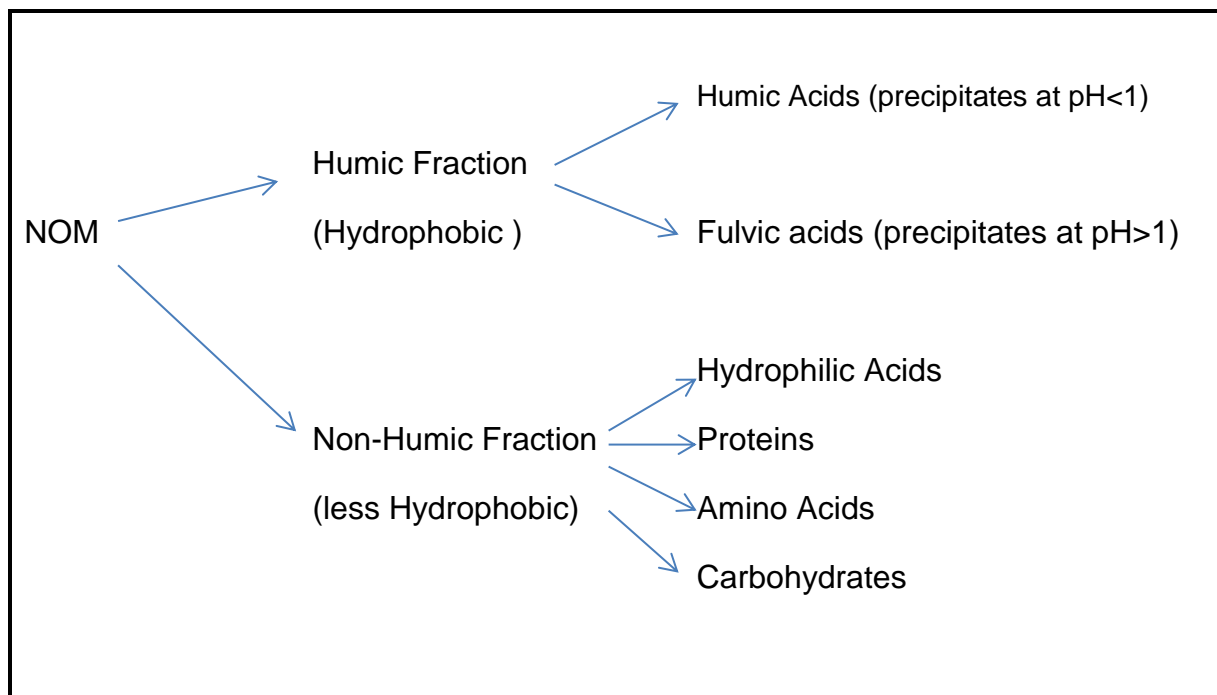


Figure 2.1 Classification of natural organic matter [7]

Hydrophilic components of NOM consist of molecules such as carbohydrates, proteins, sugars, amino acids and other hydrophilic acids [8].

Traditionally water treatment has focused on the removal of either colour or turbidity, however, recently some water treatment facilities have started to optimise their processes based purely on the removal of natural organic matter [9].

2.2.1 Hydrophobic NOM in water

Hydrophobic component is organic matter that will not readily dissolve in water or other polar solvents. It is that humic fraction that has high aromaticity, high molecular weight, is yellow to brown-black in colour and is poor in nitrogen content. They are described as the aquatic acids or humic substances comprising of humic and fulvic acids. They amount to approximately 50% of the total NOM in surface water [8].

(i) Humic acids

It is the more reactive hydrophobic NOM and can be removed easily by coagulation due to its higher molecular weight, larger size, and lower solubility in water. Low coagulant doses when reacting with humic acid are sufficient to form flocs that can be removed by filtration of water. The dark brown colour of hydrophobic NOM is due to double bonds found in the humic acids. Figure 2.2 is a proposed structure of humic acid molecule.

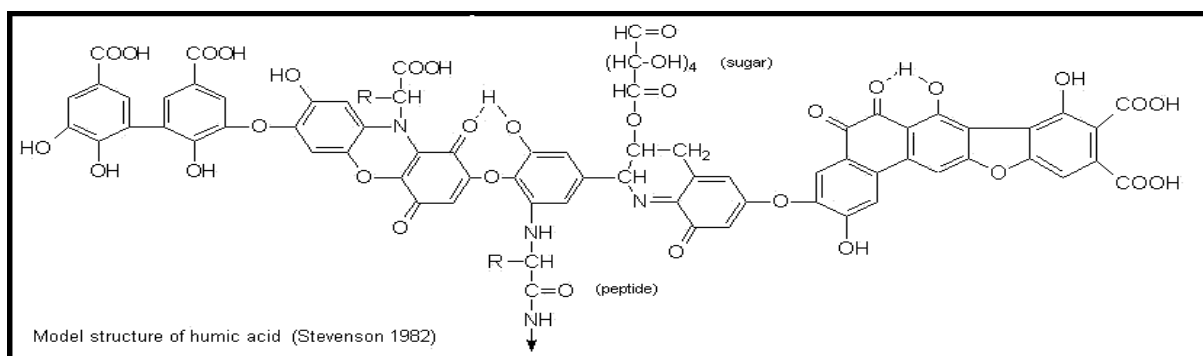


Figure 2.2: Model structure for humic acid [10]

(ii) Fulvic acid

It is a less reactive hydrophobic NOM, and therefore requires higher coagulant dosages in order for it to be removed optimally. Fulvic acid has a low molecular weight, smaller size and has a greater solubility in water relative to humic acid. It is characterised by varying colour from yellow to dark brown. Figure 2.3 is a proposed model structure for fulvic acid molecule.

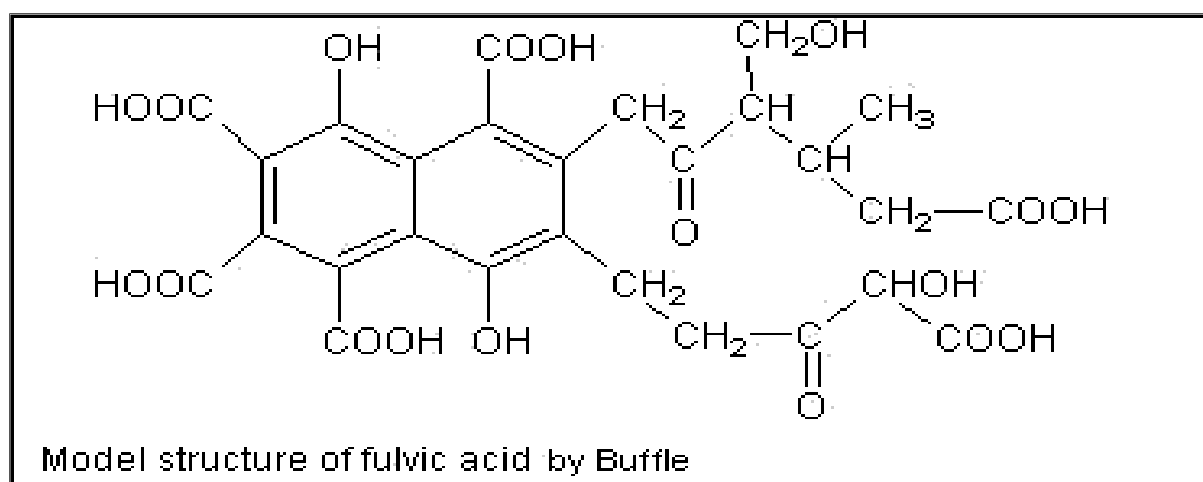


Figure 2.3: Model structure of fulvic acid [10]

2.2.2 Hydrophilic NOM in water

Hydrophilic components are non-humic solutes that readily dissolve in water. They represent around 35-40 percent of dissolved organic compounds in surface water [9]. These non-humic solutes consist of organic substances such as amino acids, hydrocarbons, carbohydrates, fats, waxes, resins, and low-molecular weight acids.

The hydrophilic or non-humic fraction of NOM is less reactive with coagulants and it is rich in nitrogen. These non-humic organics have no charge density, which is more prevalent in waters with low turbidity [11]. The mentioned qualities make the removal of the non-humic organic fraction to be difficult in the water treatment processes that involves the use of flocculants and coagulants.

In order to improve the performance of NOM removal, it is key to firstly identify its (NOM) character, as the type of organics present in water will affect not only the choice of treatment process but also the performance of the selected process [12].

2.3 IDENTIFICATION OF NATURAL ORGANIC MATTER

It is difficult to detect natural organic matter by conventional methods of analysis such as pH and conductivity measurements. Specialised instruments are required for the determination of NOM, and the measurements are made in the form of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) [7].

There are currently four methods that are available for the identification and characterisation of NOM components [2]. The methods are classified as:

- Preliminary identification
- chemical and behavioral characterization
- size characterisation
- spectral signature identification

2.3.1 Preliminary identification

The method is based on measurements of TOC/DOC, suspended solids concentration and ultraviolet absorbance (UV). Its main focus is on the dissolved fraction of NOM which literature refers to as dissolved organic matter at a size fraction below 0.45 μm . These constitute >90% of NOM [14].

Previously the permanganate value was used to determine the concentration of TOC. This was sometimes supplemented by UV absorption measurements. These methods cannot differentiate between organic matter and other reactive compounds, particularly when an attempt is made to measure polysaccharides [15].

Currently TOC measurements are done by various techniques that share a common methodology [7]. The instruments used, oxidises TOC to form carbon dioxide (CO_2) that can be measured and correlated to the organic content of the water. The oxidation techniques used are;

- Chemical oxidation
- UV (ultra-violet) oxidation

- A combination of UV and chemical oxidation
- Thermal degradation

Figure 2.4 is a basic schematic diagram of a TOC analyzer.

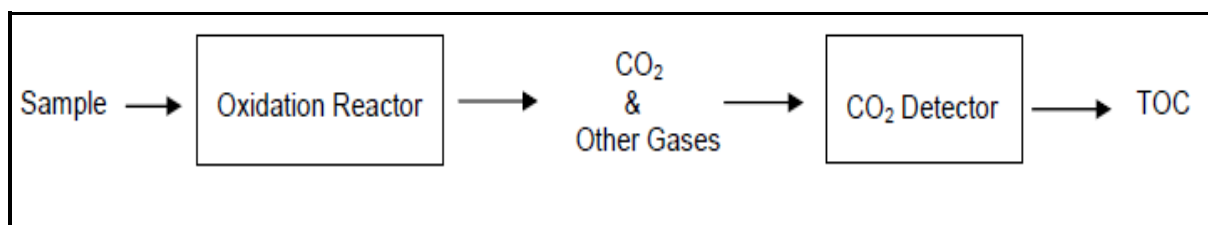


Figure 2.4: Basic TOC analyser diagram [16]

Carbon dioxide that is evolved is measured by a conductivity detector or non-dispersive infra-red absorption (NDIR) detector. The measured carbon dioxide concentration is then converted to organic carbon concentration in the water under investigation.

2.3.2 Chemical and behavioural characterisation

Analytical techniques used for chemical characterisation of NOM are Nuclear Magnetic Resonance (NMR) spectroscopy, Gas-Chromatography Mass-Spectroscopy (GC-MS) and Fourier Transform Infrared (FT-IR). Molecules are eluted from the gas chromatograph in GC-MS based on their physical properties, captured and ionised in the mass spectrometer and identified using their mass charge ratio [2]. This technique is useful for differentiating humic substances, aromatic structures, lignin, carbohydrate and protein derived compounds in NOM samples.

NMR is useful for identifying carboxyl carbons and carbohydrates in fulvic acids over humic acids.

Another method used for characterizing NOM spectrometrically and by its behaviour is called specific ultraviolet absorption (SUVA). It is an analysis of water that uses ultraviolet (UV) absorbance and dissolved organic carbon (DOC) values. SUVA value gives an indication of the humic acid content of the water. Basically SUVA is a calculated parameter equal to the ultraviolet (UV) absorption at a wavelength of 254 nm divided by the dissolved organic carbon (DOC) content of the water (in mg/L). Equation 2.1 is used for calculating SUVA value [7].

$$SUVA = \frac{UV_{254} (cm^{-1}) * 100}{DOC (\frac{mg}{L})}$$

.....Equation 2.1

The measurement principle is based on the observation that UV-absorbing constituents will absorb UV light in proportions to their concentration in solution [12]. A guideline for interpreting SUVA values and the suggested water treatment chemicals is given in table 2.1

SUVA (L/mg-m)	Composition	Coagulation	DOC Removals
< 2	Mostly Non-Humics Low Hydrophobicity Low molecular weight	NOM has little influence Poor DOC removals	< 25% for Alum Slighter greater for ferric
2 – 4	Mixture of Aquatic Humic and other NOM Mixture of Hydrophobic and Hydrophilic NOM Mixture of Molecular Weights	NOM influences DOC removal should be fair to good	25-50% for Alum Slightly greater for ferric
> 4	Mostly Aquatic Humics High Hydrophobicity High Molecular weight	NOM control Good DOC removals	50% for Alum Slightly greater for ferric

Source: Edzwald and Tobiason, 1999.

Table 2.1 Guideline on SUVA values and expected %DOC removal [7]

2.3.2 Size characterization

Isolation of NOM into different fractions is sometimes essential before analysis to ensure correct quantification of the organic specie. This fractionation is commonly achieved by using membrane technology or absorption of NOM compounds onto resins that are contained in a column. The membrane technologies that fractionate NOM involve the use of ultrafiltration (UF) and reverse osmosis (RO). In this technology, NOM is fractionated by using molecular weight (MW) of a species in a pressure-driven process [2].

UF is a physical separation process that is easy to use and has ability to handle large volumes of sample. There are problems associated with UF, and it resides with inconsistent production of NOM fractions due to blockages of pores by higher molecular weight of solutes.

Another size exclusion method used is high performance size exclusion chromatography (HPSEC). It operates at high pressures and requires small sample volume. Separation is achieved through porous gel resin column to distinguish molecular size and size distribution of molecules. Larger molecules cannot access the internal pore volume of the resin gel column, as a result, they are eluted first. They are followed by the smaller particles that are able to penetrate the gel pores.

Resin fractionation is also used as a method of separating NOM fractions. In this technique isolation and characterisation of NOM is based on the hydrophilic and hydrophobic properties of the compounds. The method is mainly used for bulk property fractionation, and has the disadvantage of requiring a pH reduction to 2 in order for adsorption of particles to be possible [2]. This condition can result in irreversible adsorption of NOM on the resin, and as well cause an alteration in the physical and chemical properties of the NOM compounds.

2.3.4 Spectral signature identification

The identification of NOM in this instance is using the fluorescence spectroscopy technique. When an electron in an atom absorbs energy due to it being exposed to ultraviolet light, it is excited to a higher energy level and a fluorescence signature occurs [2]. These organic molecule fluorescence is mainly due to structural characteristics of humic and fulvic acids in water. The technique is easy to use, quick and is characterised by quick analysis time and excellent sensitivity and selectivity.

2.3.5 Other methods of detection and analysis

NOM when analysed for by TOC-analysers, mainly gives quantification values not qualitative information. However, there is a technique that gives more details about NOM, and it is called Liquid Chromatography - Organic Carbon Detection (LC-OCD) [17].

This technique, firstly, separates NOM into different fractions by standard liquid chromatography. This is followed by detection of organic carbon (OCD), UV-absorbance (UVD) and organic nitrogen (OND). Figure 2.5 is a schematic diagram for a typical LC-OCD instrument.

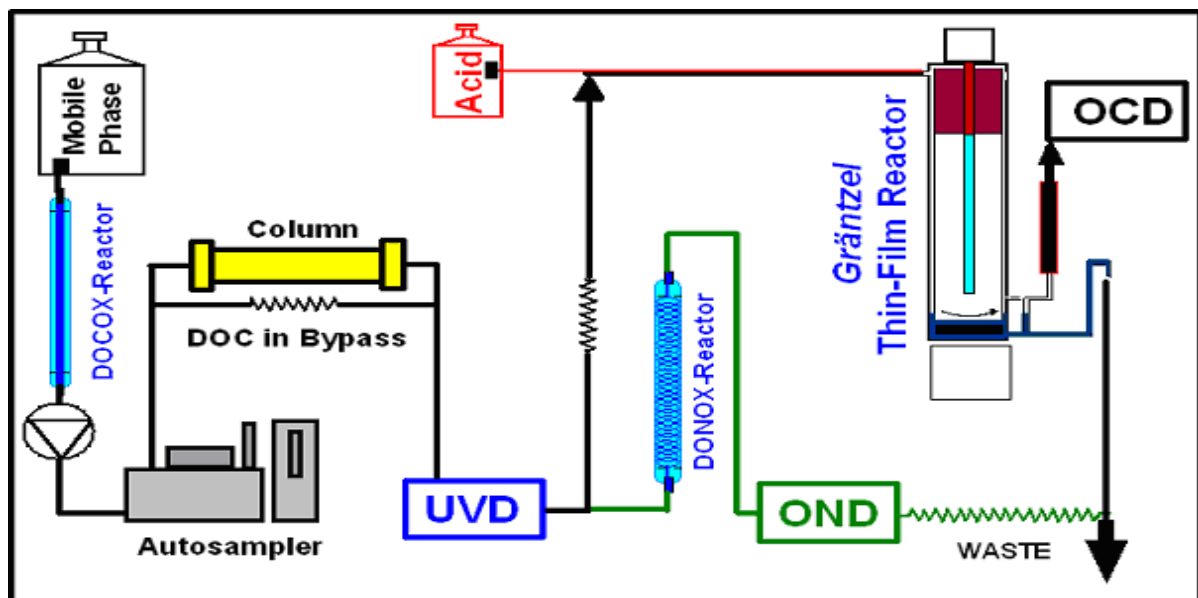


Figure 2.5: Schematic diagram for an LC-OCD instrument

The advantage of an LC-OCD instrument is that, it does not only measure DOC, but it also separates NOM into the following constituents,

- Hydrophobic organic carbon (HOC)

- Polysaccharides/Proteins
- Humics (including aromaticity and molecularity)
- Building Blocks (breakdown products of humics)
- Low-molecular weight neutrals and amphiphilics
- Low-molecular weight organic acids.

The results from the LC-OCD technique can be used to trend the performance of treatment processes and treatment chemicals in terms of the removal efficiency of the various organic species.

The LC-OCD was used in this study for identifying the nature of organic matter in the raw water supplied to the two power stations (Kriel and Arnot).

2.4 REMOVAL OF ORGANIC MATTER IN WATER TREATMENT PROCESSES

Processes such as flocculation, clarification and filtration are used for removal of suspended matter [14]. Suspended matter refers to a wide range of undissolved substances of various types and sizes. The larger particles of suspended matter (1 - 50 microns) are referred to as "silt" and will settle out of the water upon standing. This size range of suspended matter includes sand, clay, iron and manganese compounds/particles.

Particles that are less than 1 micron in size are called colloids. They are too large and complex to be classed as molecules of a simple compound, owing to their unique properties such as:

- adsorption, i.e. a tendency to attract particles to its outer surface from the surrounding medium
- electrokinetic, i.e. tendency to develop a charge on their surfaces in relation to the surrounding medium.

Colloid dispersions in aqueous media carry an electric charge [18]. The origin of this surface charge depends upon the nature of the particle and the surrounding medium. The liquid layer that surrounds the particle exists as two parts as depicted in figure 2.6, namely;

- an inner region (Stern layer) where the ions are strongly bound and an
- outer (diffuse) region where they are less firmly bound

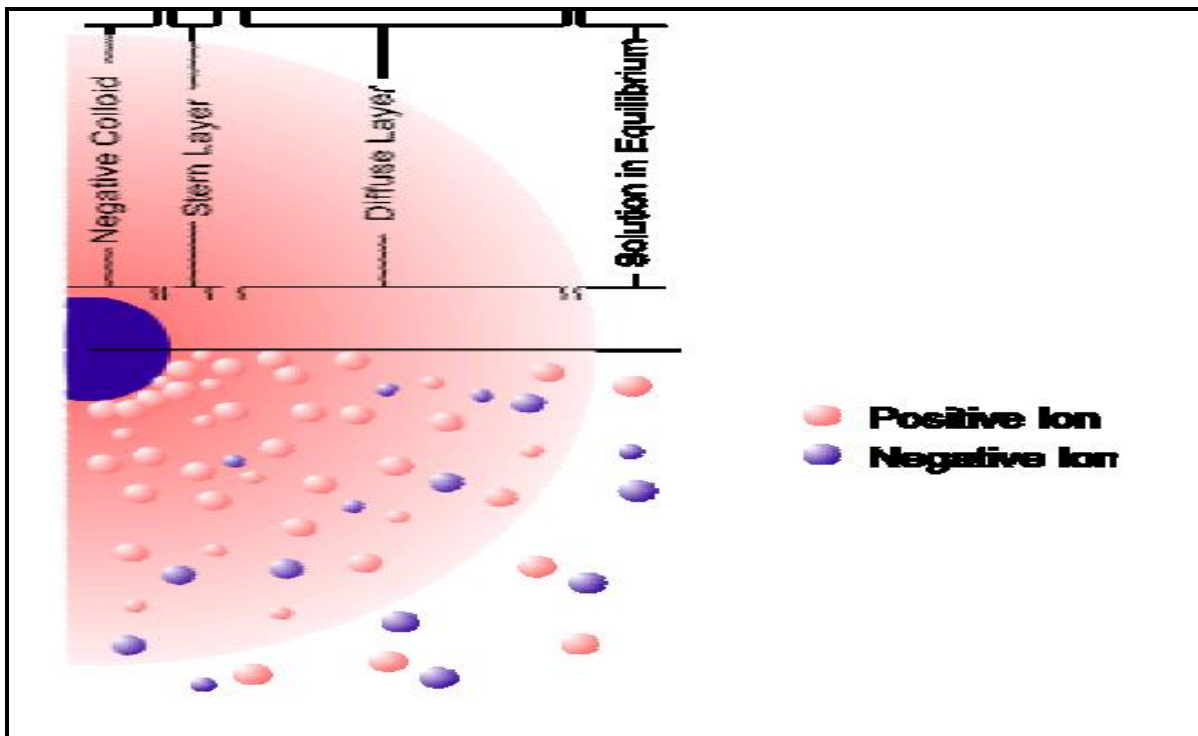


Figure 2.6: Visual double layer model of a particle in water [18]

The diffuse layer has a notional boundary inside within which the ions and particles form a stable entity. When a particle moves due to gravity, ions within the boundary moves with it. Those ions beyond the boundary stay with the bulk solution. The potential at this boundary (surface of hydrodynamic shear) is called the zeta potential. Coagulation and flocculation processes in water treatment are used to decrease the zeta potential, thereby allowing particles to settle out of solution.

2.4.1 Removal of NOM by Coagulation and Flocculation

Purification of raw water from rivers and dams involves flocculation and coagulation processes to remove turbidity/colour, ionic matter and NOM in a water treatment plant. Coagulation is a process whereby a positively charged coagulant (eg aluminium or a ferric) is added to the water to neutralise the charge particulates present and to help to induce the Van der Waal forces within the particles [19]. Flocculation is the rapid mixing (under turbulent conditions) of these colloids and coagulants to form floc. The insoluble matter that is formed by flocculation and coagulation is settleable and can be removed by sedimentation (in a clarifier) and filtration (in a sandfilter). A generic water treatment plant process is depicted in figure 2.7

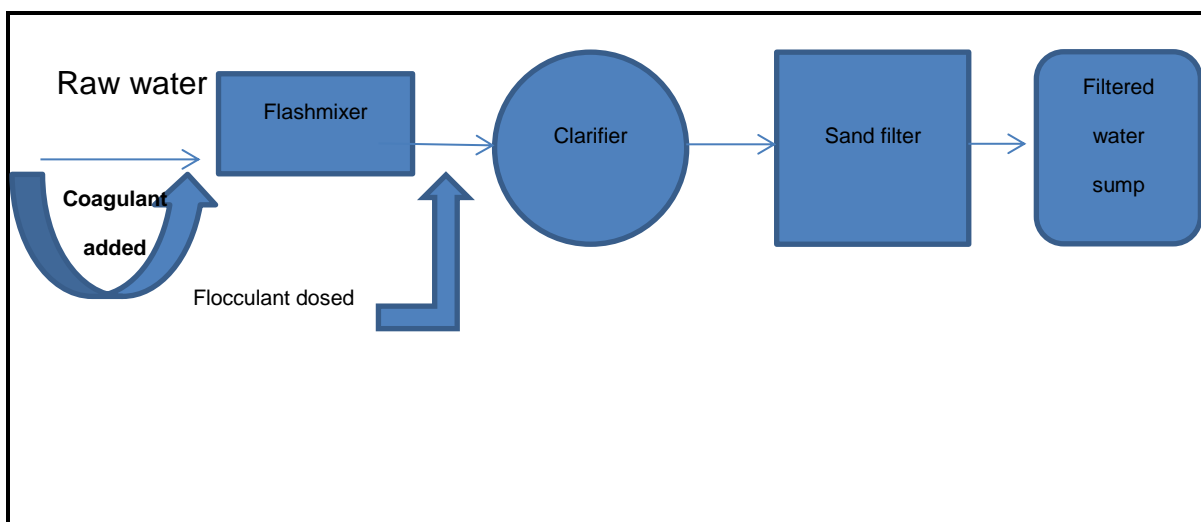


Figure 2.7: Generic water treatment process

The typical removal of NOM as per convectional processes in Figure 2.7 is depicted in Table 2.2 and it is depended on the SUVA value as discussed on section 2.3.3.

Table 2.2: SUVA-254 guideline for expected removal of TOC [7]

SUVA Value	% TOC Removal
> 1-2	35
>2-3	40
>3-4	40
> 5	55

Removal of NOM can further be achieved by other processes such as demineralisation and ultrafiltration. For the purpose of this study, only demineralisation will be discussed.

2.4.2 Removal of NOM by demineralisation

Steam generation systems (boilers) for electricity generation is dependent on water purity of specified target values, as per Original Equipment Manufacturer's (OEM) requirements [20].

The first phase of water treatment process (coagulation and flocculation), is not capable of producing the required quality as per targets on Table 2.3 [26] as a result demineralisation plant is employed to produce water of a required quality. The process of demineralisation is essentially the removal of all cations and anions due to the dissolution of inorganic salts in the water.

Table 2.3:Demineralised water quality target required for electricity production [26]

Parameter	Value	Unit
Conductivity	0.055	$\mu\text{S/cm}$
Sodium	0.002	mg/l as Na
Silica	<0.010	mg/l as SiO_2
Chloride	<0.002	mg/l as Cl
Sulphates	<0.002	mg/l as SO_4
Total Organic Carbon	<0.250	mg/l as C

A generic demineralisation plant is composed of a cation resin vessel, a degasser vessel, a weak anion vessel, a strong anion vessel and a mixed-bed vessel as depicted in figure 2.8.

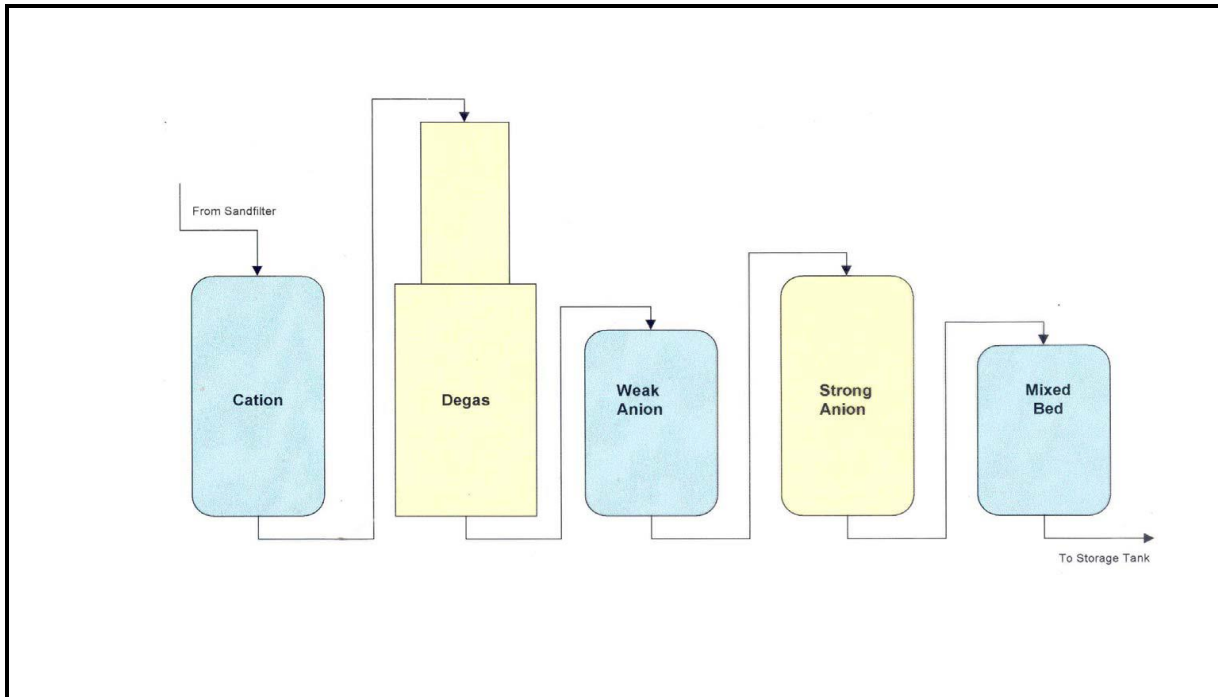


Figure 2.8: Generic outlay of a demineralisation plant

The ion exchanger vessels (with the exception of the degas vessel) contains ion exchanger resins. Ion-exchange resins are complex organic structures comprising of many smaller organic molecules that are joined together (polymerised) into three-dimensional networks which are very porous (like a sponge) [21]. These very big molecules can, in turn, be joined and bridged to each other (cross-linked). When a demineralisation plant is in service/operation, the following happens in that specific part of the plant;

- (i) **Cation Exchange vessel** - Cations in the water are exchanged with the hydrogen in the resins. The effluent from the cation exchanger column consists of a very weak mixture of acids, due to the released H^+ ions.
- (ii) **Degas vessel** – Effluents from the cation exchanger vessel contains dissolved gases that are removed as depicted in Figure 2.9. Carbon dioxide that is

dissolved in water, exists as carbonic acid due to the acidic nature of the cation exchanger outlet effluent. The weak Van Der Waal's force that exists between the carbon dioxide and water, makes it possible for the bond to be easily broken [13]. Water containing carbon dioxide as a dissolved gas is sprayed through the nozzles into a packed inert material of a degas vessel and at the same time, air is blown by a fan from the bottom of the vessel counter to the flow of water spray. As a result, carbon dioxide is displaced from the acidic water and exit the vessel at the top through an exhaust [22].

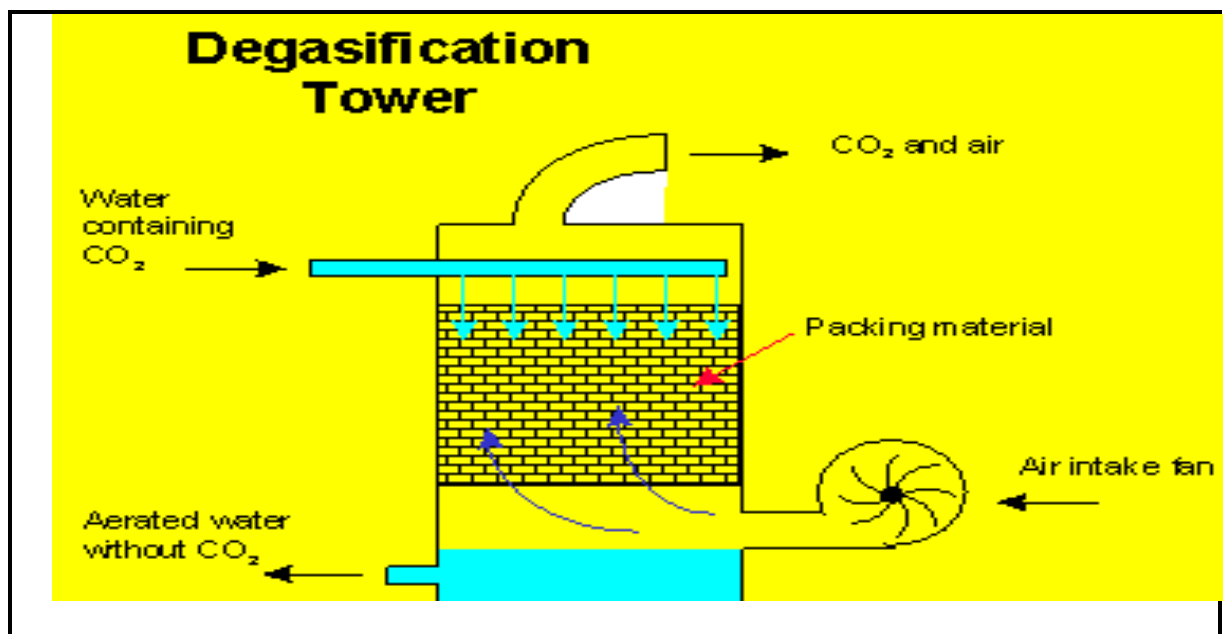


Figure 2.9: Removal of the dissolved gases from water [22]

- (iii) **Weak Anion Exchange vessel** - Water from the degas vessel now passes through a third vessel containing anion exchange resin in the hydroxide form. The exchange process is as depicted in figure 2.10

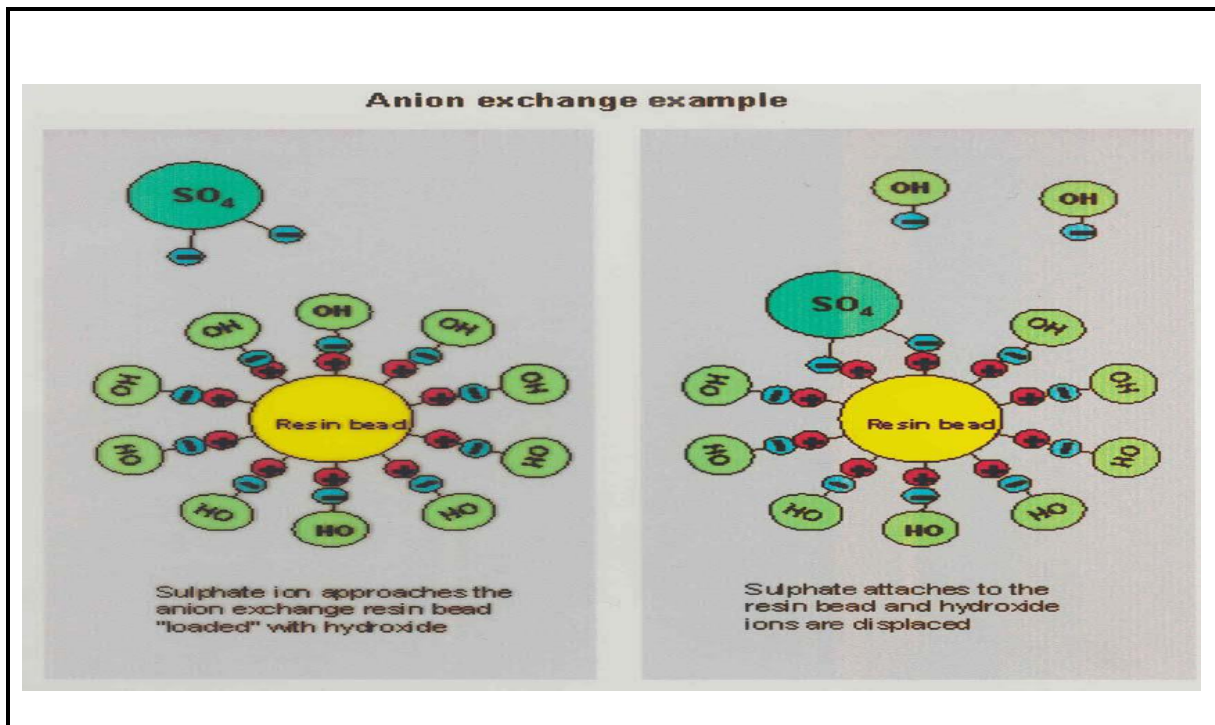


Figure 2.10: Anion exchange process model [22]

The anions in this vessel are exchanged for hydroxide ions, which react with the hydrogen ions to form water.

(iv) Strong Anion Exchange vessel – The anions that could not be removed by the weak anion exchanger resins are removed by the strong anion exchanger resins. Those are mainly large molecule complex structure like silica and organic molecules [22]. The organic molecules have a tendency of causing fouling on the exchanger resins, the only effective way to remove them (organics) from the surface of the resin is by brine washing [22]. A full procedure on how brine washing is done is in Appendix F

(v) Mixed Bed Exchange vessel – The vessel contains a mixture of cation and anion exchange resins. The purpose of which is to exchange both the cations

and anions that might have 'slipped' through without being exchanged for by the anion and cation exchange vessels.

Ultra-pure water at the outlet of a mix-bed exchange vessel (Make-up water) can only be used if it meets the quality requirements as per Table 2.3, i.e, for organic matter (NOM measured as TOC) to be acceptable, it should be less than 250 ppb [25].

2.5 NATURAL ORGANIC MATTER IN STEAM-BOILER WATER

The main and common source of organic matter contamination in steam-boiler water system is makeup water [13]. These natural organic matter contaminants might be from the treated raw water or from deionisation resin break-down or degradation. It is for this reason that organic content of steam-boiler water is preferably measured as Total Organic Carbon (TOC), which describes organic content of water (taking into consideration all the possible sources of organic carbon) [23].

Previously, monitoring the cycle chemistry in a power plant was mainly based on acid cation conductivity (ACC) measurement [13]. These measurements were based on the formation of mineral acids as the result of inorganic contaminants. It was later observed that the dissolved carbon dioxide mask the measured ACC values [15]. The other observation made was that of low molecular mass organic acids contributing to the ACC measurement [13, 15, 16, 17].

Therefore the presence of organic matter in the steam-boiler water can be a major

source of dissolved carbon dioxide and low molecular mass organic acids [17]. TOC measurements are therefore done to monitor the organic matter in steam-boiler water. Further-more, the formation of organic by-products (organic acids) of TOC can be measured by the use of Ion Chromatographic methods [24].

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CHAPTER 3

EXPERIMENTAL

3.1 INTRODUCTION

This chapter gives a broad explanation of the study areas, sampling, instrumentation and associated calibrations performed.

Raw water samples from two different river systems in Mpumalanga were used for this study. Komati water system supplying Arnot Power Station and Usutu water system at Kriel Power Station were the two sources used. The raw water from these two supply systems were used to profile the natural organic matter by using a Sievers GE 900 Total Organic and a Liquid Chromatography Organic Carbon Detector (LC-OCD).

The only drawback with Sievers analyser is that the technique does not differentiate/fractionate the type of organic compounds that are present in the water, i.e, it only reports the total organic carbon concentration of the sample [1].

An LC-OCD analyser on the other hand, separates NOM into different constituent such as humics, biopolymers, proteins etc and quantify the concentrations obtained [2]. It should however, be mentioned that LC-OCD analyser was used to determine the organic carbon concentrations at the different parts of the water treatment processes such as filtered water outlet, demineralisation plant and the steam/condensate cycle water from the two power stations.

As mentioned in section 2.3.5 (chapter 2) an LC-OCD analyser separates NOM into different constituents, one of which is low molecular weight organic acids (LMWOA).

It should however be noted that the results obtained from the LC-OCD analyser, only provides an indication of the total LMWOA, i.e, it does not identify the type and amount of the individual organic acids present in solution [2].

An ion chromatographic (IC) analyser was used to identify the types and concentrations of organic acids found in the demineralised and steam/condensate water. The IC analyser that was used also has the capability of analysing for inorganic anions (chlorides, sulphates and fluorides) in solution.

The sum of concentrations of the anions and organic acids, once determined, were correlated with the degas acid cation conductivity (DCC) obtained from the on-line conductivity analysers installed on the superheated steam (SUP) sample points at the two power stations.

3.2 SAMPLING AND STUDY AREAS

3.2.1 Water treatment plant samples

Raw water from the two stations were collected and analysed before being introduced to a water treatment plant. The other sampling points used were at the water treatment plant and are as follows;

- i) Filtered water/Cation inlet and
- ii) Mixed Bed outlet

The samples mentioned above were only used to evaluate if the treatment processes were effective in removing the DOC in the station make-up water [3]. The

organic removal was restricted to analysis by LC-OCD analyser for the samples mentioned. The DOC from LC-OCD analyser were then compared with the Sievers 900 TOC analyser results on the inlet raw water from both Usuthu and Komati water systems.

3.2.1 Steam/condensate water samples

Different parts of the cycle water where the organic profile change is possible were chosen for sampling, and they are as follows;

- i) Condensate Extraction Pump (CEP) 1st stage outlet
- ii) Common Condensate Polishing Plant Outlet (CPP Out)
- iii) Boiler water (Blr) for Arnot only and
- iv) Superheated Steam samples

3.2.3 Sample bottles

Amber Schott bottles with a volume of 250 ml were used for sampling. The bottles were treated as follows [3];

- Washed with a 10% solution of nitric acid and rinsed with tap water three times
- Rinsed with demineralised water three times
- Placed in a muffle furnace at 100°C for 30 minutes to dry
- Cooled at room temperature and stored in a dry and organic free environment

The samples after collection were stored in a cooler box where the temperature was maintained below 4°C. This was achieved by using ice packs and once at the laboratory, the samples were stored in a refrigerator at 4°C.

3.3 ANALYTICAL EQUIPMENT USED

Equipment used for the study were both on-line and laboratory bench-top analysers. The equipment, calibration procedures and material used are discussed in 3.3.1 to 3.3.4.

3.3.1 Sievers 900 GE TOC analyser

The instrument is calibrated once a year by the supplier at their premises (calibration certificate is attached in Appendix A [1]. Potassium Hydrogen Phthalate (KHP) solution was used as a quality control (QC) standard and the preparation was done as follows;

i) Preparation of the 1000 ppm KHP Stock Solution

Using a clean 100 ml beaker 3.0 g of the KHP salt was added and heated in an oven at about 110°C for one (1) hour. The salt was removed and cooled to room temperature in a desiccator. A 2,125 g of the cooled KHP salt was weighed into a 1000 ml volumetric flask and dissolved. The flask was filled to the mark with ultra-pure water.

ii) Preparation of working QC standards

The following QC standards were prepared by diluting the appropriate aliquots from The stock solution prepared above;

QC standards of concentrations 0.5 ppm and 5.0 ppm were prepared for low level TOC verification. High level TOC standards were verified by preparing 10.0 ppm and 20.0 ppm concentration QC standards.

Figure A1 (Appendix A) is a calibration data certificate received from the supplier after calibration of the analyser. The certificate contained the following data about the parameters determined (that should be noted):

- TOC (Total Organic Carbon)
- IC (Inorganic Carbon)
- TC (Total Carbon)

The TOC was determined by subtracting the IC from the TC results as calculated by the analyser [1].

The other information on the calibration data was the traceability to the technician who performed the calibration, time of injection of the standard/and or blank, amount of acid and oxidiser injected.

The Sievers analyser calibration includes injecting the blank in order to perform blank correction at the end of the calibration. It should however be noted that the blank correction was performed by the analyser as an automatic built-in function.

Ten blank injections were performed but only the last three injections were used for calculating the average results that was used as a blank value. The three blank values were used to calculate the average TOC result, the standard deviation and relative percentage standard deviation of the measurements. The other seven injections were rejected by the supplier's technician who carried out the calibration.

The information as received from the supplier was that it is a standard procedure that is used at the supplier's laboratory when performing Sievers TOC analyser calibration. The first seven injections were used as a process step to rinse the instrument to ensure that cross-contamination from the previous injections was prevented.

A single point calibration using a 25ppm potassium hydrogen phthalate (KHP) standard was used. Four replicates of the KHP standard were injected, and the relative percentage standard deviation (%RSD) of 0.21% was produced on the TOC. The acceptance criteria for a passed calibration as per suppliers quality procedure was based on the RSD of less than 10% (supplier's acceptance criteria for a passed calibration) [1].

3.3.2 LC-OCD instrument

Calibration of the instrument is done at Eskom Research, Testing and Development laboratory twice a year. The calibration procedure, results and report are attached in Appendix B. There are two calibration procedures carried out on the instrument, namely calibration of molar masses and calibration of detector sensitivities. The total

time required for calibration is about 14 hours, it is therefore recommended that this be carried out overnight.

(i) Mobile phase

A mobile phase was prepared by weighing 7.5 g of disodium-hydrogen phosphate dehydrate and 12.5 g potassium-dihydrogen phosphate and dissolving the two salts in a 5.0 L volumetric flask with ultra-pure water and making up to the mark.

(ii) Calibration of molar masses

Reagents required

A mass of 4.0 mg IHSS HA (Suwannee River Humic Acid Standard II) and 4.0 mg IHSS FA (Suwannee River Fulvic Acid Standard II) were weighed and dissolved in 100 ml of ultra-pure water.

Chromatographic conditions

Flow rate: 1.1 ml/min

Injection volume: 1000 μ L

Analysis time: 130 min

(iii) Calibration of Detector Sensitivities

Reagents required

Approximately 213 mg of potassium hydrogen-phthalate (KHP) and 100 mg potassium nitrate (KNO_3) were dissolved in 100 ml volumetric flask of mobile phase, to prepare 1000 ppm KHP and 139 ppm KNO_3 -N.

Chromatographic conditions

Flow rate: 1.1 ml/min

Injection volume: 1000 μ L

Analysis time: 110 min

Three of the detectors (Ultra violet, Organic carbon and Organic nitrogen) were calibrated during the normal annual calibration of the LC-OCD [2]. No operator intervention is required after loading the standards during calibration.

An LC-OCD analyser has a built in software that manipulates the data produced, and automatically integrates the calibration data produced. A failed calibration is indicated if the correlation coefficient of less than 0.9990 (three 9s after a decimal point) is obtained [2].

3.3.3 Swan Degas Conductivity On-line Analyzer

A mobile on-line analyser was used to determine the acid cation conductivity (ACC) and the degassed cation conductivity (DCC) at Kriel Power Station, but at Arnot power station, there is an on-line analyser that is permanently installed, and it was used for data collection. The calibration certificate for the mobile Swan analyser is attached at Appendix D. The instrument is calibrated by the OEM once a year [4]. A potassium chloride standard was used as a quality control standard to monitor the performance of the instrument. The solution is prepared as follows;

i) Preparation of 0,01M KCl standard

Two 100 ml beakers as well as a 1000 ml volumetric flask were thoroughly washed and rinsed by using ultra high purity water (UHP). They were placed in an oven (100

°C) to dry for 20 minutes, and then placed in a desiccator to cool. In one 100 ml beaker 1.00 g of KCl salt was weighed in a top loading balance and heated in an oven to dry for 20 minutes. The salt was taken out of the oven and put in a desiccator to cool. After cooling, the second 100 ml beaker was used to accurately weigh 0,74551 g of the dried KCl in an analytical balance. A small volume of UHP water was used to dissolve the salt and the resulting concentrated solution was transferred into a 1000.00 ml volumetric flask. The volumetric flask was filled to the mark by using UHP water.

ii) Preparation of 0,001 M KCl standard

A thoroughly washed and rinsed 1000 ml volumetric flask and a 100.00 ml pipette using UHP were used for preparing this standard. A 100 ml beaker was rinsed with a small solution of the 0,01 M KCl prepared in (i). A 100 ml pipette was also rinsed with the same 0,01 M KCl prepared. A 100 ml aliquot of a 0,01 M KCl was transferred into a cleaned volumetric flask and filled to the mark with UHP water.

iii) Preparation of 0,0001M KCl standard

A cleaned 100 ml beaker was rinsed with a small solution of the 0,001 M KCl prepared in ii). Also a 100.00 ml pipette was rinsed with the same 0,001 M KCl prepared in ii). A 100.00 ml of 0,001 M KCl was transferred into a cleaned volumetric flask and filled to the mark with UHP water.

3.3.4 Metrohm IC 850 Professional Bench-top analyser

The separation of the different anionic organic acids, namely formate, acetate, lactate and the two main inorganic anions (chloride and sulphate) were analysed using a Metrosep A Supp 16 -250/4 mm column [5]. A calibration of the IC system was done in the concentration range of between 0.5 ppb and 40 ppb using 1000 ppm mixed standard stock solutions for formate, acetate, lactate, chloride and sulphate ions.

Apparatus and Accessories

850 Professional IC	850.2190
858 Professional Sample Processor	858.0010
Metrosep A Sup 16 – 250/4 mm column	6.1031.430
Metrosep A Supp 16/ 4mm Guard column	6.1031.510

IC parameters

Sample transfer loop	10 ml
Sample amount	4000 µL
Flow	0.8 ml/min
Recording time	40 min
Column Temperature	45°C
Data source	Conductivity detector
Polarity	+

IC Reagents

Solvent

Ultrapure MilliQ water, resistivity > 18

MOhm.cm

Carbonate Eluent:

2.5 mmol/L Na₂CO₃

= 420 mg Na_2CO_3 /2L MilliQ

5.5 mmol/L NaHCO₃

= 1166 mg NaHCO₃/2L MilliQ

MSM Solutions

50 mmol/L Sulfuric acid (H_2SO_4) =

2.75 ml Conc. $\text{H}_2\text{SO}_4/\text{L}$

Table 3.1: Standards used for calibration of the IC instrument

Anion	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7
Formate, ppb	40	20	10	4	2	1	0.5
Acetate, ppb	40	20	10	4	2	1	0.5
Lactate, ppb	40	20	10	4	2	1	0.5
Chloride, ppb	40	20	10	4	2	1	0.5
Sulphate, ppb	40	20	10	4	2	1	0.5

The rationale of calibrating the instrument at concentrations between 0.5 ppb and 40 ppb was mainly due to the sensitivity consideration. Any values obtained that are above the highest calibration standard, resulted in the instrument rejecting the value and automatically diluting the sample and re-analysing the sample.

3.4 ANALYSIS OF SAMPLES

Different sample volumes were used for analysis on the different instruments mentioned in subsection 3.3. The following section details the volume used for the different instruments.

3.4.1 Analysis by Sievers 900

The samples were poured into a 5 ml glass vials and placed in an auto-sampler rack. KHP quality control standards of different concentrations were also included as part of verifying the validity of the instruments before commencement of any batch analysis. Each analysis took a period of 30 minutes for complete analysis.

Each measurement (monthly analysis over the experimental period of 12 months) was done in triplicate and only the averages for the entire experimental period were tabulated. It should be mentioned that the KHP standard that was used by the analyst for verification, was independent from the KHP standard used for calibrating the analyser, i.e, the standard was prepared by a different person from a different salt batch.

3.4.2 Analysis by LC-OCD

Samples were transferred into 5 ml glass vials and placed in a sample rack of an auto-sampler. Each analysis, including rinsing time takes approximately 130 minutes before the results are produced.

The water used for preparation of reagents in the laboratory was obtained from a Millipore water system in the laboratory. This water was injected into a Sievers analyser and LC-OCD analyser to determine the correlation of the TOC/DOC results between the two analysers. This was done as a form of quality control measure. Five samples were collected in five separate vials (5 samples for each analyser) and injected in each analyser.

It should however be noted that a 0.45µm filter was used to filter the Millipore water before being injected into the Sievers analyser. The rationale behind this was to remove the suspended matter from the Millipore water and ensure that only DOC was measured on a Sievers analyser. It was not necessary to do the same on LC-OCD analyser because it has a 0.45µm filter incorporated in the sample inlet port.

3.4.3 On-line analysis by Swan conductivity analysers

A sample that was continuously flowing into the conductivity analysers was used for data capturing. Three data points were captured and recorded at a 1 minute interval and an average of 3 readings was used. The samples that were analysed by these analysers were the following;

- Condensate Extraction Pump (1st stage)
- Common Condensate Polishing Plant Outlet (CPP Out)
- Boiler water (Blr) from Arnot and
- Superheated Steam samples

Degassed cation conductivity (DCC) was only determined on the SUP samples.

3.4.4 Analysis by Metrohm 850 Professional IC

A 4000 µL of the Standard solution as well as the samples were analysed by direct injection (by the sample processor) using the pre-concentrator with matrix elimination technique. This technique involves the injection of a sample of known volume through a trap resin column that retains anions of interest. This is done in order to ensure that the sample matrix is eluted and separated from the anions that will be analysed. An eluent is then injected counter to the flow of sample (after all the sample matrix has been eluted), and thereby removing and transporting the trapped anions to the guard and analytical column for analysis [5].

Automatic integration was done with MagIC Net 3.0™ software using peak area for all analyses to set up a calibration for the standard solutions containing acetate, formate, lactate, chloride and sulphate ions. Calibration graphs and chromatographs are in Appendix C.

3.5 CHEMICALS USED

All the chemicals used were AR grade and they were purchased from Merck, with the exception of the following:

- Ion chromatography calibration and quality control standards – supplied by Metrohm (they were purchased by the supplier from Sigma-Aldrich, Switzerland)
- LC-OCD calibration standards – purchased from International Humic Substances Society, USA

REFERENCES

1. Sievers Datapro Operating and Maintenance Manual, version 1.40, 2009
2. LC-OCD-OND Manual Model 8, version 2012-08-27
3. Determination of Total Organic carbon in liquid samples by TOC combustion analyser, Eskom Method Number 414 Rev 03, 2012
4. Swan Ami degas conductivity operating manual, 2010
5. Metrohm Professional IC operating method, 2013

CHAPTER 4

RESULTS AND DISCUSSIONS

4.0 INTRODUCTION

This chapter is divided into two sections (A and B). In section A, results of the TOC/DOC profile from both raw water inlet at Arnot power station (Komati supply system) and Kriel power station (Usutu supply system) water treatment plant are tabulated and discussed. The results of the water from the demineralisation plant systems of the two stations will also be discussed and interpreted.

Section B will present organic acids, chlorides, sulphates and cation acids conductivity results from the condensate/cycle water systems from both Arnot (Komati water scheme) and Kriel (Usutu water scheme) power stations.

SECTION A

The results from the Komati and Usutu under investigation are tabled and discussed.

i) Sievers 900 GE instrument's results

The average concentrations of the quality control standards obtained over the test period were tabulated on Table 4.0(a) with statistical calculations included.

Table 4.0(a) Average KHP quality control results from Sievers 900 analyser

Date	Prepared QC standard/ppm			
	0.50	5.0	10.0	20.0
	Measured QC standard/ppm			
Apr2014	0.56	5.33	10.4	21.4
May2014	0.54	5.01	10.4	20.2
Jun2014	0.54	5.03	10.4	20.1
Jul2014	0.55	5.05	9.92	20.0
Aug2014	0.52	4.97	10.1	20.3
Sep2014	0.49	4.98	10.0	20.7
Oct2014	0.50	5.01	10.7	19.8
Nov2014	0.50	5.66	10.3	19.4
Dec2014	0.48	5.07	10.7	21.1
Jan2015	0.53	5.19	10.2	20.8
Feb2015	0.52	5.05	9.99	20.0
Mar2015	0.51	5.08	10.5	20.6
Average	0.52	5.12	10.3	20.4
S.D*/ppm	0.0249	0.197	0.265	0.571
R.S.D/%**	4.78	3.86	2.57	2.80

Where S.D* is standard deviation and R.S.D** is relative standard deviation

Percentage R.S.D obtained where determined to be less than 5% for all the QC standards prepared, and the values were therefore acceptable for verification of an instrument's performance as per Eskom's acceptance criteria [2].

ii) LC-OCD calibration graphs for organics

The results of all the 3 calibrated detectors and discussions follow.

Organic carbon detector (OCD) calibration results

The LC-OCD analyser was calibrated and the resulting correlation coefficient of 0.9994 was obtained. The correlation coefficient was acceptable as per supplier's (OEM) recommended guideline. Figure 4.0(a) shows the calibration graph obtained after calibration of the instrument.

It should be noted that for some reasons only known by the OEM, potassium hydrogen phthalate (normally abbreviated as KHP) is denoted as PHP in the graph (x/vertical axis in the graph).

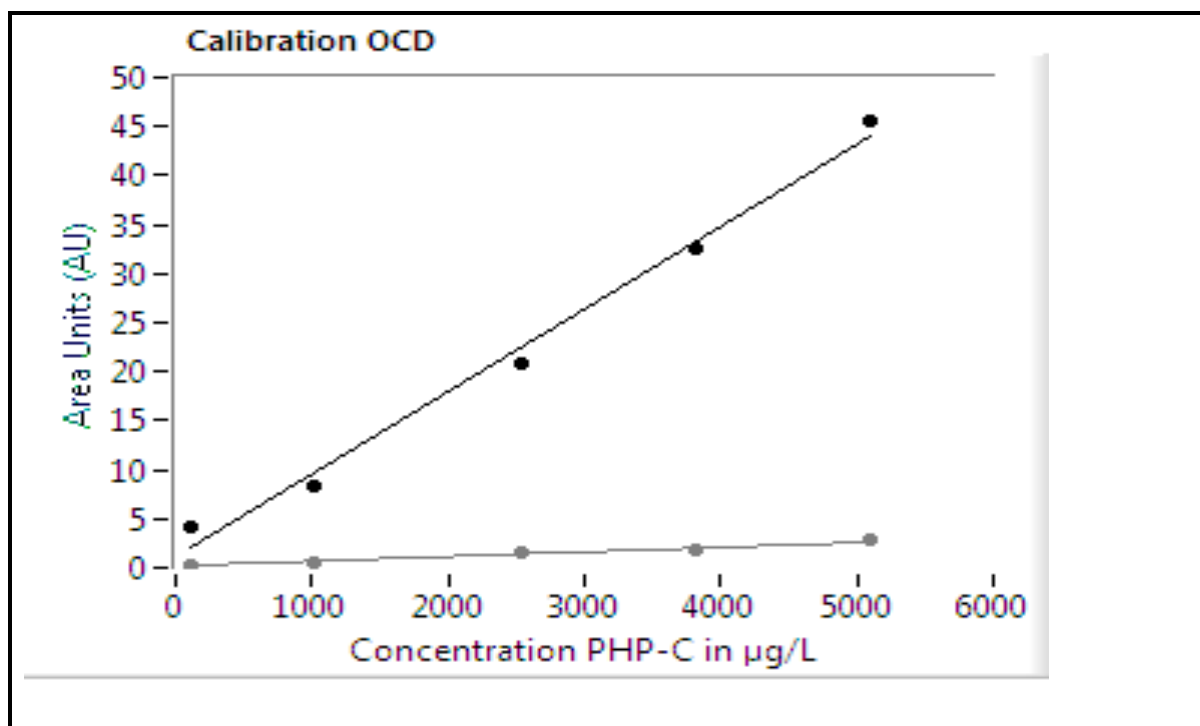


Figure 4.0(a): Organic carbon detector calibration graph

Ultra-violet detector (UVD) calibration results

The correlation coefficient result of 0.9995 was obtained after calibration of the UVD.

This still falls within the acceptance criteria. The calibration graph is shown in Figure 4.0(b).

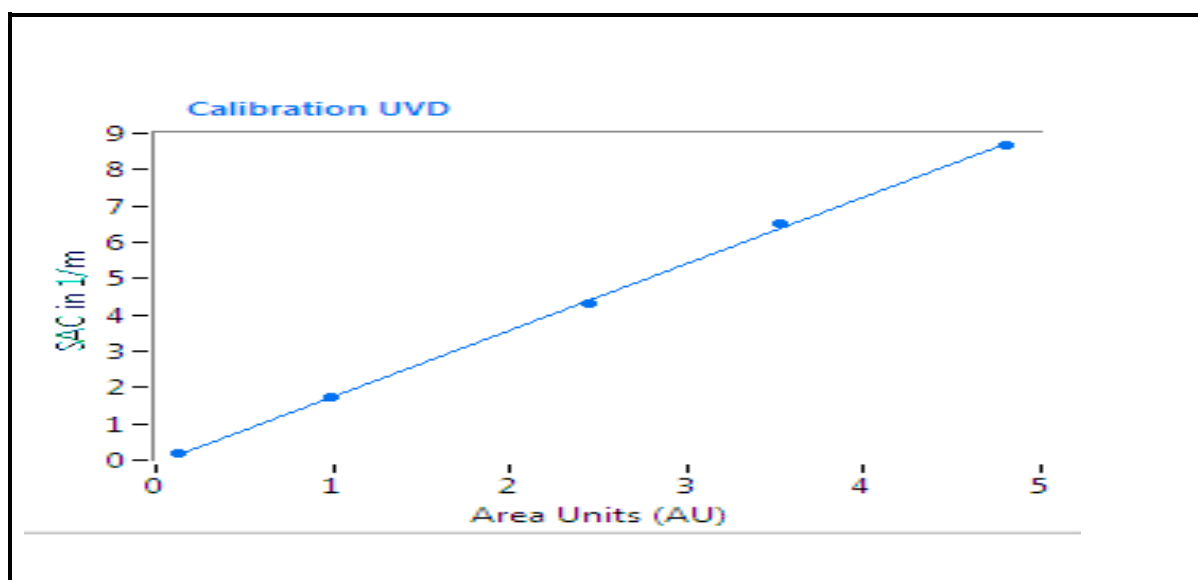


Figure 4.0(b): Ultra-violet detector calibration graph

Organic nitrogen detector (OND) calibration results

Correlation coefficient result of 0.9996 was obtained for the OND calibration. The result was as well acceptable for a successful calibration. Figure 4.0(c) shows the calibration graph obtained.

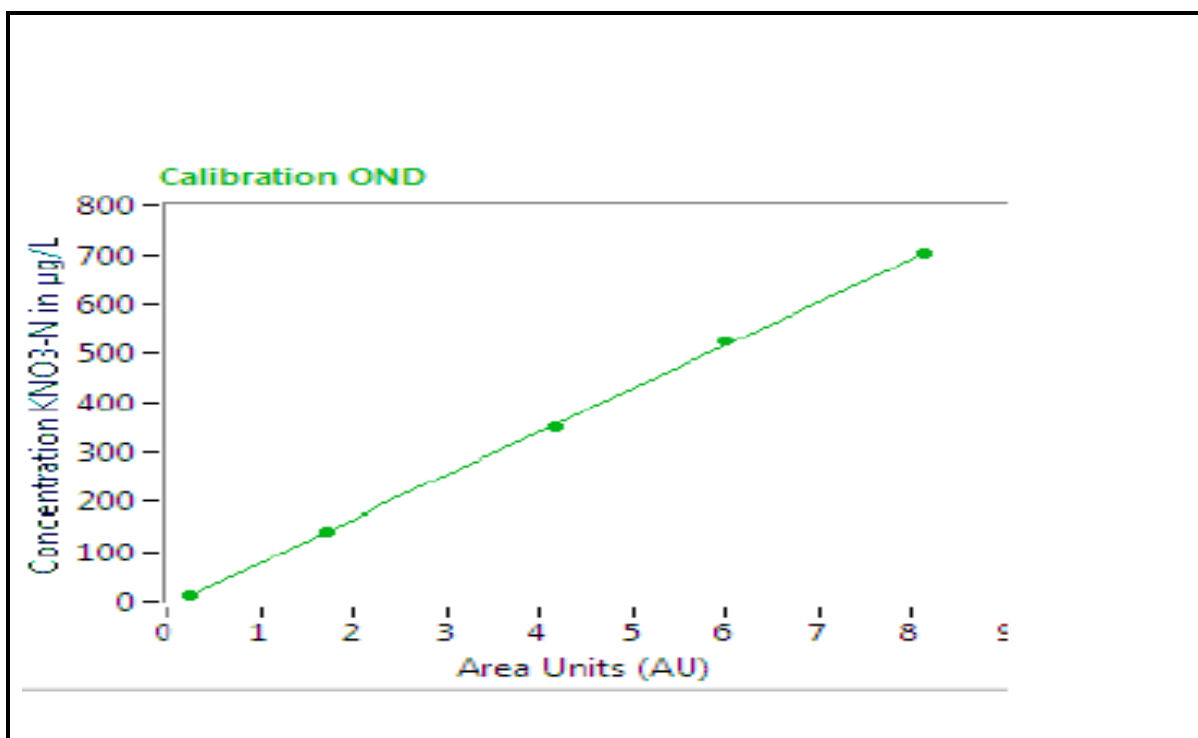


Figure 4.0(c): Organic nitrogen carbon detector calibration graph

The successful results obtained after calibration of the detectors guaranteed that the sample analysis could be undertaken with an understanding that the analyser will produce valid results.

iii) Millipore water sample results

The results obtained are shown in Table 4.0(b) and calculation of % error between the two analysers where done as follows:

$$\% \text{Error} = \frac{[(\text{Average DOC})_{\text{LCOCD}} - (\text{Average DOC})_{\text{Sievers}}]}{[(\text{Average DOC})_{\text{LCOCD}} + (\text{Average DOC})_{\text{Sievers}}]} \times 100\% \dots\dots \text{Equation 4.1a}$$

$$\% \text{Error} = \frac{34.02 \text{ppb} - 34.26}{34.02 \text{ppb} + 34.26} \times 100\%$$

$$\% \text{Error} = 0.35\%$$

Table 4.0(b): LC-OCD v/s Sievers analysers DOC results of Millipore water

Vial number	LC-OCD DOC result/ppb	Sievers DOC result/ppb
1	34.1	33.4
2	33.8	34.8
3	34.0	34.2
4	34.3	34.0
5	33.9	34.9
Average/ppb	34.02	34.26
SD/ppb	0.19	0.61
RSD/%	0.57	1.79

Based on the calculated results, the percentage error between the two analysers are acceptable with a %Error of 0.35% [2].

Sievers and LC-OCD analysers were therefore used for sample analysis after establishing/verifying that calibration and quality control checks were acceptable.

4.1 KRIEL WATER TREATMENT PLANT's RESULTS

4.1.1 Organic results from Kriel inlet raw water

Water samples collected from Kriel power station water treatment plant was analysed on a monthly basis by using Sievers TOC and LC-OCD analyser. The results obtained are graphically represented on Figure 4.1(a)

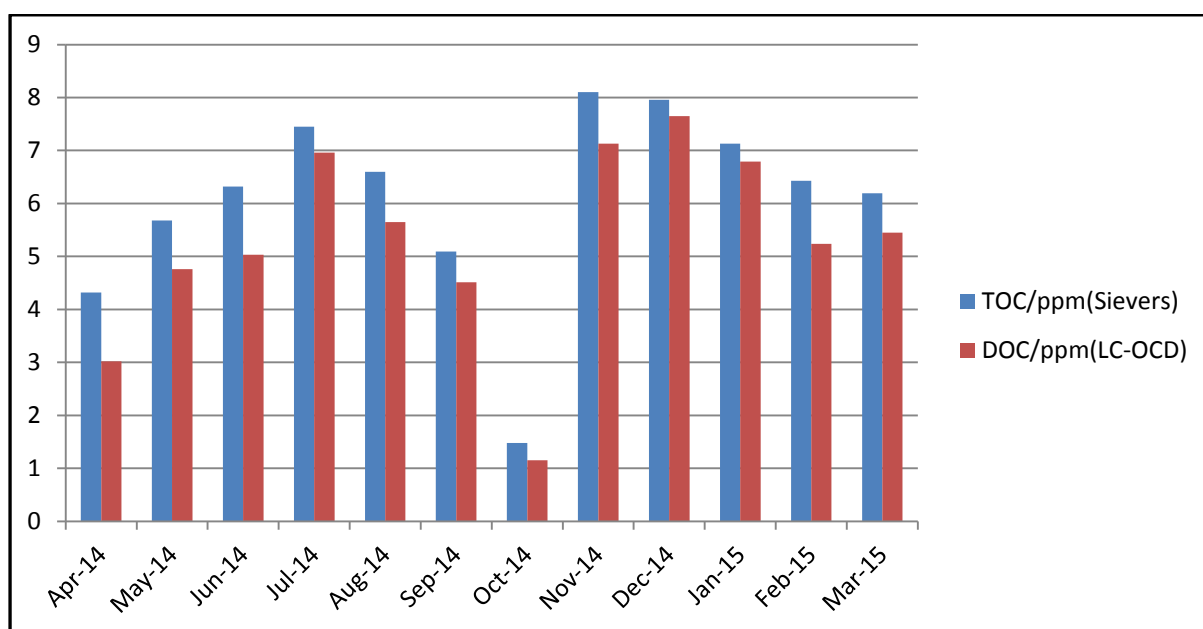


Figure 4.1(a): Kriel inlet raw water TOC v/s DOC results

There was a noticeable difference between Sievers and LC-OCD results as was expected because the sample was filtered through a 0.45 μm on a LC-OCD analyser, whereas no filtration was done on the Sievers analyser. Filtering the sample removes suspended organic matter, hence the DOC results are lower than the TOC results.

The LC-OCD results from Kriel inlet raw water in figure 4.1(b) show the composition/organic profile of the inlet raw water. An explanation of terms (legends) is as follows;

- DOC (Dissolved Organic Carbon) is made up of Hydrophobic Organic Carbon (HOC) and Chromatographic Dissolved Organic Carbon (CDOC- which only means that they were determined by chromatography, and basically they are hydrophilic organic carbons).
- CDOC is made up of Bio-polymers, Humic substances (HS), Building blocks (BB), Lower Molecular Weight (LMW) Neutrals and Lower Molecular Weight (LMW) Acids.

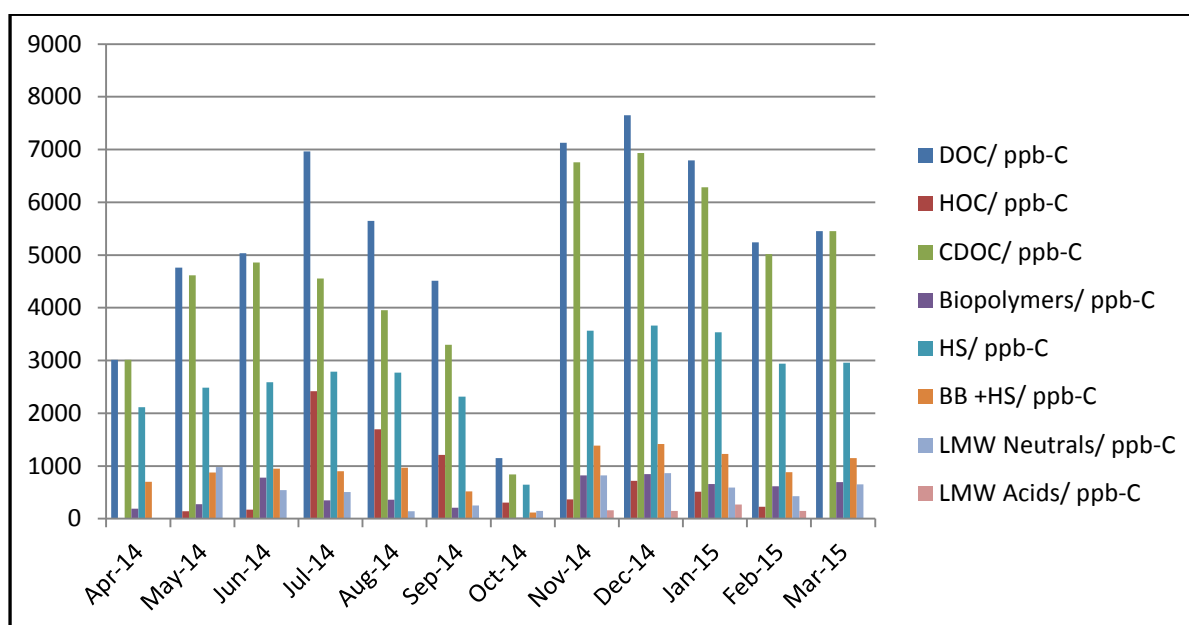


Figure 4.1(b) Kriel raw water inlet LC-OCD results

It was evident that a larger percentage of the dissolved organic carbon comprises of CDOC that are large and easy to remove by coagulation processes. A trend was observed where there was an increase in DOC concentrations in the November 2014

to January 2015 period. During that time, heavy rainfalls were experienced and an increase in farming activities which resulted in run-offs of pesticides, herbicides and fertilisers into the water supply stream.

However, low DOC results (1149 ppb) in October 2014 could not be explained, an oversight on the side of the researcher. Check samples were supposed to have been collected and analysed for, but due to time constraints as a result of work responsibilities and demands, that was not done.

4.1.2 Kriel filtered water DOC results

Filtered water results from Kriel were also analysed by using the LC-OCD analyser. The analyses were done on a monthly basis, and the results are tabulated in figure 4.1(c)

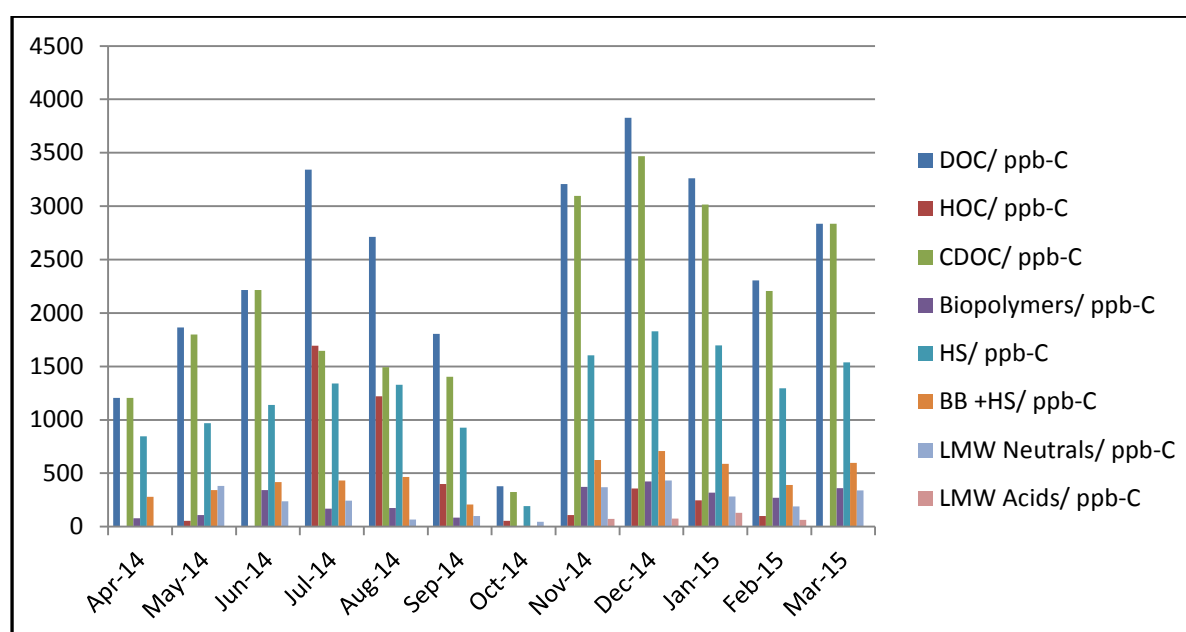


Figure 4.1(c) Kriel filtered water outlet LC-OCD results

After coagulation, flocculation, clarification/sedimentation and filtration an average of about 56.7% of the organic matter was removed from the water compared to the original DOC results of the untreated raw water (the results from filtered water DOC indicated that as shown on table 4.1(a).

The percentage organic removal for DOC, HOC and CDOC were calculated and illustrated in table 4.1(c), and the results were calculated as follows (for the purpose of showing how the calculation was done, April 2014 DOC results were used);

$$\% \text{Organic removal} = \left[1 - \left(\frac{\text{DOC of treated water}}{\text{DOC of raw water}} \right) \right] \times 100\% \quad \text{Equation 4.1b}$$

$$= \left[1 - \left(\frac{1206}{3015} \right) \right] \times 100\%$$

Organic removal = 60%

Table 4.1(a): Calculated organic removal at Kriel water pre-treatment plant

Month	DOC/ppb			CDOC/ppb			HOC/ppb		
	Raw	Filtered	%Removal	Raw	Filtered	%Removal	Raw	Filtered	%Removal
Apr2014	3015	1206	60.0	3015	1206	60	-	-	-
May2014	4760	1864	60.8	4617	1800	61	143	56	60
Jun2014	5032	2214	56.0	4860	2214	54	172	-	-
Jul2014	6963	3342	52.0	4553	1647	63.8	2420	1695	30
Aug2014	5650	2712	52	3955	1492	62.3	1695	1220	28
Sep2014	4510	1804	60	3297	1404	57.4	1212	400	77
Oct2014	1149	379	67	840	623	61.5	309	56	81
Nov2014	7125	3206	55	6755	3096	54.2	370	110	70
Dec2014	7651	3826	50	6935	3468	50.0	716	358	50
Jan2015	6794	3261	52	6283	3016	44.8	511	245	52
Feb2015	5240	2306	56	5015	2207	56	225	99	56
Mar2015	5454	2836	48	5454	2836	48	-	-	-
Average	5279	2413	55.7	4632	2084	56.1	777	471	56

Raw value in table 4.1(a) is the determined LC-OCD results of the raw water inlet of the species (DOC, CDOC and HOC) before addition of coagulants and flocculants to remove the organics from the water.

Comparison of SUVA values determined from LC-OCD analyser and percentage DOC removal is tabulated in table 4.1(b).

Table 4.1(b): Kriel SUVA values compare to %DOC removal

Month	SUVA	DOC removal /%
Apr2014	2.83	60.0
May2014	2.07	60.8
Jun2014	2.21	56.0
Jul2014	2.11	52.0
Aug2014	3.76	52
Sep2014	2.10	60
Oct2014	2.35	67
Nov2014	2.89	55
Dec2014	2.64	50
Jan2015	2.75	52
Feb2015	2.80	56
Mar2015	2.66	48
Average	2.60	55.7

The average SUVA values for the test period was determined to be 2.60 with %DOC removal of 56%. The %removal is greater than expected (for the determined SUVA values) as per table 2.2 (Chapter 2), however, it should be mentioned that the table was based on the %TOC.

4.1.3 Organic results from Kriel strong anion exchange outlet water

Further removal of organic matter occurred at the anion resin vessel of the demineralisation plant as expected, since anion resins have strong affinity for negatively charged molecules. The DOC levels dropped to a range of 350 ppb and 240 ppb as indicated in figure 4.1(d).

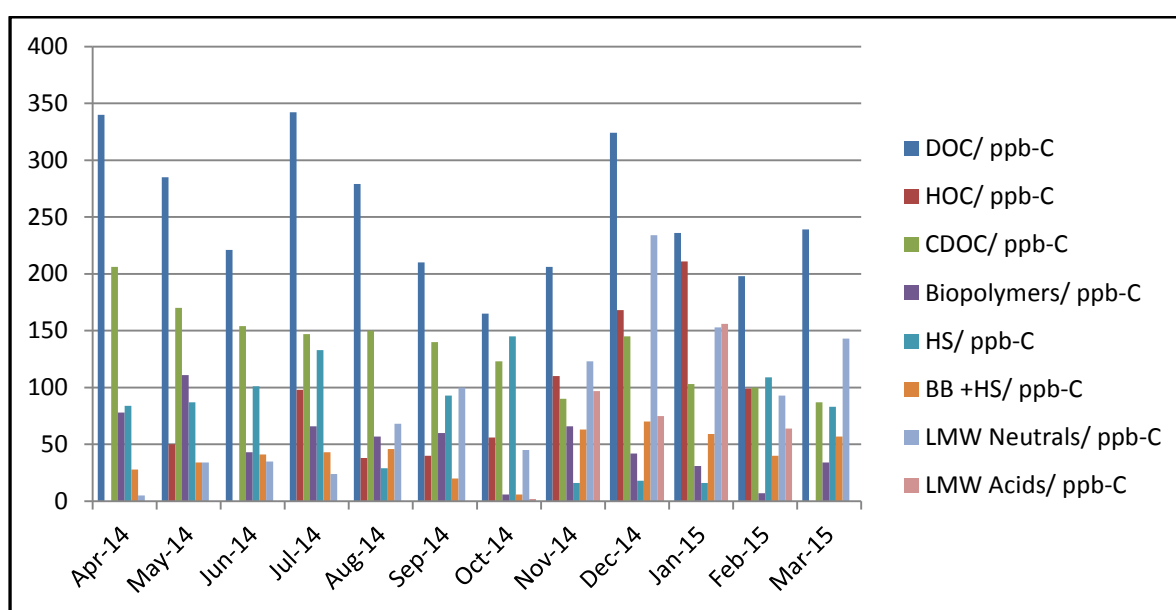


Figure 4.1 (d): Kriel strong anion exchange outlet LC-OCD results

4.1.4 Kriel mixed bed (MB) exchange outlet water results

The DOC removal in the month of August was very poor at the mixed bed exchange. At that time there was a lack of water treatment plant maintenance (brine wash to remove organics and other fouling matter) done as scheduled, hence a spike in the concentration of DOC was observed.

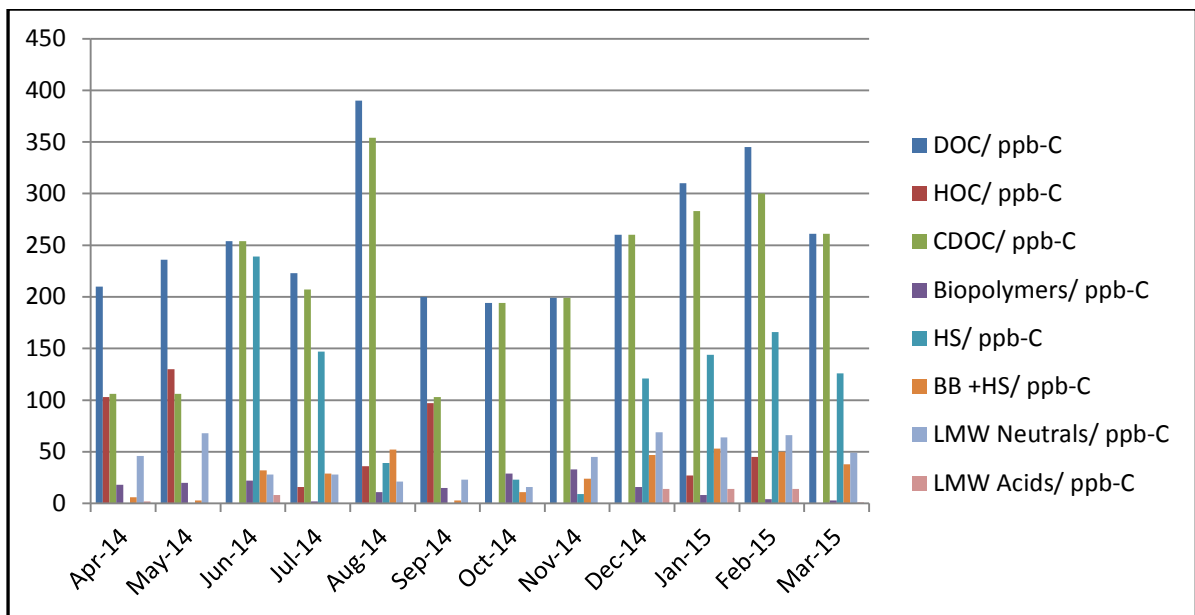


Figure 4.1(e) Kriel mixed bed exchange outlet LC-OCD results

Table 4.1(c) shows individual specie concentrations and calculated averages over the test period. One of the objectives as stated in chapter 1, section 1.3.1 was to qualify and quantify the profile of water. The intention of which was to investigate the impact in the cycle water (condensate and steam) used for power generation. The impact of the different specie determined will be shown in Section B of this report.

Table 4.1(c): Organic profile of Kriel mixed bed exchange outlet water

Month	DOC/ ppb-C	HOC/ ppb-C	CDOC /ppb-C	Biopolymers/ ppb-C	HS/ ppb-C	BB +HS/ ppb-C	LMW Neutrals/ ppb-C	LMW Acids/ ppb-C
Apr 2014	210	103	106	18	34	6	46	2
May 2014	236	130	106	20	15	3	68	-
Jun 2014	254	-	254	22	164	32	28	8
Jul 2014	223	16	207	2	147	30	28	-
Aug 2014	390	36	354	71	155	52	58	18
Sep 2014	200	97	103	30	47	3	23	-
Oct 2014	194	-	194	47	96	21	30	-
Nov 2014	199	-	199	53	77	24	45	-
Dec 2014	260	-	260	16	121	47	69	7
Jan 2015	310	27	283	8	144	53	64	14
Feb 2015	345	45	300	4	166	50	66	14
Mar 2015	261	-	261	47	126	38	49	1
Averages	256.83	64.85	218.91	28.17	107.67	29.92	47.83	9.14

Low molecular weight organic acids concentration was relatively low (undetectable, i.e below the detection limit of <1 ppb, with the highest being 18ppb) on the mixed bed outlet for the entire test period.

Figure 4.1(f) shows the comparison between Kriel raw water inlet, filtered, anion and mixed bed low molecular weight acids concentrations.

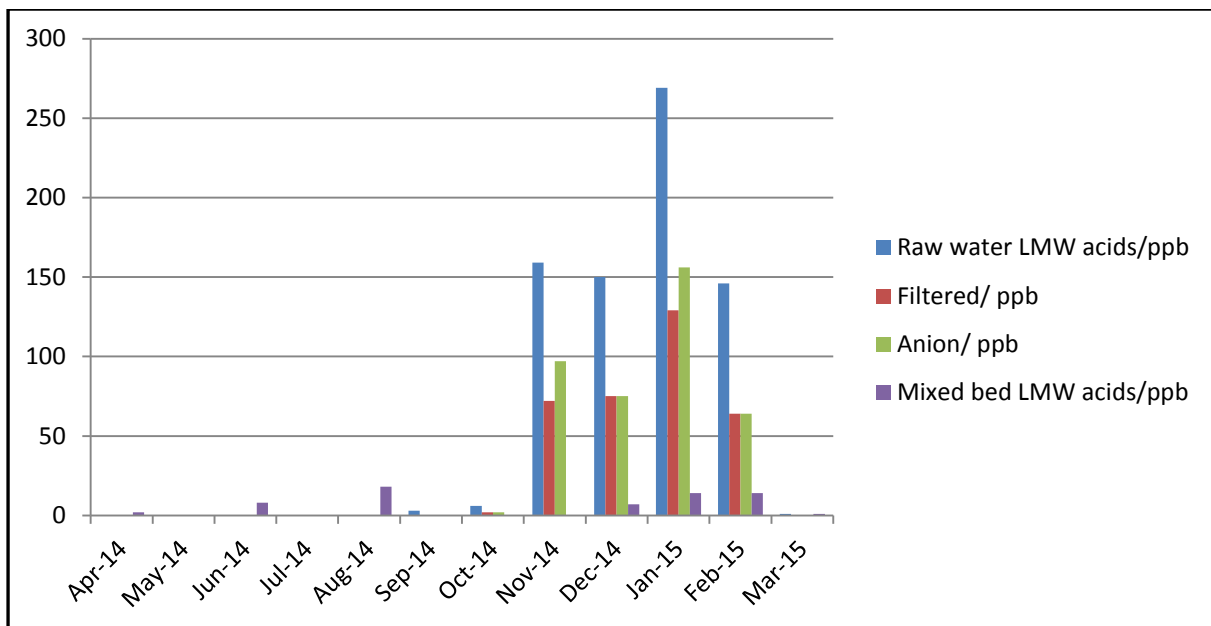


Figure 4.1(f): LMW acids results across Kriel water treatment plant

LMW organic acids were observed to be high on the mixed bed relative to the raw water from the April 2014 to August 2014, with a big spike (18 ppb) experienced in August. It can be observed that from Nov 2014 to February 2015, LMW acid from filtered water is not removed at anion exchanger vessel as expected. Actually there is an increase in acid concentration which can be attributed by the anion exchanger vessel being the source of the acid (LMW), a consequence of not brine washing the anion resin.

4.1.5 Summary of Kriel WTP organic removal

Average inlet raw water organics for Kriel power station was determined to be 5729 ppb from the period April 2014 to March 2015. A percentage organic removal averaging 55.7% was determined for the same period, which amount to half of the organics being removed across the clarification plant. This is an indication that if pre-

treatment (flocculation and clarification) is optimized properly, then good removal of organics can be expected.

Average DOC at the mixed bed outlet was determined to be 256.83 ppb, which indicates 95% removal of organics from the raw water inlet. A higher percentage (close to 98%) could be easily obtained if full maintenance of the demineralisation plant is adhered to.

4.2 ARNOT WATER TREATMENT PLANT RESULTS

4.2.1 Organic results from Arnot inlet raw water

As expected, the TOC is higher relative to the DOC results because of the suspended organic matter that was filtered on the LC-OCD (DOC analysis). The results from the two analysers (Sievers and LC-OCD) are illustrated in figure 4.2(a).

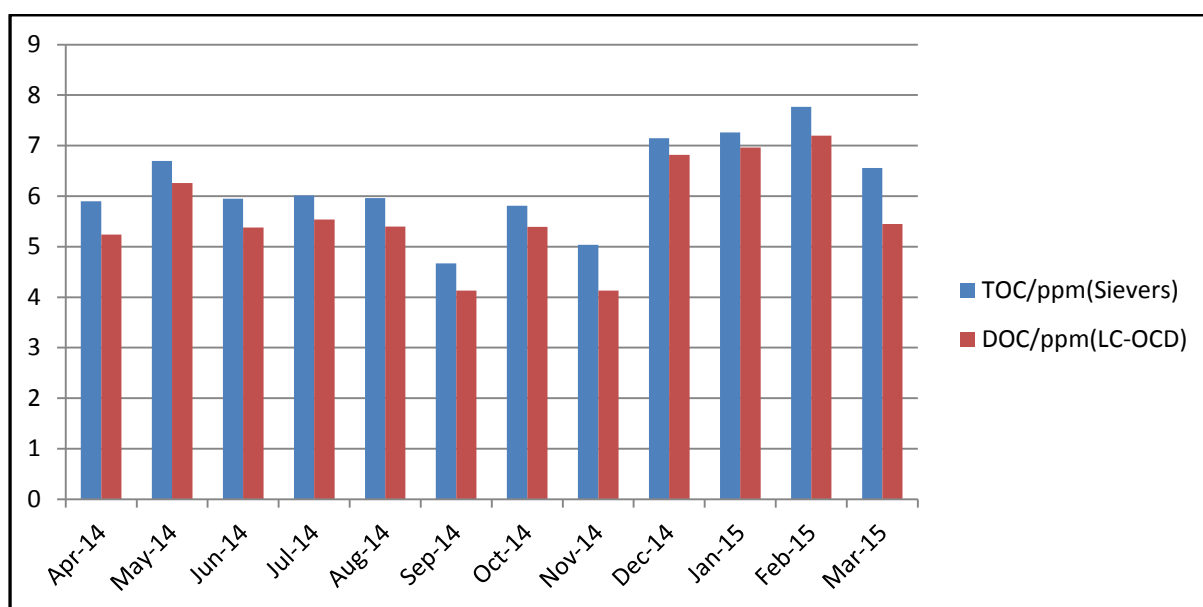


Figure 4.2(a): Arnot inlet raw water TOC v/s DOC results

Arnot power station is supplied with water from two different dams namely, Nooitgedacht and Vygeboom. Normally when the Nooitgedacht dam is in an acceptable operating level (above 70%), it is used to supply Arnot power station. On the other hand, Vygeboom (relatively better quality water when compared to Nooitgedacht) dam will only be used to supply Arnot power station when Nooitgedacht dam level decreases below 70%. A water blend that is supplied is in the ratio of 60% Nooitgedacht and 40% Vygeboom dam, and it has the advantage of

relatively better quality and low TOC concentrations when compared to water from a single source (Nooitgedacht).

There is a noticeable increase in the TOC/DOC concentrations during the rainy season (December to February) and during this period, Nooitgedacht dam was the source of water received at Arnot power station. A decrease in TOC/DOC is observed between the months of June 2014 to November 2014, due to a blend (Nooitgedacht and Vygeboom dams) being the source of water supplied to the station.

A significant increase of DOC (December 2014 and February 2015) is mainly due to CDOC as observed on an LC-OCD result from Arnot inlet raw water as shown in figure 4.2(b).

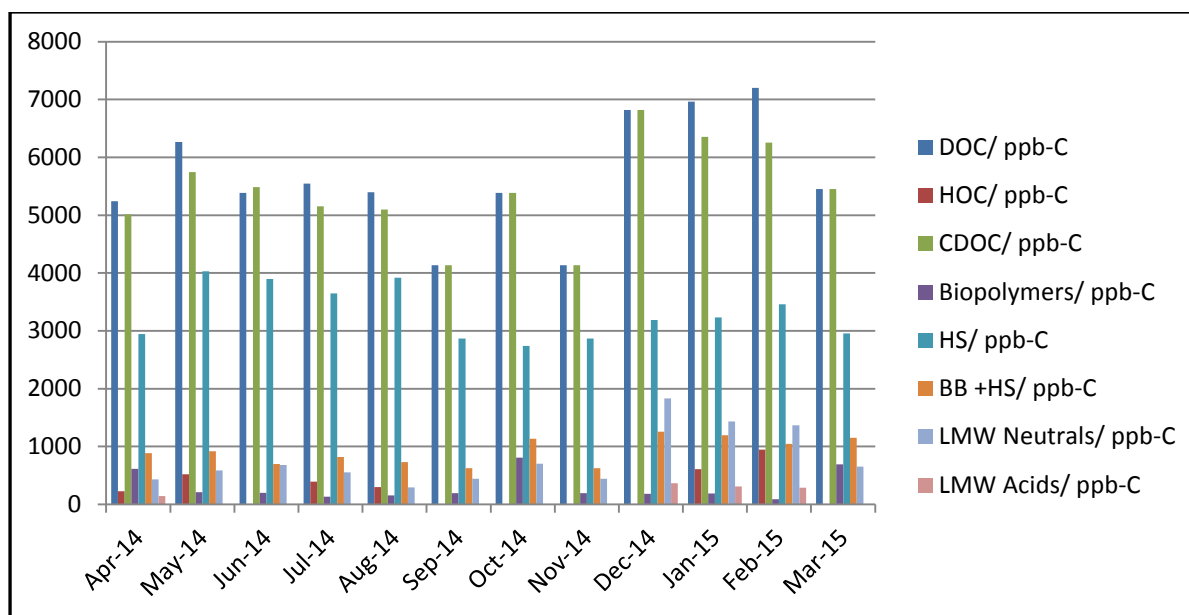


Figure 4.2(b): Arnot inlet raw water inlet LC-OCD results

4.2.2 Arnot filtered water DOC results

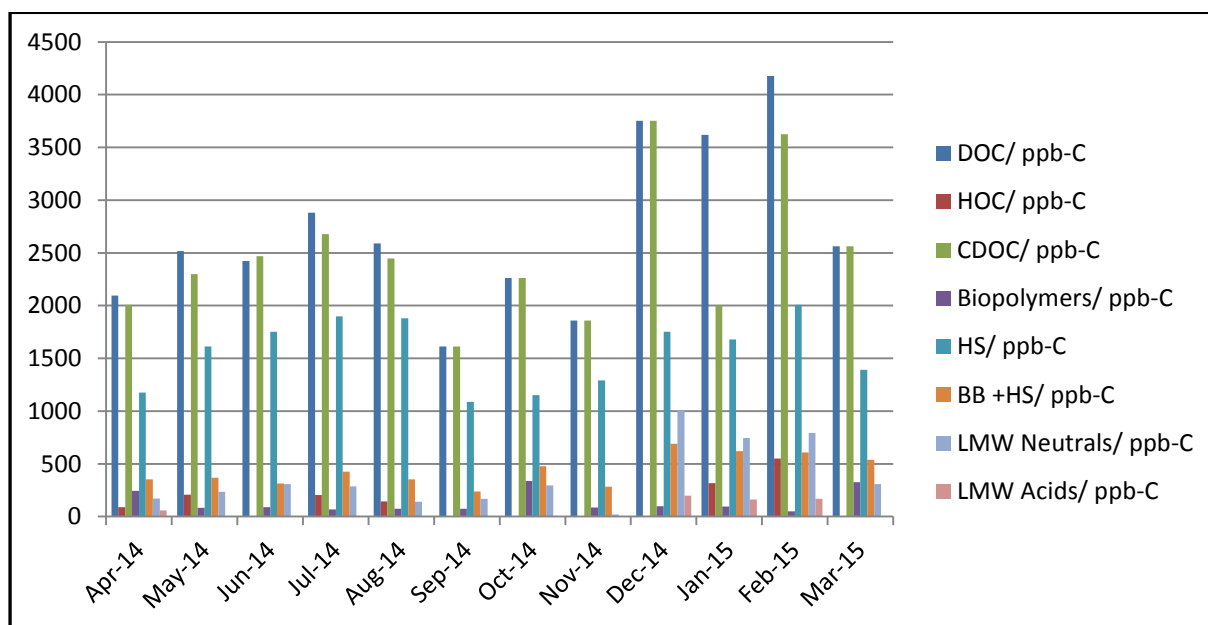


Figure 4.2(c) Arnot filtered water outlet LC-OCD results

The removal of DOC from the Arnot water treatment plant at the sandfilter common outlet indicated an average of 53.6%. Figure 4.2(c) shows a clear picture of the trends and concentration of the DOC for Arnot's filtered water.

It is clear from table 4.2(a) that when a spike in DOC was observed (December 2014 to February 2015), organic removal was very low (averaging 45%) compared to the other months and overall average of 53.6% for the entire test period.

Humic substances (HS) increased to concentrations above 3000ppb and lower molecular weight (LMW neutrals) also increased to above 700ppb during that period.

Table 4.2(a): Calculated organic removal at Arnot water pre-treatment plant

Month	DOC/ppb			CDOC/ppb			HOC/ppb		
	Raw	Filtered	%Removal	Raw	Filtered	%Removal	Raw	Filtered	%Removal
Apr 2014	5250	2096	66	5015	2006	60	225	90	60
May 2014	6263	2517	59.8	5744	2298	60	519	208	60
Jun 2014	5383	2422	55	5483	2467	55	-	-	-
Jul 2014	5544	2882	48	5152	2679	48	392	204	48
Aug 2014	5396	2590	52	5096	2446	52	300	144	52
Sep 2014	4133	1612	61	4133	1612	61	-	-	-
Oct 2014	5386	2262	58	5386	2262	58	-	-	-
Nov 2014	4133	1860	55	4133	1860	55	-	-	-
Dec 2014	6821	3752	45	6821	3752	45	-	-	-
Jan 2015	6962	3620	48	6353	2000	68.5	609	317	47.9
Feb 2015	7200	4176	42	6252	3626	42	648	550	15
Mar 2015	5454	2563	53	5454	2563	53	-	-	-
Average	5660	2690	53.6	5419	2464	54.8	449	252	47.2

Table 4.2(b) demonstrate the SUVA values with an average of 3.99 as determined from the LC-OCD analyser and the corresponding %DOC removal was found to be 53.6%.

The average percentage removal of DOC greater than 40% was expected for average SUVA value of 3.99% (as per Table 2.2, Chapter 2).

Table 4.2(b): Arnot SUVA values compared to %DOC removal

Month	SUVA	DOC removal /%
Apr2014	4.10	66.0
May2014	4.26	59.8
Jun2014	3.76	55.0
Jul2014	4.03	48.0
Aug2014	3.80	52.0
Sep2014	3.73	60.0
Oct2014	3.89	58.0
Nov2014	3.77	55.0
Dec2014	4.00	45.0
Jan2015	4.23	48.0
Feb2015	4.08	42.0
Mar2015	4.22	53.0
Average	3.99	53.6

4.2.3 Organic results from Arnot strong anion exchange water

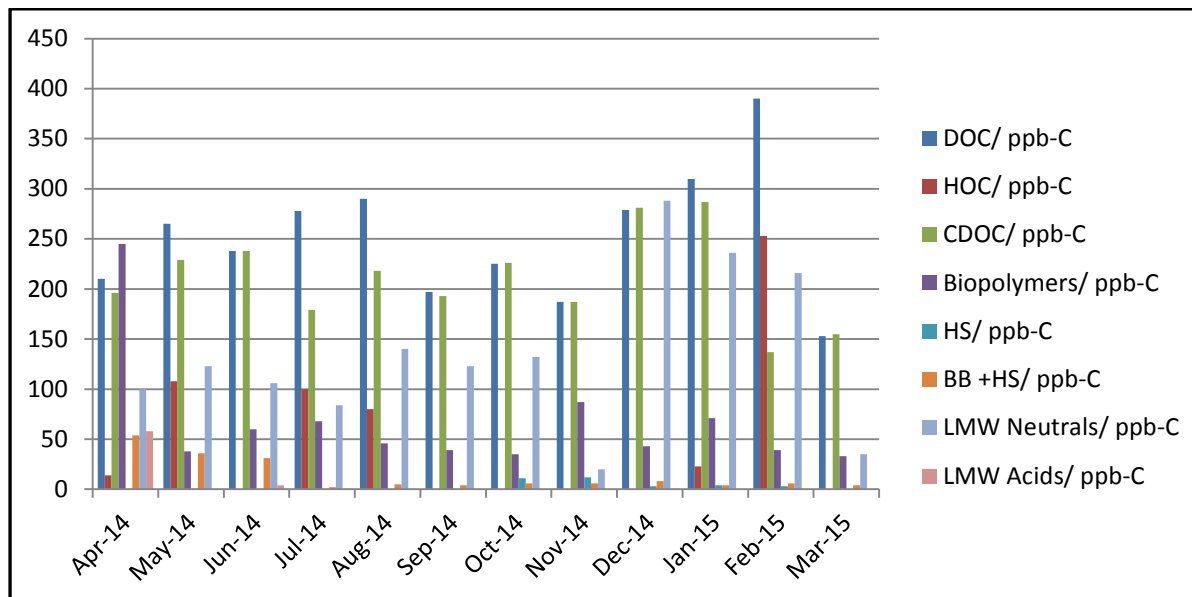


Figure 4.2(d): Arnot strong anion exchange outlet LC-OCD results

There was a significant DOC removal (from Arnot filtered water) across the strong anion exchange resin as indicated by the results plotted on figure 4.2(d). This was an indication that the resin could handle high organic loading with great efficiency.

4.2.4 Organic results from Arnot mixed bed exchange water

The mixed bed anion resin vessel's function is to remove any slippage or 'polish' the final demineralised water from the anion exchange vessel. Figure 4.2(e) clearly indicates the removal of DOC to concentrations below 120 ppb, and which was significantly lower than the Eskom's target of 250 ppb TOC in demineralised water [4].

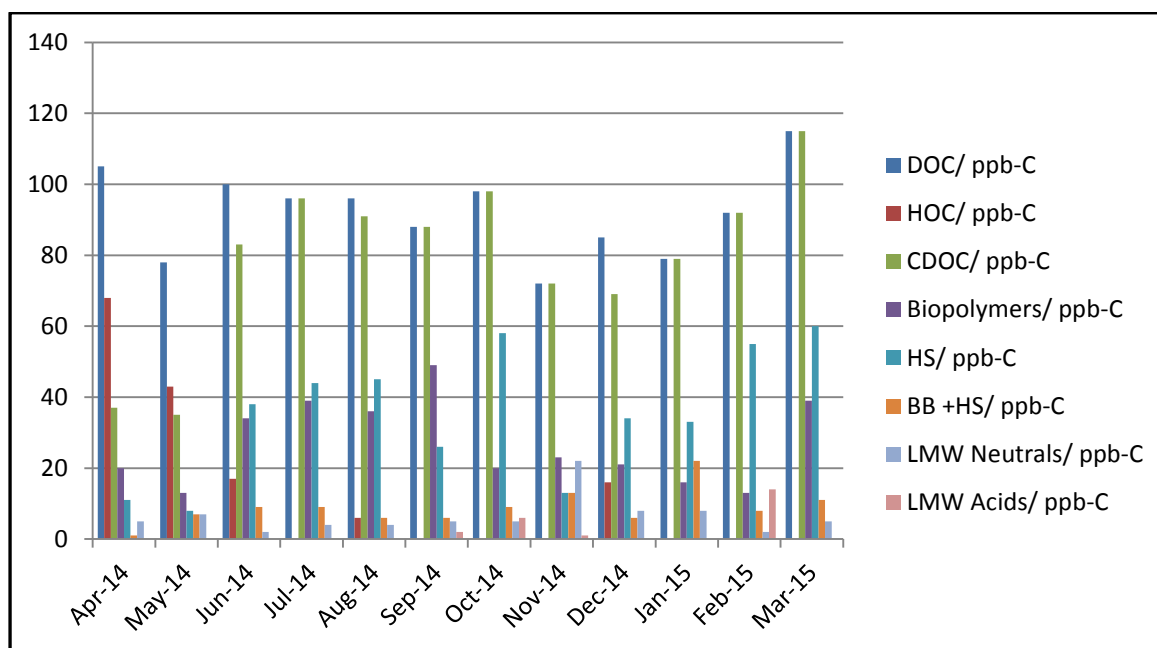


Figure 4.2(e): Arnot mixed bed exchange outlet LC-OCD results

Mixed bed exchange outlet water is the final product of water treatment plant, as a result, it is the feed water to the electricity generation. The amount of TOC/DOC concentration will therefore determine the amount of organic acids that will be present in condensate, boiler and steam samples. Organic species that are present

at the outlet of the mixed bed exchange outlet water over the test period is shown in table 4.2(c).

Table 4.2(c): Organic profile of Arnot mixed bed exchange outlet water

Month	DOC/ ppb-C	HOC/ ppb-C	CDOC/ ppb-C	Biopolymers/ ppb-C	HS/ ppb-C	BB +HS/ ppb-C	LMW Neutrals/ ppb-C	LMW Acids/ ppb-C
Apr 2014	105	68	37	20	11	1	5	-
May 2014	78	43	35	13	8	7	7	-
Jun 2014	100	17	83	34	38	9	2	-
Jul 2014	96	0	96	39	44	9	4	-
Aug 2014	96	6	91	36	45	6	4	
Sep 2014	88	0	88	49	26	6	5	2
Oct 2014	98	0	98	20	58	9	5	6
Nov 2014	72	0	72	23	13	13	22	1
Dec 2014	85	16	69	21	34	6	8	0
Jan 2015	79	0	79	16	33	22	8	0
Feb 2015	92	0	92	13	55	8	2	14
Mar 2015	115	0	115	39	60	11	5	0
Averages	92	12.5	79.58	26.91	35.41	8.92	6.42	3.29

The concentration of the DOC at the mixed bed outlet was well within the target specifications. This is an indication of a proper plant efficiency.

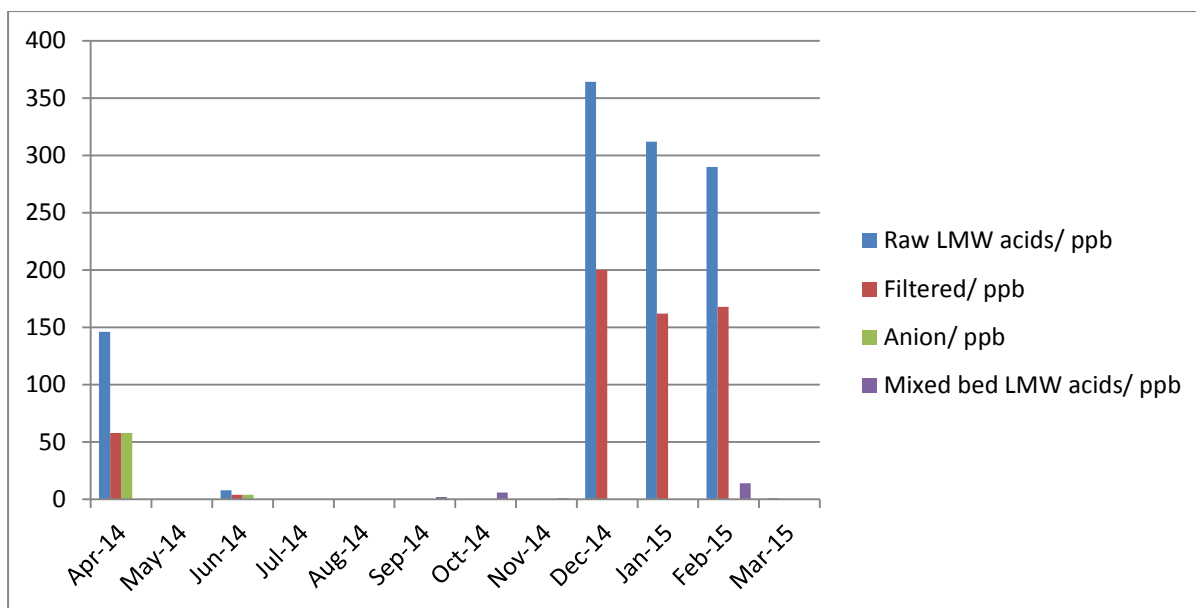


Figure 4.2(f): LMW acids results across Arnot water treatment plant

Figure 4.2(f) shows relatively high LMW acids for the months of Dec 2014, Jan and Feb 2015. The overall DOC values were high for the 3 months hence the LMW acids concentrations are expected to be high. It should however be noted that the mixed bed managed to reduce or completely remove the LMW acids from the water.

4.2.5 Summary of Arnot WTP organic removal

The average organic concentration of 5660 ppb was removed in the pre-treatment process and about 53.6% removal was achieved. On average half of the organics were removed at the pre-treatment process (flocculation and coagulation) and the rest were removed by demineralisation.

Percentage organic removal from the raw water inlet to the mixed bed was calculated to be 98.4%. That is a satisfactory removal that resulted in an average

mixed bed outlet of 92 ppb of organics, a value that is well within the specified 250 ppb Eskom's demineralized water target.

SECTION B

As already mentioned in Chapter 2 (section 2.5), that organic matter in water when exposed to high temperature and pressure, decomposes to low molecular mass organic acids and carbon dioxide. The presence of organic acids and their concentrations were determined experimentally by the LC-OCD technique, but the challenge with this method of analysis is that it gives the total lower molecular mass organic matter. There is no differentiation/speciation into different species of organics, hence an ion chromatographic method of analysis was utilised for determining the individual organic acids present and their concentration in solution.

Samples from the power plant were collected and analysed by using ion chromatography. Plant conductivities (acid cation and degased) were recorded at the time of sampling. Degased cation conductivities (DCC) were only determined at the superheated steam samples, the rationale being that at that temperature and pressure, decomposition of organics is complete at that part of the plant.

The Metrohm 850 Professional IC instrument was calibrated prior to sample analysis being done. The average calibration results are presented in table 4.3(a) with statistical calculations included.

(i) *Metrohm IC calibration results*

The IC used was calibrated with freshly prepared calibration standards from certified reagents. An example of a chromatogram produced for standard 1 (40 ppb) of the calibration is shown in Figure 4.3(a).

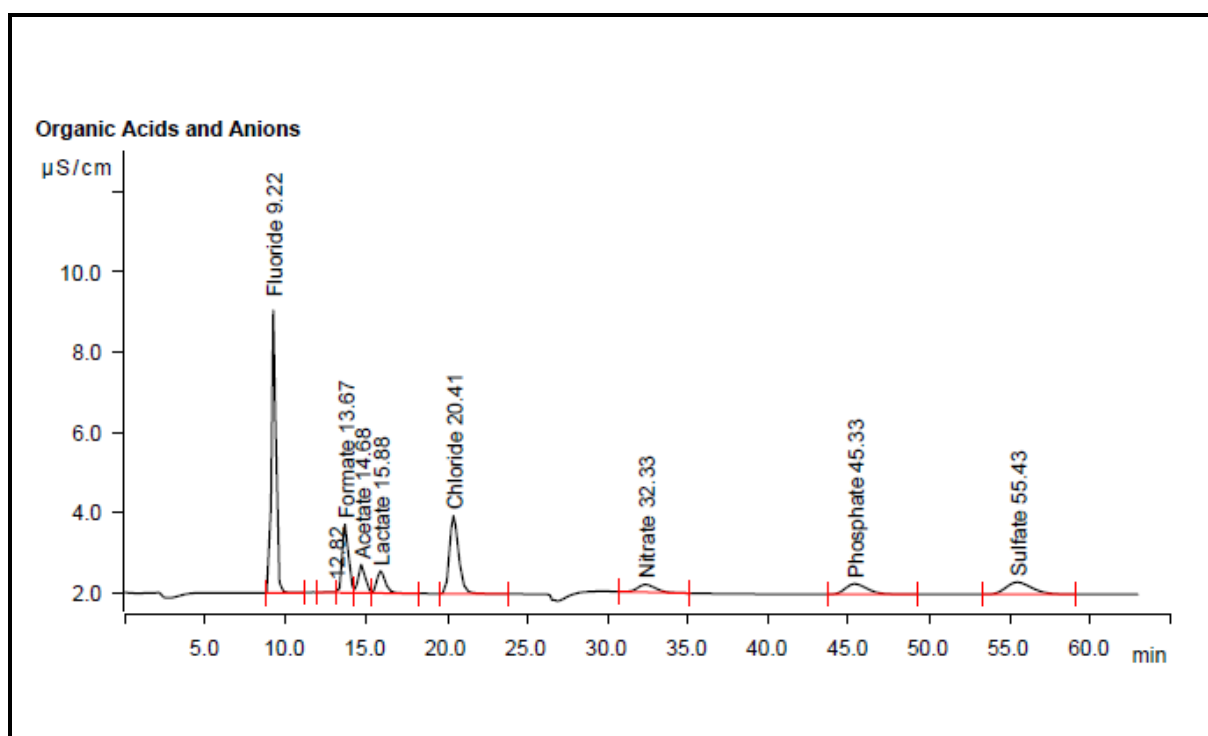


Figure 4.3(a): Metrohm 850 professional IC standard 1 chromatogram

It should be noted that even though fluoride, nitrate and phosphate peaks appear on the chromatogram, they were not part of the anions of this study. Eskom's minimum requirement for monitoring of anions in boiler, condensate and steam samples does not include fluoride, nitrate and phosphate ion measurement [5]. The calibration solution that was supplied by Metrohm contains 8 anions that appear on the chromatogram (figure 4.3(a)), and some of those anions (fluoride, nitrate and phosphate) are not part of the analysis required for Eskom's cycle water monitoring.

The calibration results (average for the 12 month period) for the ions of interest for the study viz, formate, acetate, lactate, chloride and sulphate are shown on Table 4.3(a). The calibration graph had an acceptable correlation coefficient of 0.999 and a relative standard deviation of less than 5% [2].

Table 4.3(a): Metrohm 850 Professional IC calibration results

Standards	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	%RSD	Correlation Coefficient
Formate, ppb	40	20	10	4	2	1	0.5	0.877	0.999986
Acetate, ppb	40	20	10	4	2	1	0.5	0.217	0.999999
Lactate, ppb	40	20	10	4	2	1	0.5	0.557	0.999994
Chloride, ppb	40	20	10	4	2	1	0.5	1.026	0.999980
Sulphate, ppb	40	20	10	4	2	1	0.5	0.918	0.999984

The calibrations as well as the quality control results were acceptable and the instrument was therefore used for the sample analysis. The resultant calibration graphs for individual parameters were as follows;

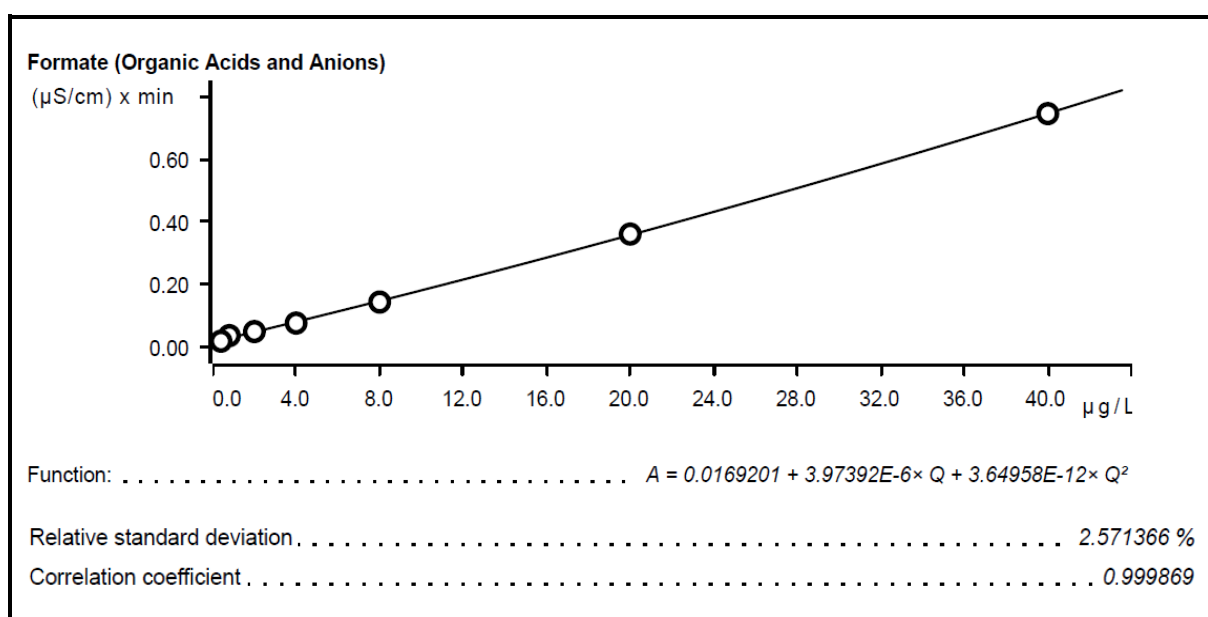


Figure 4.3(b): Calibration graph for Formate ion

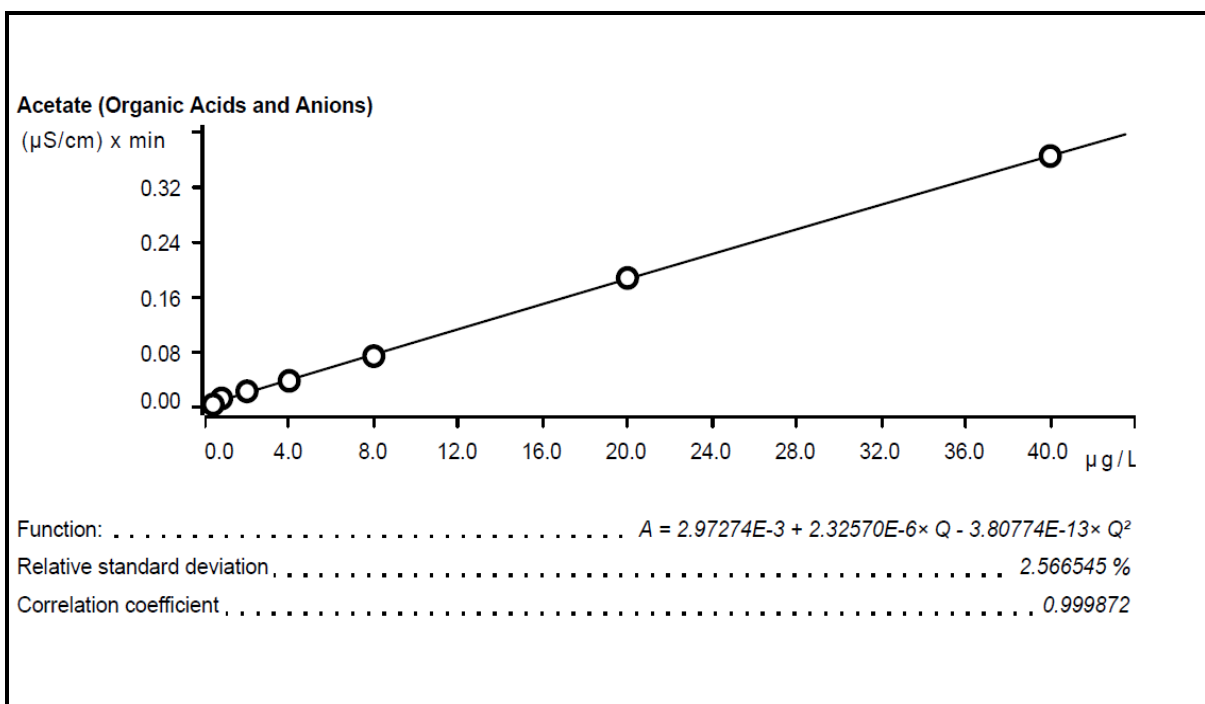


Figure 4.3(c): Calibration graph for Acetate anion

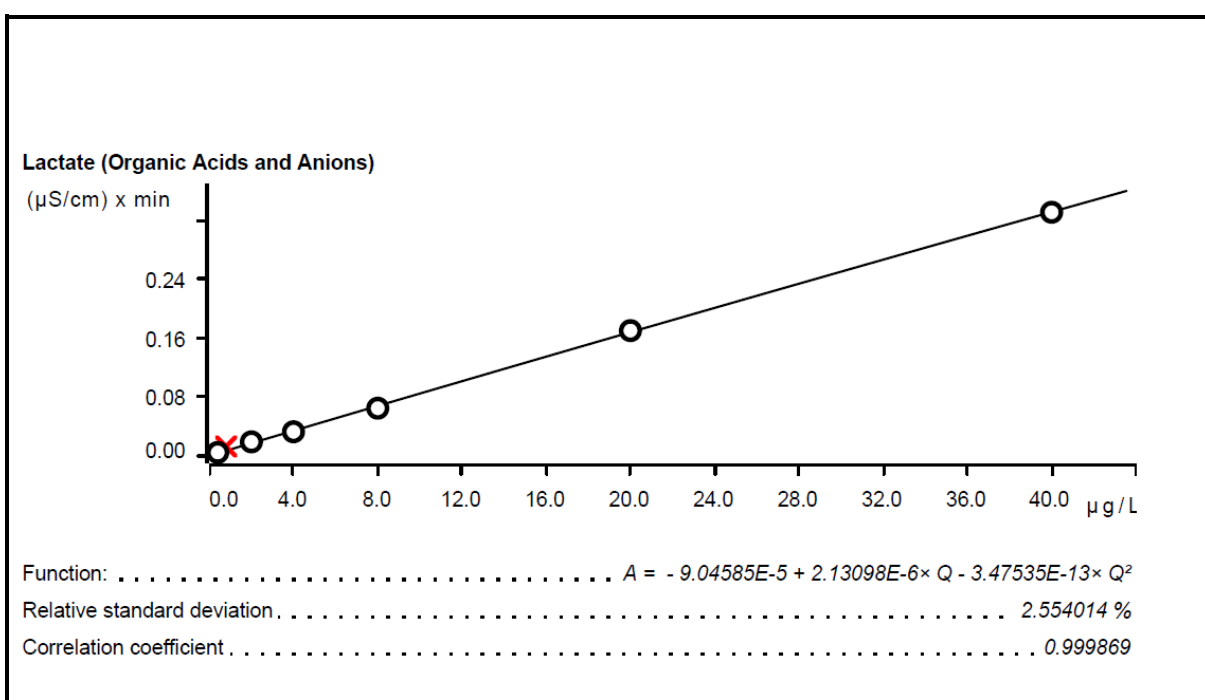


Figure 4.3(d): Calibration graph for Lactate ion

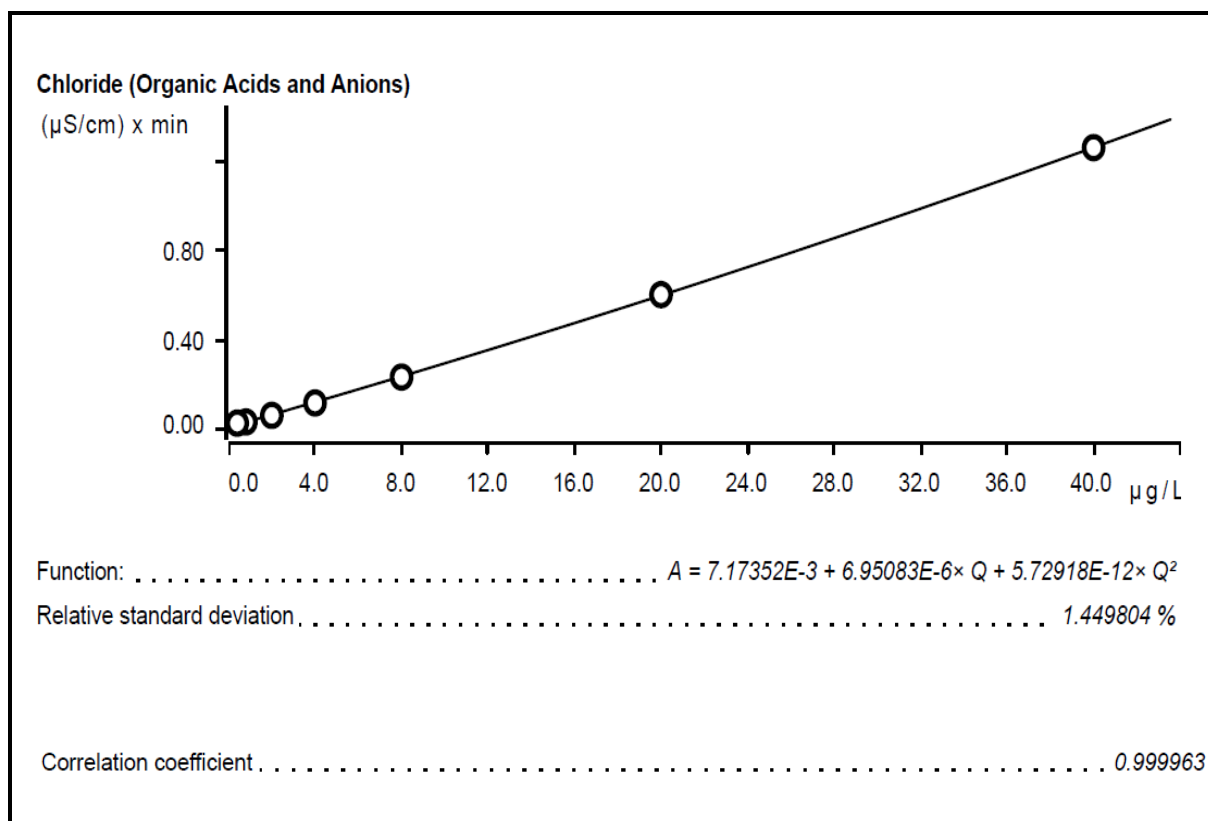


Figure 4.3(e): Ion chromatography calibration graph for chloride ion

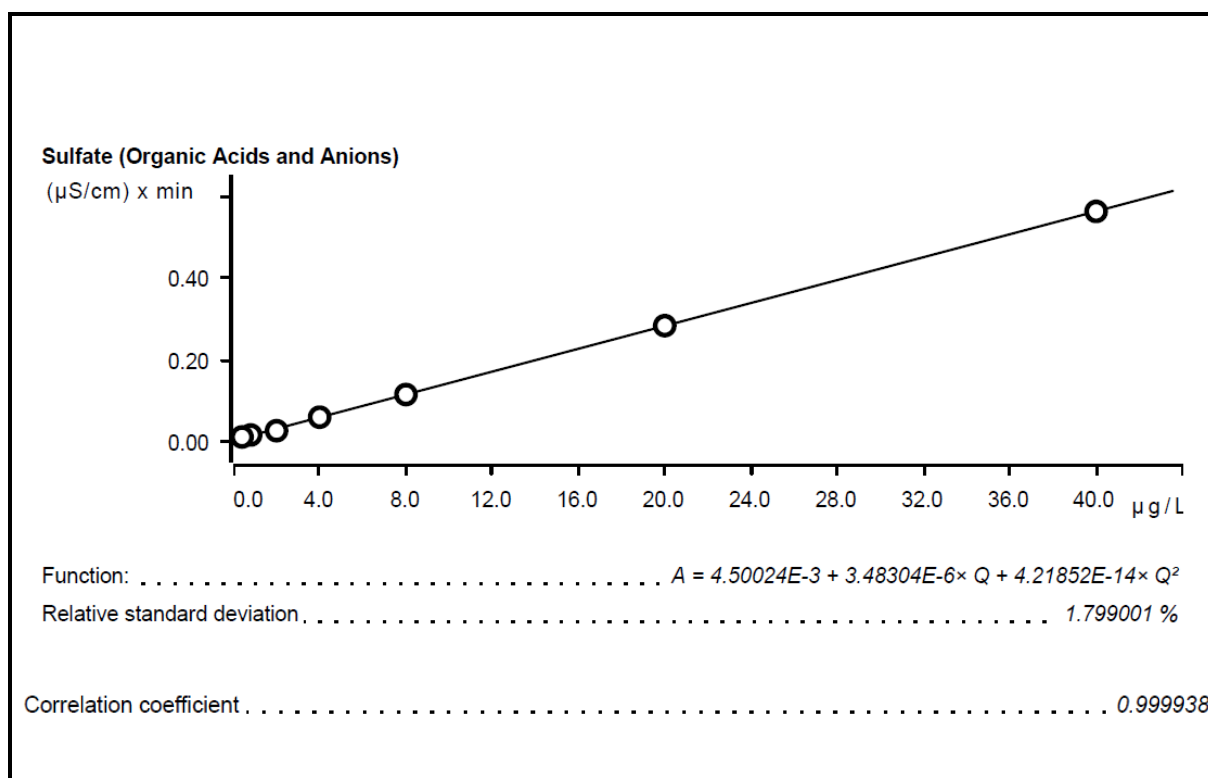


Figure 4.3(f): Ion chromatography calibration graph for sulphate ion

(ii) *Quality control (QC) standards results*

A 4.000 ppb mixed QC standard compost of chloride, sulphate, acetate, formate and lactate anions was analysed after every calibration that was performed over the entire experimental period (12 months). The analysis was done in triplicate once a month after every calibration performed. The results obtained are in table 4.1(b). It can be observed that the %RSD for all the measured anions were all below 1%, which is excellent and acceptable as per Eskom laboratory guideline [2]

Table 4.3(b): Average results for a 4.000 ppb mixed anion QC standard

Date	Chloride/ ppb	Sulphate/ ppb	Acetates/ ppb	Formates/ ppb	Lactate/ ppb
Apr 2014	3.925	3.999	4.012	3.980	3.999
May 2014	3.992	3.995	3.993	3.994	3.999
Jun 2014	3.994	4.009	3.994	3.995	4.004
Jul 2014	3.981	4.002	3.999	3.995	4.007
Aug 2014	3.997	3.967	4.001	3.990	3.998
Sep 2014	3.918	3.954	3.992	3.944	3.960
Oct 2014	3.990	4.001	4.000	3.977	3.918
Nov 2014	3.979	3.996	3.994	3.995	3.994
Dec 2014	3.995	4.000	3.991	3.999	4.001
Jan 2015	3.909	3.991	3.994	4.004	3.987
Feb 2015	3.999	4.007	3.993	4.000	3.994
Mar 2015	4.004	3.997	3.990	4.002	4.007
Average/ppb	3.9740	3.993	3.996	3.994	3.989
SD*/ppb (±)	0.0348	0.0163	0.00613	0.00814	0.0256
%RSD**	0.875	0.407	0.153	0.204	0.643

*SD- standard deviation, RSD**-relative standard deviation

4.3 KRIEL CONDENSATE-STEAM RESULTS

The condensate extraction pump, condensate polisher plant and superheated steam outlet samples were collected and analysed for inorganic and organic anions by use of an IC. The intention was to determine the concentrations of the anions in the sample and use those values for calculating the equivalents conductivities.

4.3.1 Ion Chromatography results

Condensate extraction pump (CEP) outlet, Condensate polisher plant (CPP) outlet and Superheated (SUP) outlet samples collected from Kriel were analysed for anions by using a calibrated IC. The samples were collected monthly in triplicate and the average results were recorded.

Table 4.3(c): Kriel CEP outlet results for organic, sulphate and chloride anions

Date	Chloride/ ppb	Sulphate/ ppb	Acetate/ ppb	Formate/ ppb	Lactate/ ppb
Apr-14	0.21	0.26	0.126	0.26	0.26
May-14	0.12	0.213	0.147	0.081	0.03
Jun-14	0.23	0.282	0.165	0.079	0.06
Jul-14	0.25	0.403	0.124	0.163	0.07
Aug-14	0.33	0.342	0.148	nd	0.18
Sep-14	0.26	0.464	0.187	0.086	0.000
Oct-14	0.34	0.342	0.126	0.084	0.010
Nov-14	0.32	0.432	0.054	nd	nd
Dec-14	0.23	0.459	0.151	0.05	nd
Jan-15	0.36	0.508	0.124	0.19	0.0199
Feb-15	0.27	0.394	0.157	0.16	0.16
Mar-15	0.34	0.235	0.128	0.05	0.05

*nd- non detectable

The anions that are mandatory to be analysed at Eskom's fossil fueled stations are chloride and sulphate, and they were well within the target specification as stipulated in Eskom's chemistry standard for once-through boiler (Kriel's boiler) as seen on table 4.3(c) for condensate extraction pump outlet [8]. The organic acids (acetic, formic and lactic) were detected by IC to be present in the samples. In all cases their concentration were observed to be below 1 ppb.

Table 4.3(d): Kriel CPP outlet results for organic, sulphate and chloride anions

Date	Chloride / ppb	Sulphate/ ppb	Acetate/ ppb	Formate/ ppb	Lactate/ ppb
Apr-14	0.13	0.23	0.022	0.02	0.077
May-14	0.09	0.18	0.144	0.03	0.068
Jun-14	0.11	0.17	0.018	0.05	0.057
Jul-14	0.14	0.24	0.041	0.01	0.058
Aug-14	0.21	0.29	0.049	0	0.06
Sep-14	0.25	0.32	0.098	0.03	0.067
Oct-14	0.18	0.2	0.1	0.05	0.078
Nov-14	0.21	0.29	0.082	nd	0.068
Dec-14	0.09	0.38	0.027	0.01	0.077
Jan-15	0.14	0.39	0.103	0.06	0.059
Feb-15	0.16	0.23	0.111	0.02	0.089
Mar-15	0.13	0.3	0.103	nd	0.059

A reduction in the anions (both organic and inorganic) is expected on the CPP outlet samples since ion exchange occurs at that particular part of the plant. The concentrations measured were within the maximum allowable target for once through boilers (Kriel boiler). These, therefore are meeting Eskom's target specifications [7].

However at the SUP sample, an increase in the organic anions is expected as a result of the breakdown of larger organic molecules to smaller fragments. The breakdown is mainly due to high pressure and temperature that the cycle water is exposed to. Table 4.3(e) demonstrates the results that were obtained after analysis of the sample.

Table 4.3(e): Kriel SUP results for organic, sulphate and chloride anions

Date	Chloride/ ppb	Sulphate/ ppb	Acetate/ ppb	Formate/ ppb	Lactate/ ppb
Apr-14	0.18	0.25	0.013	0.05	0.13
May-14	0.1	0.18	0.0019	0.08	nd
Jun-14	0.08	0.19	0.006	0.11	nd
Jul-14	0.16	0.21	0.023	0.05	0.27
Aug-14	0.17	0.28	0.038	nd	0.14
Sep-14	0.21	0.27	0.101	nd	nd
Oct-14	0.23	0.17	0.093	0.09	nd
Nov-14	0.19	0.21	0.042	nd	0.33
Dec-14	0.12	0.33	0.003	nd	0.87
Jan-15	0.18	0.33	0.012	0.07	0.03
Feb-15	0.12	0.19	0.0104	nd	nd
Mar-15	0.09	0.25	0.087	nd	0.12

Figure 4.3(g) is a graphical illustration of the trends of the organic acids through the different flow-path of the cycle water. As observed and expected, organic acids at the outlet of the CPP is in most cases lower than the CEP concentration because ion exchange causes a reduction of anions. An increase in organic acids at the SUP is also expected as already alluded to, due to breakdown of larger organic molecules that are found in the feed-water. However there was no regular trend observed (increase of organic acids concentration in the SUP sample), except in December 2014.

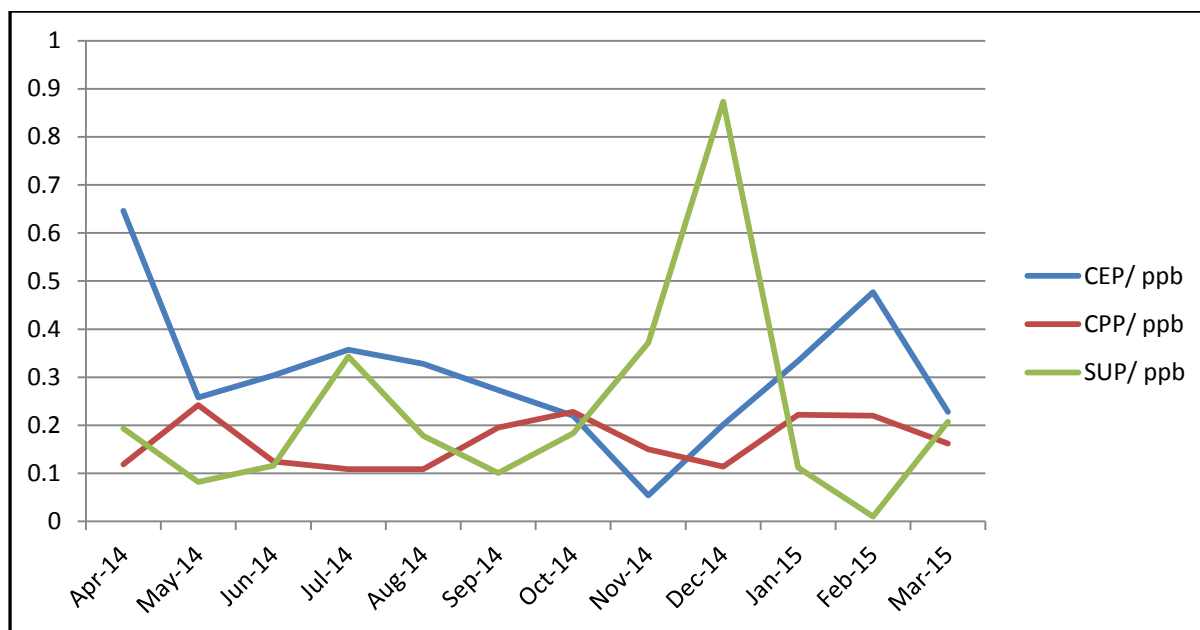


Figure 4.3(g): Kriel CEP, CPP and SUP total organic acids trends

4.3.2 Swan acid cation conductivities and calculated conductivities

A freshly prepared potassium chloride (KCl) standard of concentration 0.0001M was analysed with the Thornton 770Max calibrator as quality control standard for assurance purposes.

(i) Verification of conductivity by use of KCl standard

A freshly prepared KCl standard was used as a QC standard for verification of a Thornton 770 max calibrator that was in-turn used to verify plant analysers. The analysis was done in triplicate and the percentage error as indicated in table 4.3(f) calculated. Triplicate analysis was performed on 6 monthly basis to verify the validity of the results obtained from the conductivity on-line analysers.

Table 4.3(f): Thornton 770Max calibrator QC 147 μScm^{-1} KCl results

Reading	Measured Conductivity / 147 μScm^{-1}	%Error
1	146.79	0.14
2	145.37	1.11
3	147.55	0.37
Average	146.57	0.54

The average results on the recovery of the KCl QC standard was within the acceptable level (<5%) [2].

(ii) Acid cation conductivity readings from the plant

An average of the acid cation conductivity readings from the plant were recorded after verification of the plant on-line analysers was done. The readings were obtained from the condensate extraction pump (CEP), outlet condensate polisher plant (CPP) outlet and superheated steam (SUP) outlet. The readings from the plant on-line analysers were recorded at the time of sampling for ion chromatography (IC) analysis. It should however be noted that in order to investigate the effect of organic acids on the acid cation conductivity, SUP sample results were used. The rationale behind this is because the DCC is only done on the SUP samples, therefore the effect of dissolved gases could be eliminated from the calculation (dissolved gases were removed).

Table 4.3(g): SUP degas acid cation conductivities (DCC) and IC results in neq/L

Date	DCC/(μ S/cm)	Chloride	Sulphate
		Concentration/ neq/L	Concentration/ neq/L
Apr-14	0.071	1.874	2.603
May-14	0.062	1.041	1.874
Jun-14	0.092	0.833	1.978
Jul-14	0.063	1.666	2.187
Aug-14	0.062	1.770	2.915
Sep-14	0.059	2.187	2.811
Oct-14	0.064	2.395	1.77
Nov-14	0.064	1.978	2.187
Dec-14	0.064	1.249	3.436
Jan-15	0.09	1.874	3.436
Feb-15	0.064	1.249	1.978
Mar-15	0.064	0.937	2.603

The degas acid cation conductivity plant readings on the SUP sample point were used to calculate the conductivity contribution of organic acids by subtracting the conductivity contribution due to the inorganic anions (chloride and sulphate) and the conductivity due to the dissociation of water (K_w).

(iii) Calculated conductivities from IC results

It was stated in chapter 1 of this dissertation that the relationship between conductivity of ions in solution exists as follows:

$$\text{Measured plant degas cation conductivity } (K_m) = K_{25\text{Cl}/\text{SO}_4} + K_{\text{H}_2\text{O}} + K_? \dots \text{Equation 1.1}$$

Where $K_{25\text{Cl}/\text{SO}_4}^2$ is the conductivity contribution due to chloride and sulphate at 25°C

$K_{\text{H}_2\text{O}}$ is the conductivity contribution due to dissociation of water at 25 °C and

$K_?$ is the conductivity due to unknown specie (subject of the study)

$K_?$ was determined to be the organic acids (acetate, formate and lactate) by IC analysis.

The anion concentrations determined by IC were used to calculate the equivalent conductivities of the individual inorganic anions.

The measured DCC values and the equivalent conductivities of the inorganic anions were then used to calculate the organic acid conductivities.

The equation used was as follows;

$$\Lambda = 0.001K/c \quad \dots\dots\dots \text{Equation 4.1}$$

Where, Λ is the equivalent conductivity

K is the conductivity and

c is concentration of ion in the solution [4]

Units of Λ are mho-cm²/equivalent, K is $\mu\text{mho/cm}$ and c is measured in equivalent/litre (eq/L).

Re-arranging Equation 4.1 (to make the conductivity (K) subject of the formula),

$$K = \Lambda c / 0.001 \quad \dots\dots\dots \text{Equation 4.2}$$

It should however be noted that Λ is the equivalence conductance of a salt, and when in solution, dissociation occurs and individual ion contributes equivalent conductance (λ^\pm_0) in solution, i.e,

$$\Lambda = \lambda^0_+ + \lambda^0_- \quad \dots\dots\dots \text{Equation 4.2a}$$

Substituting equation 4.2a in equation 4.2, the result is

$$K = (\lambda^0_+ + \lambda^0_-)c / 0.001 \quad \dots\dots\dots \text{Equation 4.2b}$$

But since c is expressed in equivalent/L (N), therefore

$$K = \frac{(\lambda^0_+ + \lambda^0_-)N}{1000\text{cm}^3/\text{L}} 10^6 \mu\text{S/cm}$$

$$K = 1000(\lambda^0_+ + \lambda^0_-)N \quad \dots\dots\dots \text{Equation 4.2c}$$

Calculated individual conductivities from the inorganic anions were obtained from the IC results by using Equation 4.2c. For the SUP sample point was done (demonstration of the April 2014 chloride and sulphate results) was as follows;

$$K = [1000(\lambda^0_H + \lambda^0_{Cl})N]_{HCl} + [1000(\lambda^0_H + \lambda^0_{SO4})N]_{H2SO4}$$

$$K = [1000(350 + 76.4)1.874 \times 10^{-9} + 1000(350 + 80)2.603 \times 10^{-9}]$$

*NB, specific ionic conductivity table in Appendix E

$$K = (0.000799 + 0.00112) \mu S.cm^{-1}$$

$$K = 0.00192 \mu S.cm^{-1}$$

Values on table 4.3(h) where calculated by using equation 4.2c and the results are as follows:

Table 4.3(h): SUP chlorides and sulphates calculated conductivities

Date	Chloride Conductivity/ $(\mu S.cm^{-1})$	Sulphate Conductivity/ $(\mu S.cm^{-1})$	Chloride+ Sulphate $K_{25Cl/SO4}/(\mu S.cm^{-1})$
Apr-14	0.000799	0.00112	0.00192
May-14	0.000443	0.000805	0.00125
Jun-14	0.000355	0.000851	0.00121
Jul-14	0.000710	0.000940	0.00165
Aug-14	0.000754	0.00125	0.00201
Sep-14	0.000932	0.00121	0.00214
Oct-14	0.00102	0.000761	0.00178
Nov-14	0.000843	0.000940	0.00178
Dec-14	0.000532	0.00148	0.00201
Jan-15	0.000799	0.00148	0.00228
Feb-15	0.000532	0.000850	0.00138
Mar-15	0.000399	0.00112	0.00152

Conductivity due to water (K_{H2O}) calculated by using equation 4.2c is as follows [7]:

$$K_{H_2O} = [(1000 \lambda_{H^+}) \times (N_{H^+})] + [(1000 \lambda_{OH^-}) (N_{OH^-})]$$

$$K_{H_2O} = (1000 \mu S.cm^{-3}S^{-1} \times 350 Scm^2eq^{-1} \times 1.004 \times 10^{-7} eq/L) + (1000 \mu S.cm^{-3}S^{-1} \times 192 Scm^2eq^{-1} \times 1.004 \times 10^{-7} eq/L)$$

$$K_{H_2O} = 0.0351 \mu S.cm^{-1} + 0.0193 \mu S.cm^{-1}$$

$$K_{H_2O} = 0.055 \mu S.cm^{-1}$$

$$\text{Measured plant degas cation conductivity } (K_{25M}) = K_{25Cl/SO_4} + K_{H_2O} + K_{\text{organic acids}},$$

$$\text{Therefore, } K_{\text{organic acids}} = DCC - (K_{25Cl/SO_4} + K_{H_2O}) \dots \dots \dots \text{Equation 4.2d}$$

Example (Apr-14 calculation on table 4.3(i)):

$$K_{\text{organic acids}} = DCC - (K_{25Cl/SO_4} + K_{H_2O})$$

$$K_{\text{organic acids}} = 0.071 \mu S.cm^{-1} - (0.00192 + 0.055) \mu S.cm^{-1}$$

$$K_{\text{organic acids}} = 0.01408 \mu S.cm^{-1}$$

Table 4.3(i): Kriel SUP calculated anion conductivities

Date	DCC _{25M} /($\mu S.cm^{-1}$)	K _{25Cl/SO₄} /($\mu S.cm^{-1}$)	K _{H₂O} /($\mu S.cm^{-1}$)	K _{organic acids} /($\mu S.cm^{-1}$)
Apr-14	0.071	0.00192	0.055	0.01408
May-14	0.066	0.00125	0.055	0.00975
Jun-14	0.062	0.00121	0.055	0.00579
Jul-14	0.092	0.00165	0.055	0.03535
Aug-14	0.063	0.00201	0.055	0.00599
Sep-14	0.062	0.00214	0.055	0.00486
Oct-14	0.059	0.00178	0.055	0.00222
Nov-14	0.064	0.00178	0.055	0.00722
Dec-14	0.064	0.00201	0.055	0.00699
Jan-15	0.064	0.00228	0.055	0.00672
Feb-15	0.09	0.00138	0.055	0.03362
Mar-15	0.064	0.00152	0.055	0.00748

Figure 4.3(h) is a graphical representation of the ionic and plant measured cation conductivities of the species present in the SUP sample from Kriel. The y-axis (vertical) is the conductivity in $\mu\text{S}\cdot\text{cm}^{-1}$ whilst the x-axis is the month when the data was collected.

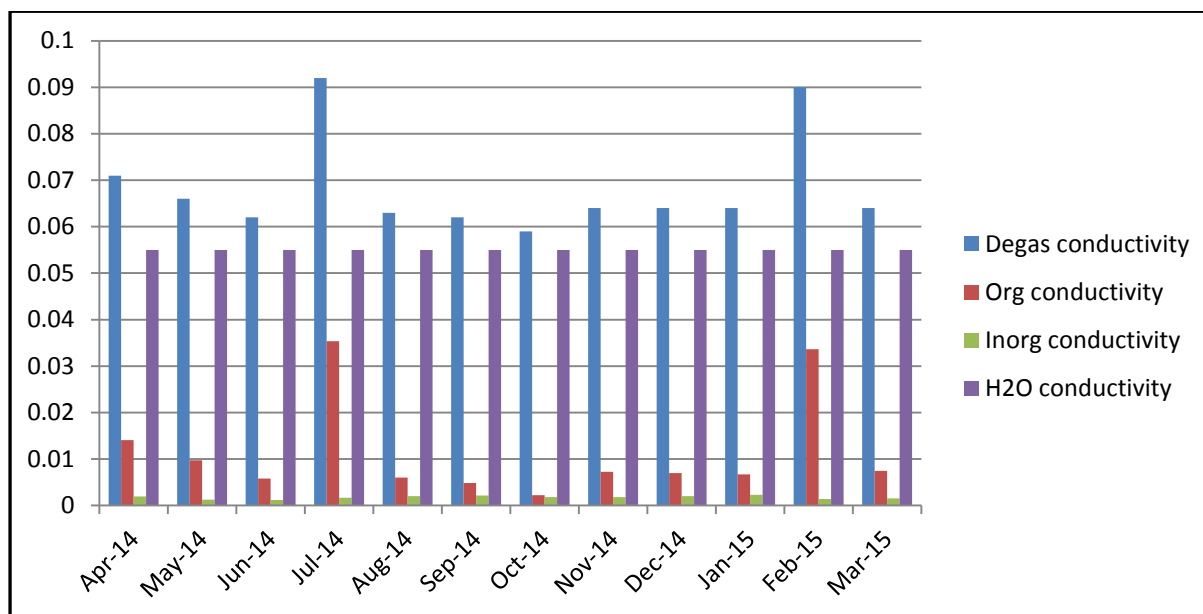


Figure 4.3(h): Kriel SUP conductivity graph

There is a clear indication as demonstrated in figure 4.3(g) that organic acids do have a significant impact on the degas cation conductivity, and it is predominant where the conductivity was above the Eskom specification of $0.08 \mu\text{S}/\text{cm}$ (July 2014 and February 2015).

Comparison of the organic acids determined by both the IC and LC-OCD is shown in Figure 4.3(i). It can clearly be observed that the LC-OCD organic acids results for both the CPP and SUP are greater than that of the IC.

Summary of Kriel SUP sample results

The DOC (obtained by using LC-OCD) results of the CPP outlet sample were compared with the organic acids of the SUP sample (Figure 4.3(i)). That was done in order to determine whether the breakdown of the organics (DOC from CPP) at high temperature and pressure will result in an increased concentration of organic acids of the SUP sample.

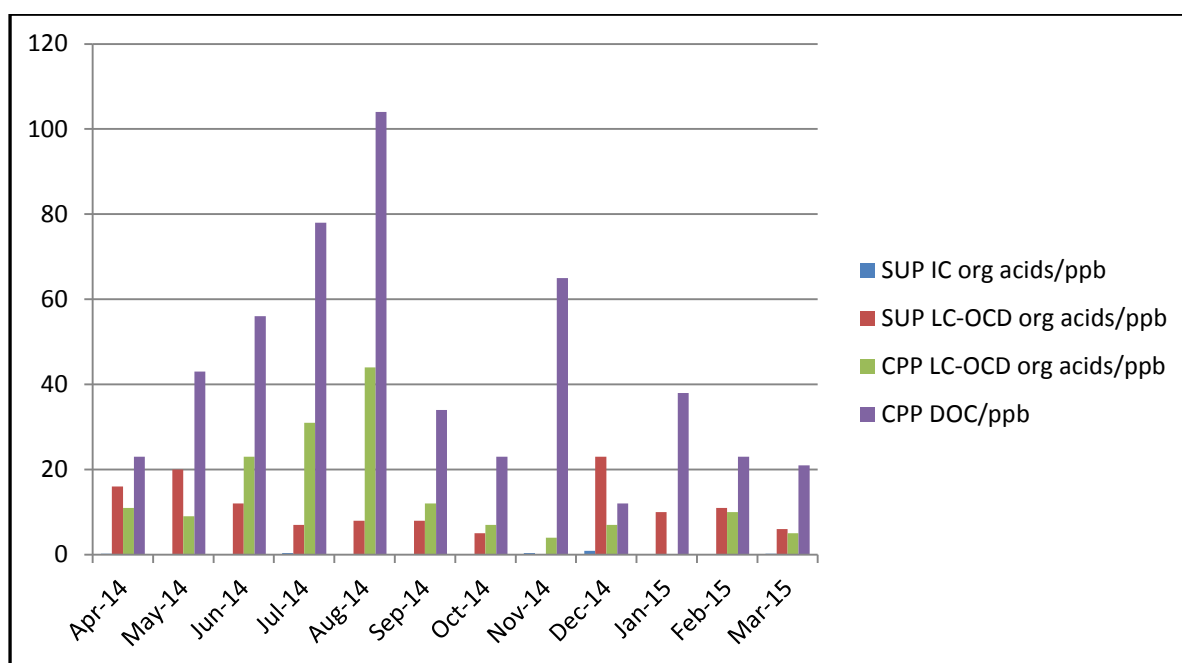


Figure 4.3(i): Comparison of organic acids results for LC-OCD v/s IC

The expectation/hypothesis was met as an observation of higher organic acids concentration of the SUP sample relative to the CPP DOC results.

4.4 ARNOT CONDENSATE-STEAM RESULTS

The same Metrohm IC instrument that was used for analysing Kriel sample was also used for analysing Arnot samples. Quality control and calibration results obtained in section 4.3.1 (i) and (ii), are also applicable to on this section since the anlysis were performed on the same days as those of Kriel power station.

4.4.1 Condensate, boiler and steam sample results

The IC results of the condensate extraction pump outlet sample points are tabulated in Table 4.4(a).

Table 4.4(a): Arnot CEP outlet results for organic, sulphate and chloride anions

Date	Chloride/ppb	Sulphate/ppb	Acetate/ppb	Formate/ppb	Lactate/ppb
Apr-14	0.096	0.26	0.18	0.26	0.26
May-14	0.262	0.291	0.17	0.25	0.1
Jun-14	0.076	0.282	0.15	0.303	0.065
Jul-14	0.089	0.403	0.08	0.26	0.01
Aug-14	0.197	0.342	0.16	0.34	nd
Sep-14	0.084	0.464	0.09	nd	1.29
Oct-14	0.098	0.342	0.11	0.23	0.09
Nov-14	0.08	0.432	0.09	0.103	0.03
Dec-14	0.083	0.459	0.1	0.11	0.28
Jan-15	0.088	0.508	0.13	0.201	0.23
Feb-15	0.092	0.394	0.09	0.093	0.3
Mar-15	0.083	0.235	0.1	0.104	0.11

The chloride and sulphate on the CEP sample point of Arnot were within Eskom's specification target. Organic acids as well were all below 1ppb at the time of sampling.

Table 4.4(b): Arnot CPP outlet results for organic, sulphate and chloride anions

Date	Chloride/ ppb	Sulphate/ ppb	Acetate/ ppb	Formate/ ppb	Lactate/ ppb
Apr-14	0.06	0.11	0.06	0.08	0.03
May-14	0.3	0.19	0.0713	0.09	0.11
Jun-14	0.18	0.25	0.15	0.21	0.019
Jul-14	0.07	0.36	0.03	0.12	0.07
Aug-14	0.11	0.21	0.06	0.19	0
Sep-14	0.13	0.23	0.07	0	0.23
Oct-14	0.05	0.27	0.18	0.1	0.12
Nov-14	0.14	0.33	0.06	0.03	0.09
Dec-14	0.2	0.18	0.032	0.08	0.09
Jan-15	0.07	0.14	0.0981	0.11	0.1
Feb-15	0.08	0.09	0.0101	0.04	0.18
Mar-15	0.14	0.17	0.0229	0.06	0.09

A reduction in anions from CEP outlet is expected at the outlet of a CPP vessel (a mixed bed exchange resin), and that is observed in figure 4.4(a).

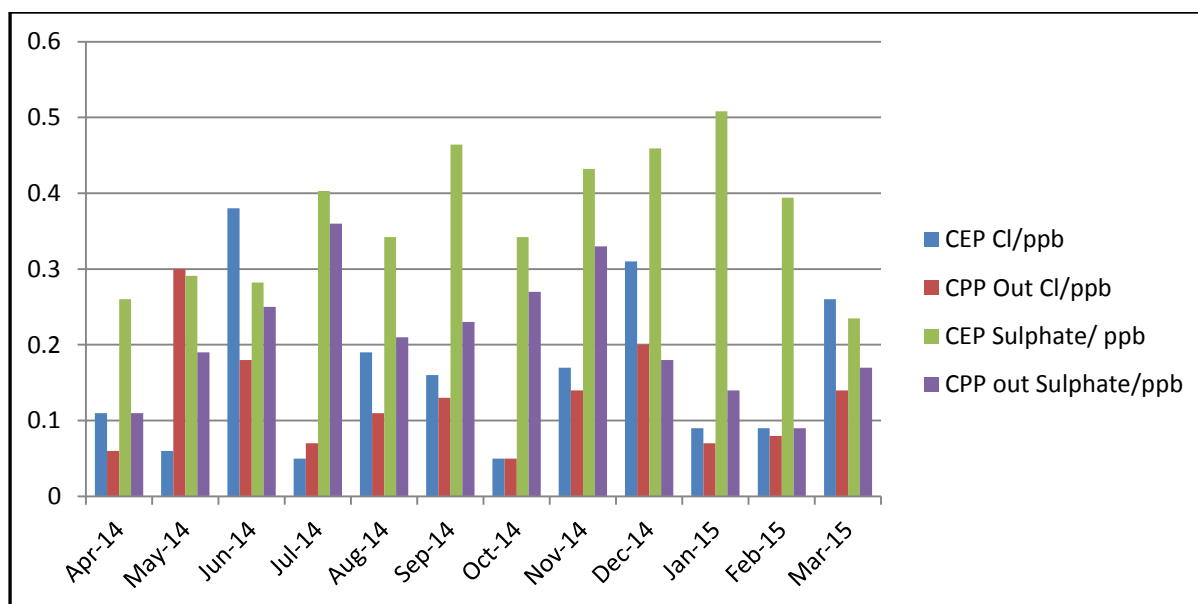


Figure 4.4(a): Graphical representation of condensate polishing by exchanger vessel

The results for the analysed anions at Arnot power station were within the target specifications level. Arnot power station has a drum boiler, and as observed in the

results, the chlorides and sulphates are higher at the boiler than in all other sample points (CEP, CPP and SUP). That was expected because the boiler drum is a 'vessel' where impurities concentrate and allow for removal by blowdowns processes.

Table 4.4(c): Arnot Boiler drum results for organic, sulphate and chloride anions

Date	Chloride /ppb	Sulphate /ppb	Acetate /ppb	Formate /ppb	Lactate /ppb
Apr-14	9.31	13.3	0.91	0.39	1.32
May-14	12.04	21.2	0.08	1.04	0.92
Jun-14	5.6	8.97	1.4	1	0.99
Jul-14	16.9	28.4	1	4.8	1.27
Aug-14	23	31.2	3.1	13.1	nd
Sep-14	28.98	133.93	nd	nd	0.38
Oct-14	7.04	18.9	0.18	10.3	3.25
Nov-14	8.79	14.2	1.18	8.9	0.1
Dec-14	3.92	10.6	2.34	1.9	0.7
Jan-15	13.7	12.1	4.22	0.99	0.23
Feb-15	28.59	5.93	1.57	0.14	0.19
Mar-15	21.08	14.9	0.99	0.11	0.11

Carryover of the inorganic anions into steam phase is not expected because of the design of the drum boiler, therefore inorganic acids are expected to be lower on the SUP sample. This is demonstrated in Table 4.4(d).

The dissolved organic acids have low boiling point, as a result, they are carried over into the SUP. Breakdown of the longer organic molecules occur and that results in shorter organic acid molecules and carbon dioxide being formed.

Table 4.4(d): Arnot SUP results for organic, sulphate and chloride anions

Date	Chloride /ppb	Sulphate /ppb	Acetates /ppb	Formates /ppb	Lactate /ppb
Apr-14	0.21	0.16	0.12	0.51	2.33
May-14	0.28	0.15	0.1	0.63	0.27
Jun-14	0.11	0.21	0.16	0.29	0
Jul-14	0.1	0.25	0.33	1.01	0.31
Aug-14	0.14	0.15	0.19	1.22	0
Sep-14	0.11	0.19	0.25	0	1.22
Oct-14	0.03	0.2	0.13	0.99	0.98
Nov-14	0.09	0.22	0.1	1.06	0
Dec-14	0.14	0.14	0.18	0.23	0.94
Jan-15	0.09	0.27	0.32	0.67	0.57
Feb-15	0.012	0.14	0.21	0.28	0.22
Mar-15	0.17	0.11	0.29	0.33	0.36

Figure 4.4(b) shows an expected trend of higher organic acids concentration on the SUP sample relative to the concentration on the CEP and CPP samples.

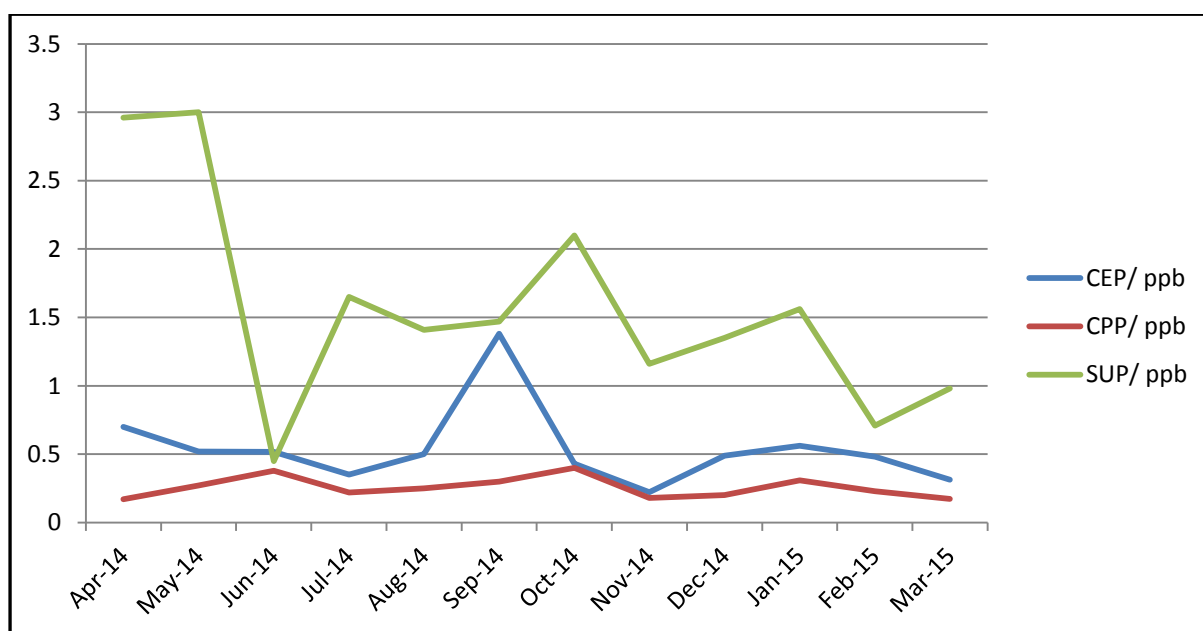


Figure 4.4(b): Arnot CEP, CPP and SUP total organic acids trends

The chloride and sulphate concentrations from table 4.4(d) were converted from ppb to neq/L in order to facilitate calculation of organic acid conductivities on table 4.4(e).

Table 4.4(e): Arnot SUP inorganic anions results for DCC and IC

Date	DCC/(μ S/cm)	Chloride	Sulphate
		Concentration/ neq/L	Concentration/ neq/L
Apr-14	0.068	2.187	1.666
May-14	0.077	2.915	1.562
Jun-14	0.071	1.145	2.187
Jul-14	0.063	1.041	2.603
Aug-14	0.059	1.458	1.562
Sep-14	0.065	1.145	1.978
Oct-14	0.072	0.312	2.082
Nov-14	0.06	0.937	2.291
Dec-14	0.081	1.458	1.458
Jan-15	0.074	0.937	2.811
Feb-15	0.079	0.125	1.458
Mar-15	0.062	1.770	1.145

Equation 4.2c was used to calculate conductivities due to concentrations of inorganic anions and the results were tabulated in table 4.4(f).

Table 4.4(f): Arnot SUP chlorides and sulphate calculated conductivities

Date	Chloride Conductivity/($\mu\text{S.cm}^{-1}$)	Sulphate Conductivity/($\mu\text{S.cm}^{-1}$)	Chloride+ Sulphate $K_{25\text{Cl}/\text{SO}_4}/(\mu\text{S.cm}^{-1})$
Apr-14	0.000932	0.000716	0.00165
May-14	0.00124	0.000672	0.00191
Jun-14	0.000488	0.000940	0.00143
Jul-14	0.000443	0.00112	0.00156
Aug-14	0.000621	0.00067	0.00129
Sep-14	0.000488	0.000850	0.00134
Oct-14	0.000133	0.000895	0.00103
Nov-14	0.000399	0.000985	0.00138
Dec-14	0.000621	0.000626	0.00125
Jan-15	0.000399	0.00121	0.00161
Feb-15	0.000053	0.00626	0.000680
Mar-15	0.000754	0.000492	0.00125

The values in table 4.4(f) were used to calculate for the organic acids conductivities that appear on table 4.4(g).

Table 4.4(g): Arnot SUP calculated anion conductivities

Date	$K_{25\text{M}}/(\mu\text{S.cm}^{-1})$	$K_{25\text{Cl}/\text{SO}_4}/(\mu\text{S.cm}^{-1})$	$K_{\text{H}_2\text{O}}/(\mu\text{S.cm}^{-1})$	$K_{\text{org acids}}/(\mu\text{S.cm}^{-1})$
Apr-14	0.068	0.00165	0.055	0.01135
May-14	0.077	0.00191	0.055	0.02009
Jun-14	0.071	0.00143	0.055	0.01457
Jul-14	0.063	0.00156	0.055	0.00644
Aug-14	0.059	0.00129	0.055	0.00271
Sep-14	0.065	0.00134	0.055	0.00866
Oct-14	0.072	0.00103	0.055	0.01597
Nov-14	0.06	0.00138	0.055	0.00362
Dec-14	0.081	0.00125	0.055	0.02475
Jan-15	0.074	0.00161	0.055	0.01739
Feb-15	0.079	0.000680	0.055	0.02332
Mar-15	0.062	0.00125	0.055	0.00575

Figure 4.4(b) graphically represents the ionic (both inorganic and organic) conductivities contribution on the total degas cation conductivity of Arnot SUP steam.

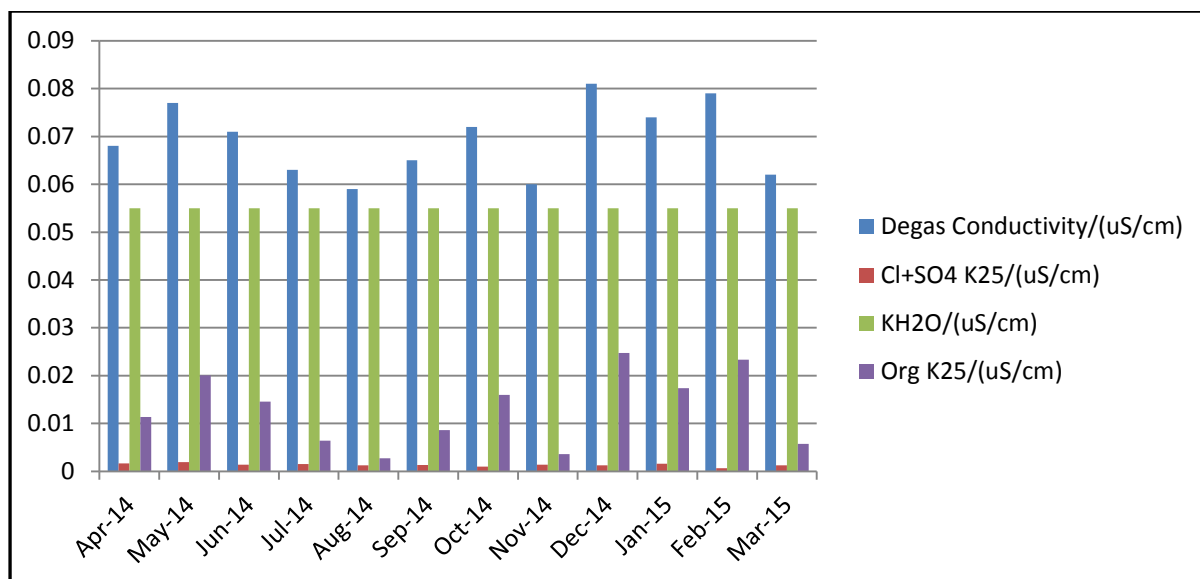


Figure 4.4(c): Arnot SUP conductivity graph

The impact of organic acids conductivities on the degas cation conductivities relative to the inorganic acids is clearly observed to be high, as not noted in the figure 4.4(c).

Summary of Arnot SUP sample results

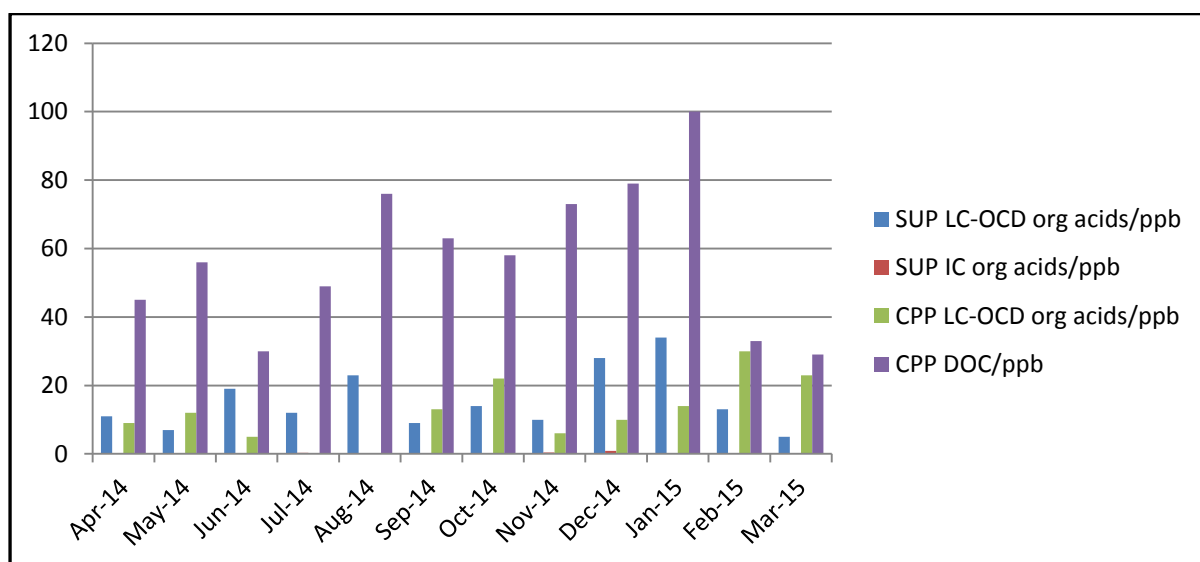


Figure 4.4(d): Comparison of organic acids results for LC-OCD v/s IC

The organic acid conductivities for the month of May 2014, Dec 2014 and Feb 2014 were found to be 0.020 $\mu\text{S}/\text{cm}$, 0.025 $\mu\text{S}/\text{cm}$ and 0.023 $\mu\text{S}/\text{cm}$ respectively (figure 4.4(c)), whereas the DOC on the CPP sample for the same months, was found to be 56 ppb, 79 ppb and 33 ppb. From this information, it shows that assumptions cannot be made that the high DOC concentration on the CPP (feed-condensate water) result in high organic acids concentrations of the SUP sample.

The conductivities (due to organic acids) were less than 0.02 $\mu\text{S}/\text{cm}$ for the other 9 months, and the related DOC concentrations of the CPP sample was ranging from 29 ppb (Mar 2015) to 100 ppb (Feb 2015) as extracted from figure 4.4(d).

Comparison of results between the DOC concentrations of the CPP (when taking into consideration that it, CPP, is the source of the make-up water, after 'polishing') and the SUP organic acids concentration cannot be clearly defined from the data on figures 4.4(c) and 4.4(d).

REFERENCES

1. Sievers Datapro Operating and Maintenance Manual, version 1.40, 2009
2. Eskom Analytical Chemistry Laboratory Method Validation Guideline, 240-55864789, Rev 01 2015
3. LC-OCD-OND Manual Model 8, version 2012-08-27
4. Determination of Total Organic carbon in liquid samples by TOC combustion analyser, Eskom Method Number 414 Rev 03, 2012
5. Metrohm Professional IC operating method, 2013
6. Swan Ami degas conductivity operating manual, 2010
7. H. Wagner, Influence of temperature on electrical conductivity of diluted aqueous solution, Power Plant Chemistry 2012, 455-469, Switzerland
8. Eskom chemistry standard for once through boilers operating at 17 MPa, 240-55864792, 2014

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 USUTU WATER SYSTEM

The organic profile of the Usutu system changes seasonally, with higher concentrations experienced in rainy seasons. That is expected because of the farming activities during that time of the year and river beds run-offs.

Processes at the station (water treatment) are expected to be able to deal with such changes due to the optimisation program that is in place. It was seen that the mixed bed outlet water quality was in most cases kept below the Eskom's specific target value of less than 250ppb (TOC).

The organic acids that were found in the main steam at Kriel power station were, acetate, formate and lactate. Their concentrations varied significantly throughout the time of the experiment. The concentrations could not be clearly linked with the concentration of the CPP-outlet sample DOC (when taking into consideration that the CPP outlet is the feed water into the cycle).

The impact of the organic acids on the acid cation conductivity was high relative to the conductivity due to inorganic anions (chloride and sulphate), but in most cases, the concentration was below 1ppb. Therefore an assumption can be made that as long as the DOC is below 250ppb, then the concentration of organic acids will be less than 1 ppb (Table 4.3(e) demonstrated that).

5.2 KOMATI WATER SYSTEM

The organic profile for Arnot power station (Komati water system) has shown that if only one dam is used (Nooitgedacht), the quality of water is affected, i.e, high DOC values are experienced. Whereas, when a blend is used, the quality improves. The

average SUVA value during the test period was determined to be 3.99, which simply indicates that the water is made up of aromatic compounds that are relatively easy to remove from water with pre-treatment processes (coagulation-flocculation and sand-filtration). An average of 53.6% organic removal was achieved for the test period.

The average DOC concentration at the mixed bed outlet was found to be 92 ppb, however the average organic acid concentrations was 1.56 ppb. The organic acid concentration was higher at Arnot relative to the results at Kriel, even though the average mixed bed DOC was higher at Kriel.

Specifications cannot be set from the results obtained in this experiment. Further experimental work needs to be done to investigate the presence of other organic acids that might be present in the steam samples. The IC column that was used was mainly developed for the food industry, not taking into consideration other parameters that can be present in the steam, for example resin fragments, oil sealants and other sources of contaminants that are possible in the power station cycle water.

Further-more it was observed that as long as the DOC concentration is lower than the Eskom target specifications of 250 ppb, then the organic acids impact does not affect the DCC values to a large extend (as observed in figure 4.4(c)).

APPENDIX A

Sievers TOC analyser

DataPro900 Results

SIEVERS®

Result File:	C:\GEA\NDataPro900A\DataGuard900\Result\2015FEB18CALIBRATION.rst
Protocol File:	C:\Program Files\Sievers\DataPro900A\DataGuard900\Protocol\Single_Point_Calibration
Analyst:	MOKGOSI MAKENA
Protocol Run On:	09:05:07 AM 18-Feb-2015 CAT
Serial Number:	4011
Firmware Version:	02.14
DataPro900 Version:	01.40

Group:	Calibration Blank	Acid Rate (µ L/min):	1.0
Group Type:	Blank	Oxid Rate (µ L/min):	0.0
Number Rejects:	7	ICR:	Off
Start Date:	18-Feb-2015	Skip:	No
Lot Number:			

Vial	Rep		TOC	IC	TC	Acid	Oxid
1	1	09:17:41 AM	31.4 ppb	168 ppb	199 ppb	1.0 µ L/min	0.0 µ L/min
	2	09:21:44 AM	29.0 ppb	172 ppb	201 ppb	1.0 µ L/min	0.0 µ L/min
	3	09:25:42 AM	26.4 ppb	172 ppb	198 ppb	1.0 µ L/min	0.0 µ L/min
	4	09:29:45 AM	25.1 ppb	171 ppb	196 ppb	1.0 µ L/min	0.0 µ L/min
	5	09:33:42 AM	21.5 ppb	175 ppb	196 ppb	1.0 µ L/min	0.0 µ L/min
	6	09:37:45 AM	20.3 ppb	172 ppb	192 ppb	1.0 µ L/min	0.0 µ L/min
	7	09:41:43 AM	19.1 ppb	176 ppb	195 ppb	1.0 µ L/min	0.0 µ L/min
	8	09:45:46 AM	18.0 ppb	186 ppb	204 ppb	1.0 µ L/min	0.0 µ L/min
	9	09:49:43 AM	16.0 ppb	198 ppb	214 ppb	1.0 µ L/min	0.0 µ L/min
	10	09:53:46 AM	14.8 ppb	208 ppb	223 ppb	1.0 µ L/min	0.0 µ L/min
Average:			16.3 ppb	197 ppb	214 ppb		
S.D.:			1.62 ppb	11.0 ppb	9.50 ppb		
R.S.D.:			9.94 %	5.58 %	4.45 %		

Group:	25 ppm TOC Calibration Std	Acid Rate (µ L/min):	1.0
Group Type:	Sample	Oxid Rate (µ L/min):	3.4
Number Rejects:	1	ICR:	Off
Start Date:	18-Feb-2015	Skip:	No
Lot Number:			

Data Summary							
Vial	Rep		TOC	IC	TC	Acid	Oxid
2	1	10:06:17 AM	26.9 ppm	102 ppb	27.0 ppm	1.0 µ L/min	3.4 µ L/min
	2	10:10:15 AM	26.9 ppm	106 ppb	27.0 ppm	1.0 µ L/min	3.4 µ L/min
	3	10:14:17 AM	27.0 ppm	107 ppb	27.1 ppm	1.0 µ L/min	3.4 µ L/min
	4	10:18:15 AM	27.0 ppm	107 ppb	27.1 ppm	1.0 µ L/min	3.4 µ L/min
	Average:		27.0 ppm	107 ppb	27.1 ppm		
	S.D.:		57.7 ppb	0.58 ppb	57.7 ppb		
	R.S.D.:		0.21 %	0.54 %	0.21 %		

Group:	25 ppm IC Calibration Std	Acid Rate (µ L/min):	1.0
Group Type:	Sample	Oxid Rate (µ L/min):	0.0
Number Rejects:	1	ICR:	Off
Start Date:	18-Feb-2015	Skip:	No
Lot Number:			

Vial	Rep		TOC	IC	TC	Acid	Oxid
------	-----	--	-----	----	----	------	------

Serial Number: 4011

Location : ESKOM

File: C:\GEA\NDataPro900A\DataGuard900\Result\2015FEB18CALIBRATION.rst

Printed on: 10:43:10 AM 18-Feb-2015 CAT

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DataPro900 Results

SIEVERS®

Group:		25 ppm IC Calibration Std			Acid Rate (µ L/min): 1.0		
Group Type:		Sample			Oxid Rate (µ L/min): 0.0		
Number Rejects:		1			ICR: Off		
Start Date:		18-Feb-2015			Skip: No		
Lot Number:							
Vial	Rep		TOC	IC	TC	Acid	Oxid
3	1	10:30:46 AM	1.67 ppm	25.7 ppm	27.4 ppm	1.0 µ L/min	0.0 µ L/min
	2	10:34:43 AM	1.63 ppm	25.8 ppm	27.4 ppm	1.0 µ L/min	0.0 µ L/min
	3	10:38:46 AM	1.61 ppm	25.8 ppm	27.4 ppm	1.0 µ L/min	0.0 µ L/min
	4	10:42:44 AM	1.58 ppm	25.8 ppm	27.4 ppm	1.0 µ L/min	0.0 µ L/min
	Average:		1.61 ppm	25.8 ppm	27.4 ppm		
		S.D.:	25.2 ppb	0.00 ppb	0.00 ppb		
		R.S.D.:	1.57 %	0.00 %	0.00 %		

Signature: 
Reason: _____
Comment: _____

ID: MOKEOSI (8mm)
Date: 18/02/2015

Signature: _____
Reason: _____
Comment: _____

ID: _____
Date: _____

Serial Number: 4011

Location : ESKOM

File: C:\GEA\NDataPro900A\NDataGuard900\Result\2015FEB18CALIBRATION.rst

Printed on: 10:43:10 AM 18-Feb-2015 CAT

Page 2 of 3

DataPro900 Results

SIEVERS®

TC Calibration				
	Expected	Measured	% Diff	Adjusted
Calibration Blank	N/A	214 ppb	N/A	199 ppb
25 ppm	25.1ppm	27.1 ppm	7.97 %	25.1ppm

IC Calibration				
	Expected	Measured	% Diff	Adjusted
25 ppm	25.4ppm	25.8 ppm	1.57 %	25.4ppm

Calibration Passed

Serial Number: 4011
Location : ESKOM
File: C:\GEA\DataPro900A\DataGuard900\Result\2015FEB18CALIBRATION.rst
Printed on: 10:43:10 AM 18-Feb-2015 CAT

Page 3 of 3

Figure A1.1: Sievers calibration certificate

APPENDIX B

LC-OCD analyser

Manual Software LC-OCD
Version 2011-11-28



DOC-Labor Dr. Huber
www.doc-labor.de

3.12 Calibration of System: Print out of Application Note:

Print Application Note: Calibration of System

Preparation of calibration solutions and procedure of calibration is specified in an application note. To print the application note click on the button above.

Calibration of Molecular Masses of Humics and Detector Sensitivities

- 2 measurements for Molecular Masses (vial 1 and 2)
- 5 measurements for Detector Sensitivities (vial 3-7).

Total calibration takes 14 hrs and can be carried out over night. We recommend to calibrate for Molecular Masses. The recommended time interval is every 6 month or once a year.

A) Molecular Masses Calibration of Humics:

Prenotes:

- Allow HS-solutions to ripen for at least 3 days (HS must expand fully).
- HS-solutions are not biodegradable and are stable for at least 1 year.

- Dissolve approx. 4 mg of IHSS HA* and IHSS FA** in 100 mL of lab water respectively.
- Place 1 mL of each solution in a sample vial and add 9 mL of labwater (vial 1=HA; vial 2=FA).
- Place vials on tray and measure together with vials for Detector Sensitivities (see B below).
- Process data following instructions in ChromCALC.

Chromatographic conditions:

Flow rate: 1.1 mL/min
Injection volume: 1000 µL
Analysis time: 130 min each

*: Suwannee River Humic Acid Standard II, Catalog # 25101H
**: Suwannee River Fulvic Acid Standard II, Catalog # 25101F

B) Calibration of Detector Sensitivities (OCD - UVD - OND):

Prenotes:

- Be aware that PHP is biodegradable! Even stock solution 1 should be prepared freshly.
- It is difficult to weight-in masses in milligrams precisely. Therefore approximate masses are sufficient and will be corrected later by an algorithm.

- Dissolve approximately 213 mg potassium hydrogenphthalate (PHP) and 100 mg potassium nitrate (KNO₃) in 100 mL mobile phase (use a volumetric flask). This STOCK SOLUTION 1 has a concentration of around 1000 mg/L PHP-C and of 139 mg/L KNO₃-N. Annotate the precise weighted-in masses for PHP and KNO₃ for correction.

- Transfer 1 mL of STOCK SOLUTION 1 into a second 100 mL volumetric flask. Fill up flask with mobile phase. This STOCK SOLUTION 2 has a concentration of around 10 mg/L PHP-C and of 1.39 mg/L KNO₃-N. Organic impurities in mobile phase will have no influence on results.

- Transfer aliquots of STOCK SOLUTION 2 in vials according to the table below.

- Analyse vials 1 and 2 (see A above) followed with these 5 calibration solutions (vials 3-7) by consecutive runs with increasing analyte concentrations (increasing vial number).

Chromatographic conditions:

Flow rate: 1.1 mL/min
Injection volume: 1000 µL
Analysis time: 110 min each

- Calculate the conversion factors with ChromCALC. (see also software manual chapter: Calibration of Detectors (OCD-UVD-OND)).

Note: For a quick check of calibration factors you may inject "Vial 5" only. Calculate the results with "manual integration" (ChromCALC) and compare with target values. Should deviation be more than 5 % perform a full calibration.

Vial number	Volume of STOCK SOLUTION 2 in mL	Added Volume of mobile phase in mL	Approx. concentration of PHP-C in mg/L	Approx. concentration of KNO ₃ -N in µg/L
Vial 3	0.1	9.9	0.1	13.9
Vial 4	1	9	1	139
Vial 5	2.5	7.5	2.5	348
Vial 6	3.75	6.25	3.75	521
Vial 7	5	5	5	695

NOTE: If you use two columns in series please use 170 min analysis time

3.13 Calibration of Molar Masses

Calibration of System

After measurement of calibration solutions according to AN1 start calibration routine by clicking the button above.

As columns are not absolutely identical, retention times will differ slightly. Therefore it is necessary to create a set of default files for each column. These files are used by ChromCALC for:

1. calculating the HS (Biopolymer) peak.
2. Integration of the fractions.
3. HS calibration factors for molecular masses.

Each column gets a distinctive number with 3 digits (column A: **501**; column B: **502**; "50" stands for resin type HW50S, "1" stands for column 1 and "2" for column 2. A new column should get "503"). A further digit will be added after calibration, indicating the calibration number of this column (e.g. **5097** means: column #9 of HW50S type, calibration #7).

Columns were calibrated before delivery of system. The numbers are: **5010** and **5020** (if two columns were ordered). At site the columns will be re-calibrated and numbers will be **5011** and **5021**.

On the following screen insert the file # for IHSS HA and IHSS FA chroms and the column # in 3 digits. The calibration # will be added automatically. Now click on the yellow button: "continue calib. routine".

Calibration of Molar Masses (MM) of Humic Substances

Insert data and continue with yellow button

IHSS HA File # 00 (Vial 1)

IHSS FA File # 00 (Vial 2)

Column # 00

3 digits (calibration # will be added automatically)

continue calib. routine

back to main screen

Figure B 1.1: LC-OCD calibration procedure

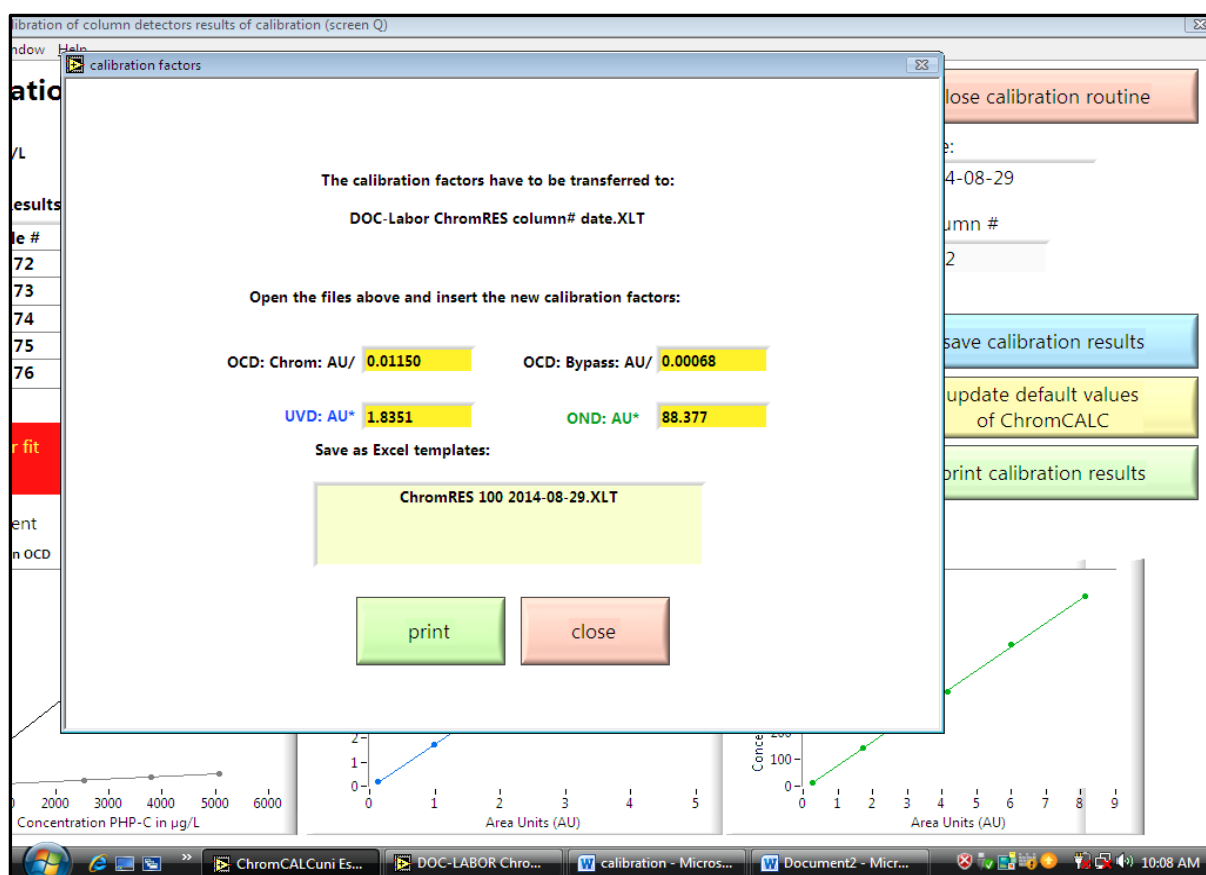


Figure B 1.2: Calibration factor results (August 2014)

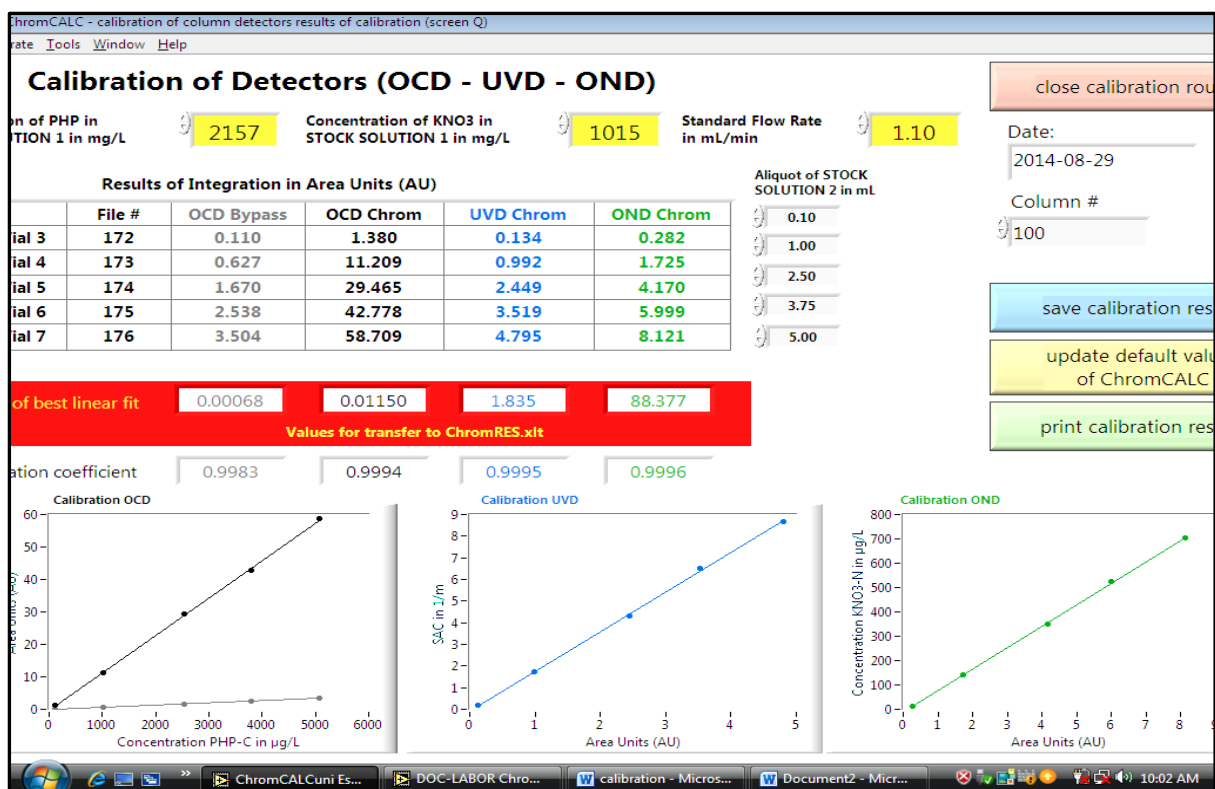



Figure B 1.3: LC-OCD 3 detectors calibration results (August 2014)

			DOC		HOC*		CDOC		Approx. Molecular Weights in g/mol:										300-500			<350		<350		Inorg. Colloid. SAC (m ⁻¹)		SUVA L/(mg*DOC)	
			>>20,000		~1000 (see separate HS-Diagram)		300-500		<350		<350																		
Project:	0	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC	BIO-polymers				Humic Subst. (HS)				Aromaticity (SUVA-HS)		Mol-Weight (Mn)		Position in HS diagram		Building Blocks		LMW Neutrals		LMW Acids						
					ppb-C % DOC	ppb-N	µg/l	% Proteins in BIOPol.*	ppb-C % DOC	ppb-N	µg/l	L/(mg*nm)	g/mol	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC													
UNIT 1 MB		194	n.q.	194	47	38	0.82	100	96	47	0.49	1.94	281	A	21	30	nq	0.03	2.51										
		100%	--	100.0%	24.2%	--	--	--	49.5%	--	--	--	--	--	10.8%	15.5%	#####	--	--										
Raw Kriel		1149	309	840	20	n.q.	--	--	544	n.q.	--	2.78	263	B	119	151	6	0.02	2.73										
		100%	26.9%	73.1%	1.7%	--	--	--	47.4%	--	--	--	--	--	10.4%	13.2%	0.5%	--	--										
Unit 1 CPP Out		23	nq	23	4	n.q.	--	--	n.q.	n.q.	--	--	#VALUE!	--	14	17	7	0.02	17.33										
		100%	#VALUE!	100.0%	19.5%	--	--	--	--	--	--	--	--	--	60.9%	75.4%	30.4%	--	--										
Unit 1 SUP		6	n.q.	6	3	n.q.	--	--	2	n.q.	--	0.18	353	D	21	91	5	0.01	5.35										
		100%	--	100.0%	43.1%	--	--	--	28.3%	--	--	--	--	--	344.3%	#####	83.3%	--	--										
Kriel Filtered		379	56	323	n.q.	n.q.	--	--	193	n.q.	--	18.00	0	E	6	45	2	n.q.	#DIV/0!										
		100%	14.8%	85.2%	--	--	--	--	50.9%	--	--	--	--	--	1.6%	11.9%	0.5%	--	--										
Kriel anion		165	56	123	6	n.q.	--	--	145	n.q.	--	40.00	0	F	6	45	#####	n.q.	#DIV/0!										
		100%	33.9%	74.5%	3.6%	--	--	--	87.9%	--	--	--	--	--	3.6%	27.3%	#DIV/0!	--	--										
standard deviation		319	140	251	16	38	0.82	100	196	47	0	12.58	#VALUE!	--	31	63	#####	0.02	#DIV/0!										
		428	146	311	19	#####	#####	#DIV/0!	207	#####	#####	16.91	#VALUE!	--	44	50	#DIV/0!	0.01	#DIV/0!										
in ppb		449	153	326	20	#####	#####	#DIV/0!	217	#####	#####	17.75	#VALUE!	--	46	52	#DIV/0!	0.01	#DIV/0!										
in %		140.7	109.2	129.8	122.3	#####	#####	#DIV/0!	110.9	#####	#####	141.1	#VALUE!	--	147.1	82.5	#DIV/0!	60.4	#DIV/0!										

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

***: pale green: cross sensitivity inferred

Figure B 1.4: Kriel LC-OCD sample results (October 2014)

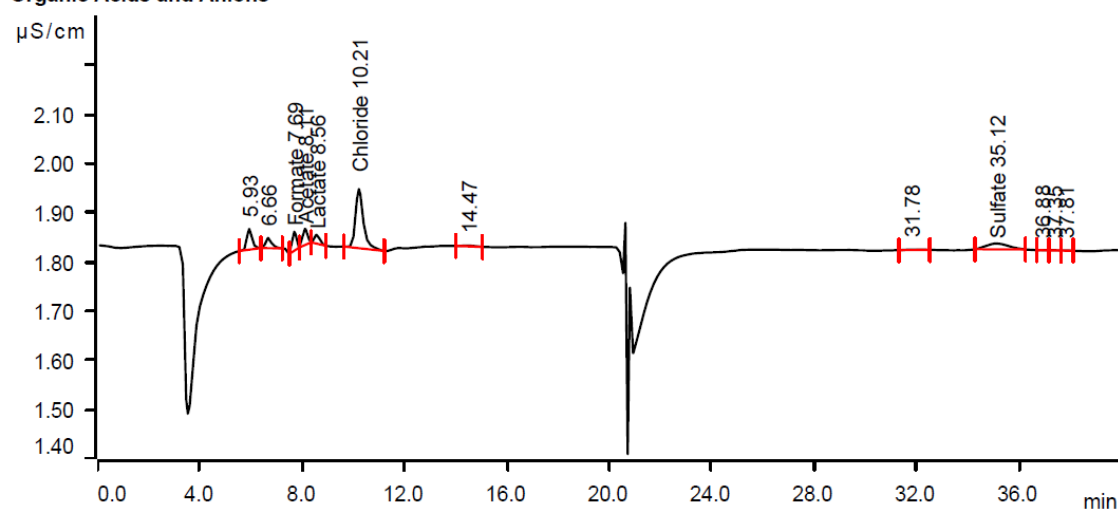
APPENDIX C

Metrohm 850 profesional IC



2014-09-25 10:24:31

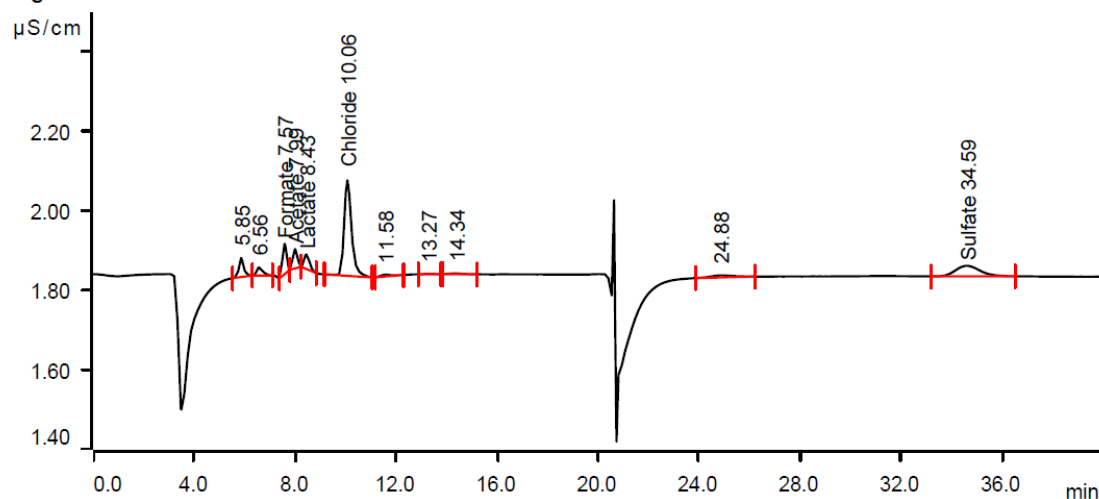
Organic Acids and Anions



Peak number	Retention time min	Area ($\mu\text{S}/\text{cm}$) x min	Height $\mu\text{S}/\text{cm}$	Concentration $\mu\text{g}/\text{L}$	Component name
1	5.930	0.0097	0.042	invalid	
2	6.658	0.0058	0.021	invalid	
3	7.688	0.0073	0.039	0.500	Formate
4	8.108	0.0075	0.033	0.500	Acetate
5	8.558	0.0045	0.018	0.500	Lactate
6	10.212	0.0428	0.120	0.500	Chloride
7	14.468	0.0009	0.002	invalid	
8	31.782	0.0007	0.001	invalid	
9	35.118	0.0121	0.012	0.500	Sulfate
10	36.883	0.0001	0.000	invalid	
11	37.352	0.0002	0.001	invalid	
12	37.808	0.0002	0.001	invalid	

Figure C 1.1: Ion chromatography 0.500 ppb mixed calibration standard (September 2014)

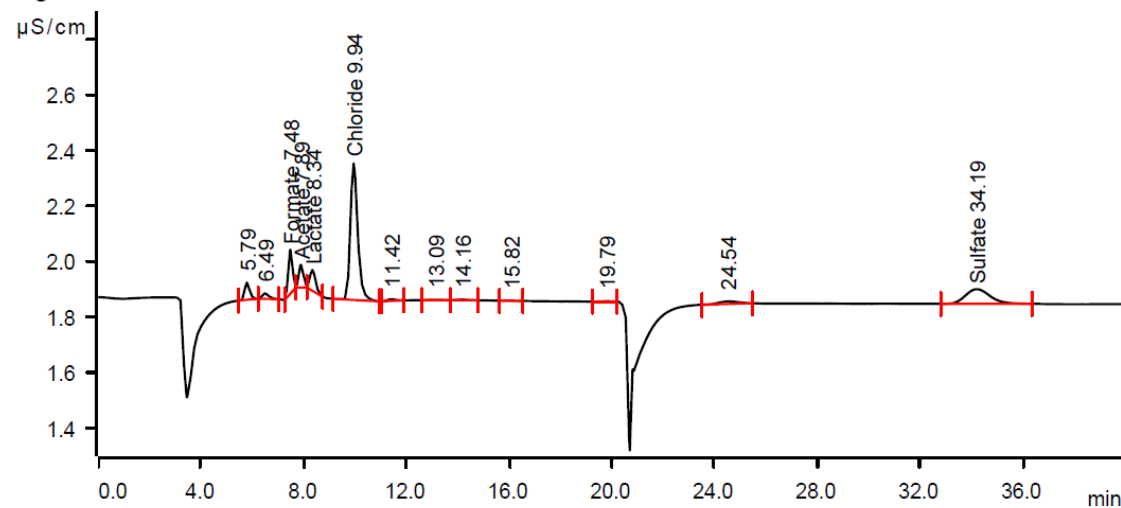
Organic Acids and Anions



Peak number	Retention time min	Area ($\mu\text{S/cm}$) x min	Height $\mu\text{S/cm}$	Concentration $\mu\text{g/L}$	Component name
1	5.852	0.0107	0.048	invalid	
2	6.562	0.0057	0.020	invalid	
3	7.572	0.0149	0.077	0.999	Formate
4	7.987	0.0107	0.049	0.988	Acetate
5	8.433	0.0093	0.037	1.012	Lactate
6	10.063	0.0815	0.241	1.017	Chloride
7	11.580	0.0021	0.004	invalid	
8	13.273	0.0004	0.001	invalid	
9	14.340	0.0010	0.002	invalid	
10	24.878	0.0054	0.005	invalid	
11	34.588	0.0301	0.027	1.063	Sulfate

Figure C 1. 2: Ion chromatography 1.000 ppb mixed calibration standard (September 2014)

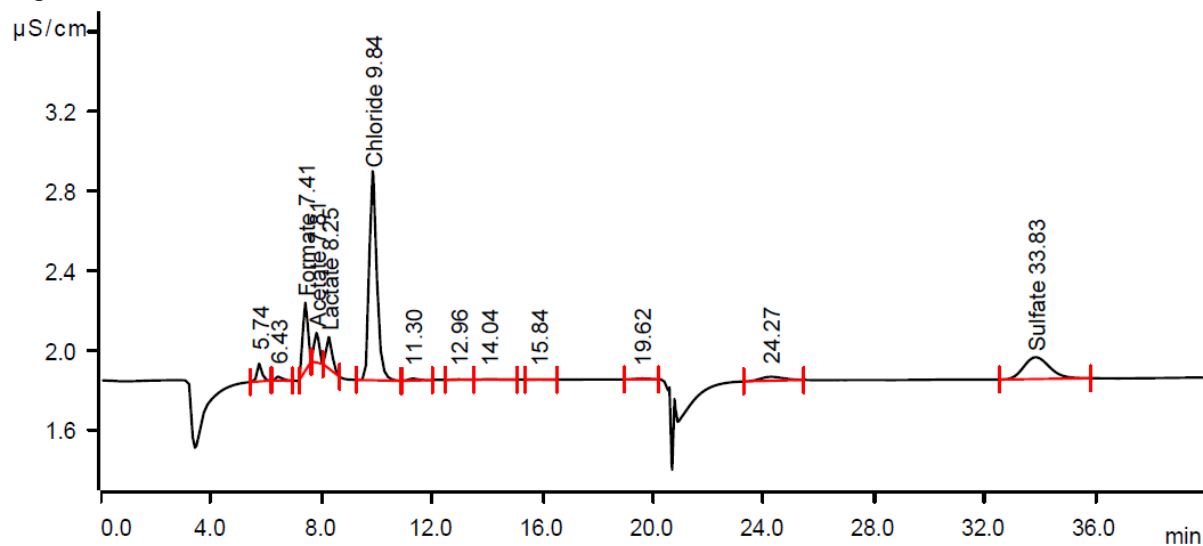
Organic Acids and Anions



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration µg/L	Component name
1	5.788	0.0136	0.062	invalid	
2	6.485	0.0057	0.020	invalid	
3	7.482	0.0318	0.158	1.943	Formate
4	7.890	0.0176	0.082	1.986	Acetate
5	8.335	0.0189	0.075	1.972	Lactate
6	9.943	0.1615	0.492	1.963	Chloride
7	11.420	0.0024	0.006	invalid	
8	13.088	0.0006	0.001	invalid	
9	14.162	0.0011	0.002	invalid	
10	15.822	0.0003	0.001	invalid	
11	19.793	0.0008	0.001	invalid	
12	24.538	0.0083	0.009	invalid	
13	34.193	0.0590	0.053	2.020	Sulfate

Figure C 1.3: Ion chromatography 2.000 ppb mixed calibration standard (September 2014)

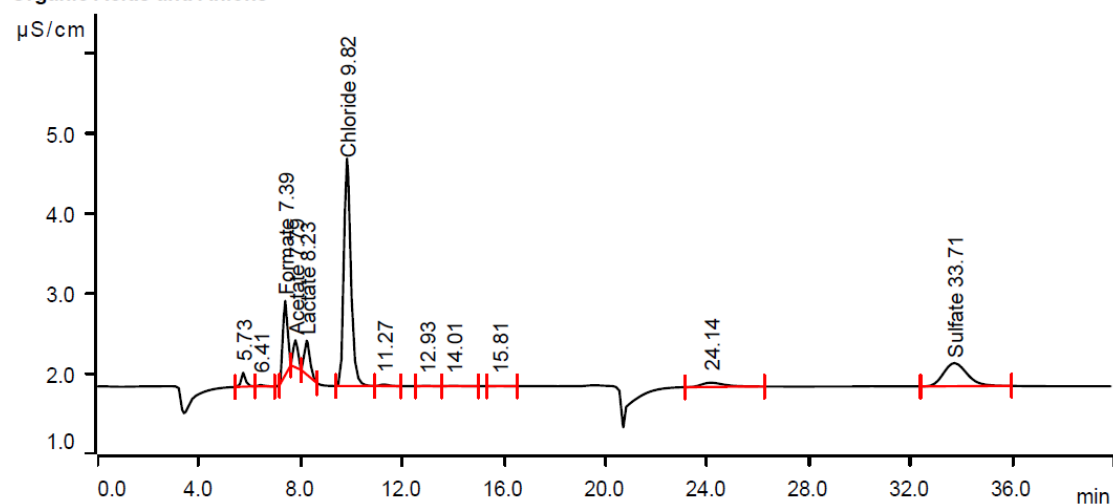
Organic Acids and Anions



Peak number	Retention time min	Area ($\mu\text{S}/\text{cm}$) x min	Height $\mu\text{S}/\text{cm}$	Concentration $\mu\text{g}/\text{L}$	Component name
1	5.740	0.0189	0.090	invalid	
2	6.425	0.0056	0.020	invalid	
3	7.407	0.0688	0.342	3.944	Formate
4	7.812	0.0312	0.149	3.992	Acetate
5	8.253	0.0396	0.157	3.960	Lactate
6	9.843	0.3327	1.050	3.918	Chloride
7	11.303	0.0041	0.010	invalid	
8	12.962	0.0009	0.002	invalid	
9	14.035	0.0017	0.003	invalid	
10	15.840	0.0006	0.001	invalid	
11	19.615	0.0026	0.004	invalid	
12	24.265	0.0192	0.020	invalid	
13	33.828	0.1194	0.110	3.954	Sulfate

Figure C 1.4: Ion chromatography 4.000 ppb mixed calibration standard (September 2014)

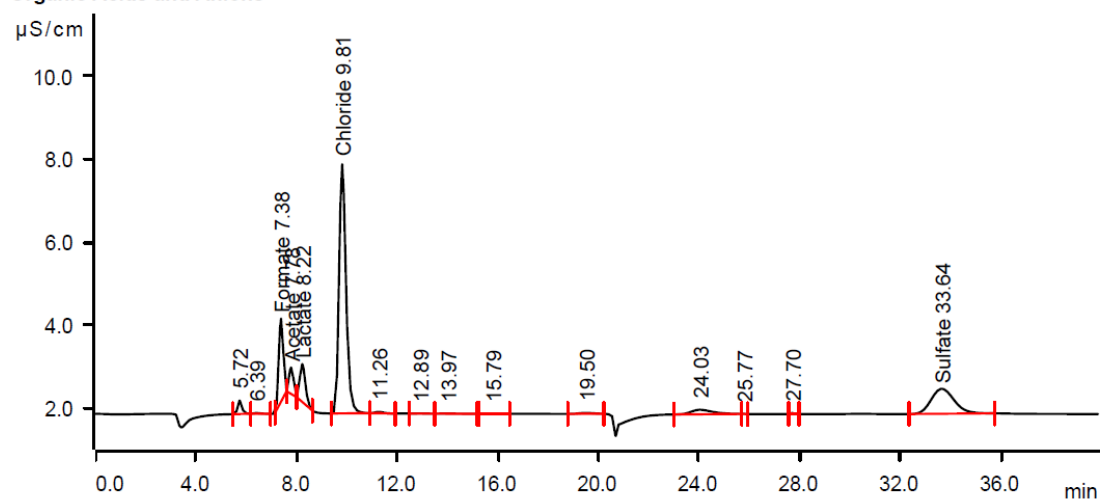
Organic Acids and Anions



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration µg/L	Component name
1	5.732	0.0360	0.175	invalid	
2	6.413	0.0048	0.017	invalid	
3	7.390	0.1879	0.928	10.000	Formate
4	7.792	0.0704	0.341	10.000	Acetate
5	8.233	0.1063	0.424	10.000	Lactate
6	9.818	0.8937	2.849	10.000	Chloride
7	11.268	0.0080	0.020	invalid	
8	12.925	0.0016	0.004	invalid	
9	14.005	0.0020	0.004	invalid	
10	15.812	0.0014	0.003	invalid	
11	24.137	0.0571	0.054	invalid	
12	33.712	0.3131	0.289	10.000	Sulfate

Figure C 1.5: Ion chromatography 10.000 ppb mixed calibration standard (September 2014)

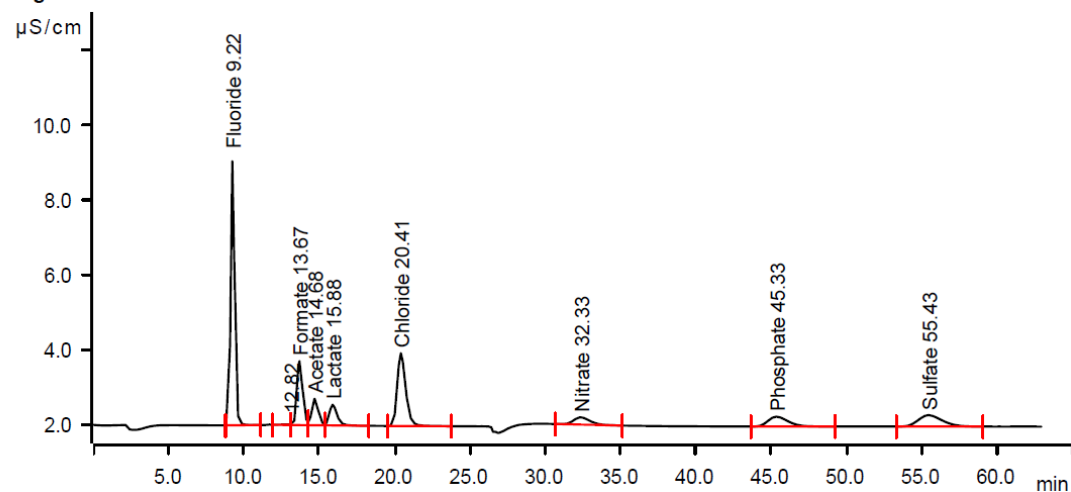
Organic Acids and Anions



Peak number	Retention time min	Area ($\mu\text{S/cm}$) x min	Height $\mu\text{S/cm}$	Concentration $\mu\text{g/L}$	Component name
1	5.723	0.0645	0.323	invalid	
2	6.387	0.0053	0.018	invalid	
3	7.375	0.4090	2.003	20.000	Formate
4	7.775	0.1313	0.637	20.000	Acetate
5	8.218	0.2299	0.916	20.000	Lactate
6	9.805	1.8998	6.018	20.000	Chloride
7	11.255	0.0139	0.036	invalid	
8	12.893	0.0026	0.006	invalid	
9	13.967	0.0029	0.005	invalid	
10	15.785	0.0026	0.005	invalid	
11	19.498	0.0147	0.022	invalid	
12	24.028	0.1086	0.109	invalid	
13	25.770	0.0002	0.002	invalid	
14	27.697	0.0026	0.027	invalid	
15	33.637	0.6410	0.604	20.000	Sulfate

Figure C 1.6: Ion chromatography 20.000 ppb mixed calibration standard (September 2014)

Organic Acids and Anions



Peak number	Retention time min	Area ($\mu\text{S/cm}$) x min	Height $\mu\text{S/cm}$	Concentration $\mu\text{g/L}$	Component name
1	9.217	2.0544	7.060	39.953	Fluoride
2	12.822	0.0090	0.011	invalid	
3	13.673	0.7456	1.710	39.972	Formate
4	14.683	0.3651	0.705	39.969	Acetate
5	15.875	0.3316	0.553	39.951	Lactate
6	20.407	1.2652	1.948	39.979	Chloride
7	32.330	0.2453	0.194	40.017	Nitrate
8	45.333	0.4078	0.265	39.990	Phosphate
9	55.433	0.5627	0.305	39.990	Sulfate

Figure C 1.7: Ion chromatography 40.000 ppb mixed calibration standard (September 2014)

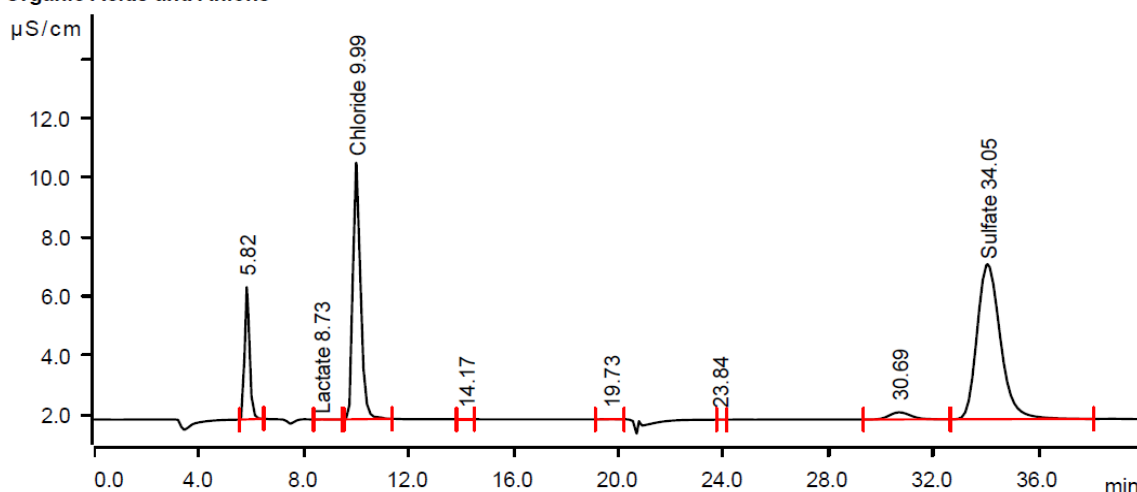
Sample data

Ident ARN BLR 6
Sample type Sample
Determination start 2014-09-23 12:39:00 UTC+2
Method Organic Acids and Anions_MiPCT_ME
Operator

Organic Acids and Anions

Data source Conductivity detector 1 (850 Professional IC 1)
Channel Conductivity
Recording time 40.0 min
Integration Automatically
Column type Metrosep A Supp 16 250/4.0
Eluent composition A Supp 16_2 - 2.5 mmol/L NaHCO₃, 5.5 mmol/L Na₂CO₃
Flow 0.800 mL/min
Pressure 13.32 MPa
Temperature 45.0 °C

Organic Acids and Anions



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration µg/L	Component name
1	5.820	0.9171	4.459	invalid	
2	8.730	0.0011	0.002	0.380	Lactate
3	9.988	2.9106	8.645	28.984	Chloride
4	14.170	0.0007	0.002	invalid	
5	19.733	0.0038	0.007	invalid	
6	23.840	0.0002	0.002	invalid	
7	30.685	0.2271	0.239	invalid	
8	34.050	5.4051	5.224	133.928	Sulfate

Figure C 1.8: Arnot boiler sample anions (IC) results

Swan degasser conductivity

Figure D 1.1: Swan degasser conductivity on-line analyser calibration certificate (April 2015)

APPENDIX E

EQUIVALENT CONDUCTIVITY OF ELECTROLYTES IN AQUEOUS SOLUTION

Petr Vanýsek

This table gives the equivalent (molar) conductivity Λ at 25 °C for some common electrolytes in aqueous solution at concentrations up to 0.1 mol/L. The units of Λ are $10^{-4} \text{ m}^2 \text{ S mol}^{-1}$.

For very dilute solutions, the equivalent conductivity for any electrolyte of concentration c can be approximately calculated using the Debye–Hückel–Onsager equation, which can be written for a symmetrical (equal charge on cation and anion) electrolyte as

$$\Lambda = \Lambda^\circ - (A + B\Lambda^\circ)c^{1/2}$$


For a solution at 25 °C and both cation and anion with charge [1], the constants are $A = 60.20$ and $B = 0.229$. Λ° can be found from the next table, “Ionic Conductivity and Diffusion at Infinite Dilution.” The equation is reliable for $c < 0.001 \text{ mol/L}$; with higher concentration the error increases.

Compound	Infinite dilution Λ°	Concentration (mol/L)						
		0.0005	0.001	0.005	0.01	0.02	0.05	0.1
		Λ ($10^{-4} \text{ m}^2 \text{ S mol}^{-1}$)						
AgNO ₃	133.29	131.29	130.45	127.14	124.70	121.35	115.18	109.09
1/2BaCl ₂	139.91	135.89	134.27	127.96	123.88	119.03	111.42	105.14
1/2CaCl ₂	135.77	131.86	130.30	124.19	120.30	115.59	108.42	102.41
1/2Ca(OH) ₂	258	—	—	233	226	214	—	—
CuSO ₄	133.6	121.6	115.20	94.02	83.08	72.16	59.02	50.55
HCl	425.95	422.53	421.15	415.59	411.80	407.04	398.89	391.13
KBr	151.9	149.8	148.9	146.02	143.36	140.41	135.61	131.32
KCl	149.79	147.74	146.88	143.48	141.20	138.27	133.30	128.90
KClO ₄	139.97	138.69	137.80	134.09	131.39	127.86	121.56	115.14
1/3K ₃ Fe(CN) ₆	174.5	166.4	163.1	150.7	—	—	—	—
1/4K ₄ Fe(CN) ₆	184	—	167.16	146.02	134.76	122.76	107.65	97.82
KHCO ₃	117.94	116.04	115.28	112.18	110.03	107.17	—	—
KI	150.31	148.2	143.32	144.30	142.11	139.38	134.90	131.05
KIO ₄	127.86	125.74	124.88	121.18	118.45	114.08	106.67	98.2
KNO ₃	144.89	142.70	141.77	138.41	132.75	132.34	126.25	120.34
KMnO ₄	134.8	132.7	131.9	—	126.5	—	—	113
KOH	271.5	—	234	230	228	—	219	213
KReO ₄	128.20	126.03	125.12	121.31	118.49	114.49	106.40	97.40
1/3LaCl ₃	145.9	139.6	137.0	127.5	121.8	115.3	106.2	99.1
LiCl	114.97	113.09	112.34	109.35	107.27	104.60	100.06	95.81
LiClO ₄	105.93	104.13	103.39	100.52	98.56	96.13	92.15	88.52
1/2MgCl ₂	129.34	125.55	124.15	118.25	114.49	109.99	103.03	97.05
NH ₄ Cl	149.6	147.5	146.7	143.9	141.21	138.25	133.22	128.69
NaCl	126.39	124.44	123.68	120.59	118.45	115.70	111.01	106.69
NaClO ₄	117.42	115.58	114.82	111.70	109.54	106.91	102.35	98.38
NaI	126.88	125.30	124.19	121.19	119.18	116.64	112.73	108.73
NaOOCCH ₃	91.0	89.2	88.5	85.68	83.72	81.20	76.88	72.76
NaOH	247.7	245.5	244.6	240.7	237.9	—	—	—
Na picrate	80.45	78.7	78.6	75.7	73.7	—	66.3	61.8
1/2Na ₂ SO ₄	129.8	125.68	124.09	117.09	112.38	106.73	97.70	89.94
1/2SrCl ₂	135.73	131.84	130.27	124.18	120.23	115.48	108.20	102.14
ZnSO ₄	132.7	121.3	114.47	95.44	84.87	74.20	61.17	52.61

Figure E.1: Ionic conductance of substances

APENDIX F

Brine wash procedure



DOWEX Ion Exchange Resins

Procedure for Brine Cleaning of Anion Resins

Brine cleaning is an effective treatment for removing organic contaminants on strong and weak base anion resins in demineralizers, organic traps and Dealkalizer units. If organic levels in the feed water are high, it is advised to carry out regular brine treatments as part of a preventative maintenance program, as heavily fouled resins may not be completely restored with this treatment. An alternative is to install an organic filter as pretreatment to the demineralization line.

The recommended procedure is as follows:

1. Exhaust the resin.
2. Backwash at the regular flow rate for 10-20 minutes, if possible with air-lance at 4 resin bed volumes air/minute. Drain the bed.
3. Apply 1.5 bed volumes (10 gal/cu.ft) of a 10% NaCl/1% NaOH solution. Drain to bed level over 1 hour and allow to soak for a further 3-16 hours. It is preferable to use an alkali brine solution warmed up to approximately 50°C (120°F) for type 1 and weak base anions or 40°C (105°F) for type 2.
4. Displace with 2-3 bed volumes water (15-20 gal/cu.ft) over 20-30 minutes.
5. Rinse out with 3-5 bed volumes DI water fast rinse (20-40 gal/cu.ft).
6. Double regenerate the resin (same NaOH or brine concentration, double time).
7. Rinse and return the unit to service.

Notes: Expect the first run to give an earlier conductivity break.

Cation effluent or soft water must be used for the solutions make up and rinse. Hot solutions will increase the efficiency of the cleaning and regeneration. Recirculation of the cleaning solution, for the contact time specified, will also increase the efficiency of the cleaning.

*Trademark of The Dow Chemical Company

DOWEX® Ion Exchange Resins

Form No. 177-01843-802XQRP

Figure F1: Brine wash procedure(*Source, Dionex technical data on maintenance of resin)

Cycle chemistry steam flow diagram

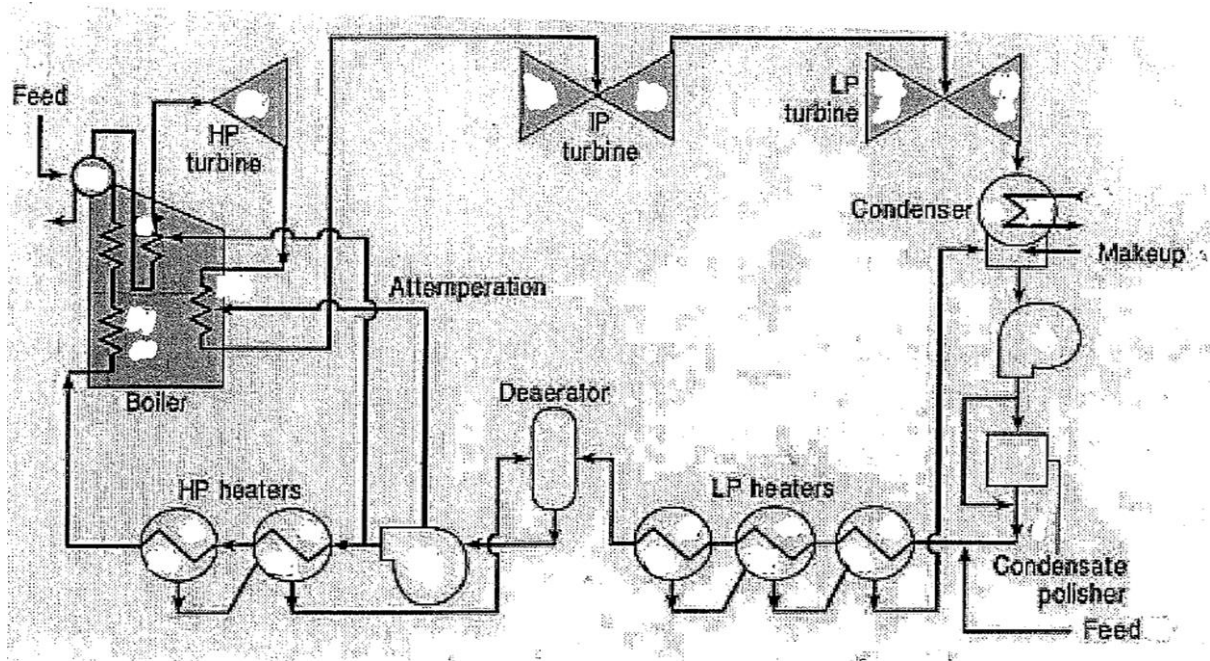


Figure G1: Generic plant layout showing different sampling points