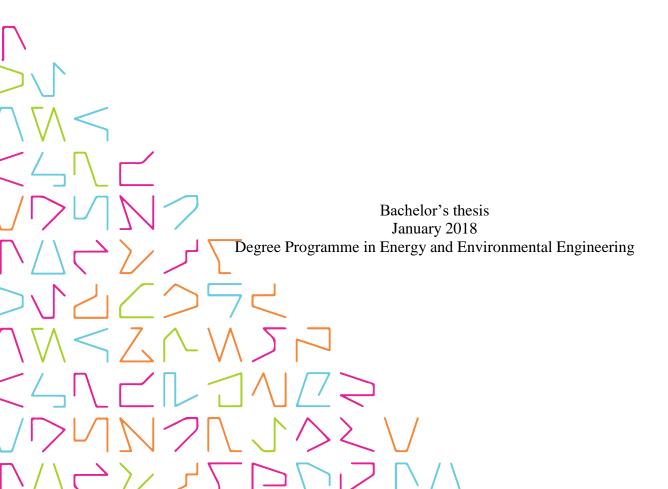


FEASIBILITY OF ELECTROLYSIS IN NUTRIENT RECOVERY

Alexandra Gorbatova



ABSTRACT

Tampereen ammattikorkeakoulu Tampere University of Applied Sciences Degree Programme in Energy and Environmental Engineering

ALEXANDRA GORBATOVA Feasibility of Electrolysis in Nutrient Recovery

Bachelor's thesis 42 pages, appendices 10 pages January 2018

The need for developing nutrient management systems, in particular, nutrient recycling and reuse, arises from rapid increase in population, which in turn causes nutrient imbalance. Nitrogen and phosphorus, leaching to the environment through fertilization and sewage release, can cause adverse environmental effects, such as eutrophication of water bodies, causing biodiversity loss in the ecosystem. Instead, water treatment technology can be developed for effective nutrient removal and recovery.

Previously, it was tested that phosphorus can be efficiently precipitated in a form of struvite. Tests were carried out on the possibility of nitrogen capturing from the reject water from struvite precipitation process, which did not lead to effective nitrogen capturing. At best, 18% of the total nitrogen was captured in the testing. If capturing nitrogen is not efficient, concentrating nitrogen in the solution with a possibility of volume reduction could be explored, which is the aim of this thesis.

Electrochemistry has earlier been applied for treatment and nutrient recovery from urine. Feasibility of electrolysis in nitrogen recovery from struvite precipitation reject water is yet to be researched. The main findings after conducting the electrolysis and analyzing the electrolyte in comparison to the initial solution include the potential for volume reduction and nitrogen capturing. Volume reduction rate of the system was 60ml/hour, which is 20% of the total volume. Nitrogen levels decreased with the duration of electrolysis, but not significantly. Possible losses can be caused by nitrogen escaping in a gaseous form, such as chloramine and nitrogen gas.

Application of electrolysis in nutrient recovery could be feasible with a few structural modifications to the experimental set-up and testing. Additional nitrogen and foam analyses should be carried out to obtain more reliable results and numerous duplicates of fresh electrolyte samples would provide a better understanding of the chemical process behind the electrolysis of struvite precipitation reject water.

CONTENTS

1	INTRODUCTION	5
	1.1. Nitrogen	6
	1.2. Wastewater treatment – nitrogen removal	7
	1.3. Electrolytic cell and electrolysis	8
	1.4. Electrolysis of urine	9
	1.5. Previous use of electrochemistry in urine treatment	12
2	AIMS AND SCOPE	13
3	MATERIALS AND METHODS	14
	3.1. Electrolysis	14
	3.2. Analyses	16
	3.2.1 Nitrogen measurements	16
	3.2.2 pH, conductivity, and temperature	18
	3.2.3 Ion chromatography	19
4	RESULTS AND DISCUSSION	21
	4.1. Nitrogen analyses	22
	4.1.1 Total Kjaldahl nitrogen	22
	4.1.2 HACH total nitrogen	23
	4.1.3 Ammonia-nitrogen measurements	23
	4.1.4 Nitrogen recovery: discussion	26
	4.2. pH	28
	4.3. Conductivity	28
	4.4. Temperature	30
	4.5. Ion chromatography	30
	4.5.1 Ion chromatography: discussion	33
	4.6. Power consumption	35
	4.7. General discussion	36
5	CONCLUSION	38
RI	EFERENCES	39
Al	PPENDICES	43
	Appendix 1. HACH total nitrogen data table.	43
	Appendix 2. Raw data collected throughout the measurements	44
	Appendix 3. Data for ammonia ISE calibration curve.	47
	Appendix 4. Ammonia measurements with an ISE	48
	Appendix 5. Ion chromatography summary sheets and table	49

ABBREVIATIONS AND TERMS

Cl ₂	Chlorine gas	
$CO(NH_2)_2$	Urea	
E^{0}	Standard reduction potential in aqueous solution at 25 $^{\circ}C$	
H_2	Hydrogen gas	
H_2SO_4	Sulphuric acid	
HClO	Hypochlorous acid	
IC	Ion chromatography	
ISA	Ionic strength adjustor	
ISE	Ion selective electrode	
N_2	Nitrogen gas/dinitrogen	
N_2O	Nitrous oxide	
Na ₂ CO ₃	Sodium carbonate	
NaHCO ₃	Sodium bicarbonate	
NH ₃	Ammonia	
NH ₃ -N	Ammonia nitrogen	
\mathbf{NH}_{4}^{+}	Ammonium	
NO ₂ ⁻	Nitrite	
NO ₃ -	Nitrate	
O ₂	Oxygen gas	
ТАМК	Tampere University of Applied Sciences	
TKN	Total Kjeldahl nitrogen	
TN	Total nitrogen	
UHP water	Ultra-high purity water	

1 INTRODUCTION

Nutrient recovery is defined as an action, which enables extraction, purification or concentration of a nutrient from a substrate. (Buckwell A., Nadeu E., 2016). The need for nutrient recovery arises primarily from the developing concepts of sustainability and circular economy, where the materials, in this case, nutrients, are used and reused during their life-cycle as many times as possible.

Nutrient management becomes an increasingly important topic now as continuous population growth and the changes this brings to various economic, environmental and social sectors are being acknowledged. (SDGs, 2015). The worldwide nutrient management system is currently not able to utilize all the valuable nutrients to their full potential – the nutrients end up leaking out from the system to the environment, which is disadvantageous from two angles: environmental pollution and inefficient use of nutrients. Examples of such sectors, from which the nutrients leak to the environment, are agricultural fertilization and management of human waste. Nutrient release via untreated sewage can cause adverse effects on the environment. (EPA. Nutrient Pollution. 2016).

Human waste, especially urine, is very rich in nutrients, such as nitrogen, potassium, and phosphorus. All the three nutrients mentioned above are main constituents of commercially available mineral fertilizers. When released to the environment, urine, containing phosphorus and nitrogen, can cause eutrophication of natural water ecosystems, causing severe harm to the aquatic environment. Thus, such nutrients are removed in wastewater treatment plants but are not efficiently recycled. The fate of sludge, containing the nutrients, depends on the scale of the treatment plant and the concentration of the nutrient in the sludge. Often, sludge is anaerobically or aerobically digested, composted and sometimes even incinerated. (Tchobanoglous G., Schroeder E., 1985). There are ways, which could enable more efficient utilization of nutrients, even from human waste. (Miso, A., Spuhler, D. 2009).

Urine can be applied in agriculture as a fertilizer, however, it should be diluted first, since the nutrient content can be overwhelming to certain crops. The dilution factor should be calculated based on the nutrient requirement of the crops and the nutrient content of urine. There are, however, certain challenges associated with the use of urine as a fertilizer. Logistic challenges: if the urine is acquired from elsewhere than locally, transportation and storage costs are too high, due to the volume. There are also certain requirements for pre-storing the urine before using it as a fertilizer in order for pH to stabilize at high enough value and pathogens to be eliminated. The minimum storage requirement for viruses and bacteria to be eliminated from urine according to WHO is over 6 months at a temperature of 20 °C. (WHO, 2006). Legislative challenges are also present – the use of urine for commercial fertilization is yet to be accepted statutory, since the use of urine involves risks of contamination, due to pathogens and medicinal residues present in urine. (Biourea Loppuraportti, 2017).

To minimize logistically imposed and statutory challenges, urine can be processed to obtain urine-based fertilizers. For example, production of struvite via the addition of magnesium salts and subsequent phosphorus precipitation is a viable alternative. The rates of struvite precipitation can be rather high, but the method requires pH adjustment to 8-10 and temperature range in-between 25 and 90 °C, which can make the process costly. Struvite is a very light phosphorus-rich powder, which can be easily and effectively applied as a fertilizer, as was demonstrated throughout the Biourea project. (Biourea Loppuraportti, 2017, p.50).

The concept of nutrient recovery can be taken even further, by attempting to utilize the nutrients that were left over in the struvite precipitation reject water.

1.1. Nitrogen

Nitrogen, as a nutrient, can be present in wastewater in several forms, since nitrogen is an element, which can exist in seven (7) oxidation forms. When thinking about water quality, the main forms of nitrogen of interest are organically bound nitrogen, ammonianitrogen (NH₃-N), ionic species: nitrate and nitrite, and nitrogen gas. One more nitrogenous compound, which can be found from wastewater is urea. Urea is formed in the liver as a result of de-amination of amino acids. (PubChem, 2017).

Nitrogen cycle is a process, where nitrogen is changed from one form to another and passes from atmosphere to soil and plants and then to living organisms, after which it

returns back to the atmosphere. Nitrogen is cycled between its organic and inorganic forms. (Kimball J., 2016).

Animals and humans cannot make use of nitrogen when it is present in its inorganic form. Dinitrogen from the atmosphere is converted to organically bound nitrogen and ammonia by plants. Organically bound nitrogen (proteins) are broken down by bacteria to urea and ammonia. Urea can be converted to ammonia through enzyme activity. Then ammonia is bacterially oxidized to nitrite and even further to nitrate. The process of bacterial oxidation is called nitrification. Nitrate can be reduced by bacteria to nitrite, which is then reduced back to nitrogen gas through the process called denitrification. (Tchobanoglous G., Schroeder E., 1985, p.73, 183).

The sum of ammonia-nitrogen and organically bound nitrogen is called total Kjeldahl nitrogen (TKN). If nitrate and nitrite-nitrogen are added to the TKN, the result would be total nitrogen (TN). The two terms should not be confused since they do not account for the same forms of nitrogen present in the wastewater. The use of having the two different tests for different groups of nitrogen forms is to derive organic nitrogen from the equation if the total ammonia is known and vice versa. Knowing the concentrations of the TKN, nitrate- and nitrite-nitrogen, the total nitrogen can be calculated. (Total Nitrogen in Wastewater, ASA Analytics).

1.2. Wastewater treatment – nitrogen removal

Removal of nitrogen, as well as phosphorus, form wastewater is a crucial part of wastewater treatment, before water can be released back to natural reservoirs. Nitrogen in several of its forms can cause adverse environmental and health effects, if not properly removed from the wastewater. Nitrogen can cause eutrophication, which is defined as excessive algae growth due to the abundance of readily available nutrients, which leads to excessive oxygen consumption. Oxygen becomes a limiting factor, being at the same time insufficient for supporting all the life forms in the ecosystem. (Chislock, M., et al., 2013).

Nowadays, nitrogen removal can be done in several ways, for example, biological treatment, breakpoint chlorination, gas stripping and ion exchange. Biological systems are based on the principle of nitrification and denitrification. The systems facilitate natural nitrifying and denitrifying bacterial growth, which enables the process of nitrate and nitrite reduction to nitrogen gas. Breakpoint chlorination is done by adding sufficient amount of chlorine to facilitate chemical reactions, resulting in the production of nitrous oxide and nitrogen gas. This technique can eliminate residual ammonia in the water. (Tchobanoglous G., Schroeder E., 1985). Ion exchange is a method, where ions, such a NH_4^+ , are removed by exchange with a mineral, resin or synthetic ion-selective medium. (Blumhof S., 2010).

In the aforementioned processes, the nitrogen, in its final form is not recovered, instead, it is released back into the atmosphere. Air stripping, on the other hand, provides an alternative to collecting the gas after, for example, ammonia removal. Nitrogen gas can be used for the manufacture of nitrogen-based fuels, which could potentially serve as an alternative to fossil fuels. (Dana A., et al., 2016).

1.3. Electrolytic cell and electrolysis

Electrolysis is a technology of applying electric current to a system in order to facilitate reactions, which would not happen spontaneously without application of external force. One of the examples of such reactions is separating a solution into its components, such as breaking down water molecules (H₂O) into hydrogen gas (H₂) and oxygen gas (O₂). (Chemistry Libre Texts, 2014).

A conventional electrolytic cell is composed of a vessel with electrolyte, two electrodes: anode and cathode and a power source. An example of an electrolytic cell is demonstrated in FIGURE 1.

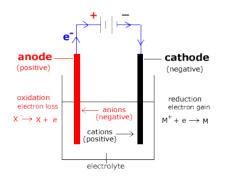


FIGURE 1. Schematic representation of an electrolytic cell. (AUS-e-TUTE, 2017).

As it can be seen from FIGURE 1, the anode is the electrode connected to the positive terminal of the power supply, where oxidation happens. Oxidation is the process of an electron loss by a substance. A cathode is an electrode connected to the negative terminal of the power source, where reduction happens. Reduction is the process of accepting electrons. From the definitions of oxidation and reduction, free electrons formed during oxidation are gained in the process of reduction, which defines the electron flow from the anode to the cathode.

The elements are characterized by their ability to donate or accept electrons in an electrochemical series. The elements with the most negative reduction-oxidation potential are placed at the top of the series and the most positive at the bottom. The electrode reductionoxidation potentials are measured relative to a standard hydrogen electrode. In practice, the elements on the top of the electrochemical series are stronger reducing agents, so they readily give out electrons. The elements on the bottom of the series are oxidizing agents, so they more readily accept electrons. (Clark J., 2013). The electrochemical series determines the order of the reactions happening in the cell if the solution is complex, consisting of numerous substances. Some substances are going to be reduced and oxidized over the others.

Cell potential can be calculated using the half reactions and the half-cell potentials acquired from the electrochemical series. That can be done if all the compounds in the solution are defined and all the half-reaction can be written down. In case of the reject water from struvite precipitation, calculating the cell potential for electrolysis of the solution is practically impossible, since the exact chemical composition of the solution is unknown. That is why sufficient potential difference should be induced across the cell during the testing, to make sure that the required potential demand of the cell is met.

1.4. Electrolysis of urine

The major components present in urine, which could be present in struvite precipitation reject water are sodium (Na⁺), magnesium (Mg⁺), ammonia (NH₃), chloride (Cl⁻), hydroxide (OH⁻) and water (H₂O). (Helmenstine A.M., 2017). The positive ions (cations) will be attracted to the negative electrode – cathode and the negative ions (anions) will be

attracted to the anode. This means, that theoretically, magnesium and sodium will be oxidized, while chloride and hydroxide will be reduced.

The possible reactions, which can happen at the anode according to the electrochemical series are the following:

$4OH^{-} \leftrightarrow O_2(g) + 2H_2O + 4e^{-}$	$E^0 = +0,401 V$
$2\mathrm{Cl}^{-} \leftrightarrow \mathrm{Cl}_{2}(\mathrm{g}) + 2\mathrm{e}^{-}$	$E^0 = +1,358 V$
$Cl^{-}(aq) + H_2O \leftrightarrow HClO(aq) + H^{+}(aq) + 2e^{-}$	$E^0 = +1,482 V$

A possible reaction happening at the cathode:

$$2H_2O(1) + 2e^- \leftrightarrow H_2(g) + 2OH^-(aq)$$
 $E^0 = -0.8277 V$

The electrode potentials are given in a form of standard reduction potentials. Some reaction pairs can be formed, for example, the electrons from chloride ion oxidation can be used in the reduction of water for hydrogen gas formation. The final cell potential is calculated by subtracting the reduction potential of the reaction happening at the anode from that happening at the cathode.

Oxidation:	$2\mathrm{Cl}^{-}(\mathrm{aq}) \leftrightarrow \mathrm{Cl}_{2}(\mathrm{g}) + 2\mathrm{e}^{-}$	$E^0 = +1,358 V$
Reduction:	$2H_2O(l) + 2e^- \leftrightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0,828 V$
	$2\mathrm{Cl}^{-}(\mathrm{aq}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \leftrightarrow \mathrm{Cl}_{2}(\mathrm{g}) + \mathrm{H}_{2}(\mathrm{g}) + 2\mathrm{OH}^{-}(\mathrm{aq})$	$E^0 = -2,186 V$

In addition, the electrons formed from reduction of hydroxide ion can be used for hydrogen gas formation at the cathode.

Oxidation:	$4OH^{-} \leftrightarrow O_2(g) + 2H_2O + 4e^{-}$	$E^0 = +0,401 V$
Reduction:	$4H_{2}O\left(l\right)+4e^{-}\leftrightarrow2H_{2}\left(g\right)+4OH^{-}\left(aq\right)$	$E^0 = -1,656 V$
	$2H_2O\left(l\right)\leftrightarrow O_2\left(g\right)+2H_2\left(g\right)$	$E^0 = -2,057 V$

As it can be seen, neither of the reactions has a positive reduction potential, which indicates that these reactions will not happen spontaneously, some external energy has to be applied to the system. (Harris D.C., 2007). Based on the reaction pairs, hydrogen gas bubbles should be forming on the cathode and oxygen at the anode. (Cohen P., Geffner S., 1996, pp.440 - 447.)

Electrolysis of ammonia and the half-reactions have not been described in the standard reduction potential tables and literature. The research conducted in Ohio University has shown that the electrolysis of ammonia can be written out using the following half-reactions:

Oxidation:	$2NH_3(aq) + 6OH^- \leftrightarrow N_2(g) + 6H_2O + 6e^-$	$E^0 = +0,77 V$
Reduction:	$2H_2O + 6e^- \leftrightarrow 3H_2(g) + 6OH^-(aq)$	$E^0 = -0,83 V$
	$2NH_3(aq) \leftrightarrow N_2(g) + 4H_2O + 3H_2(g)$	$E^0 = -1,60 V$

The reduction potentials have been determined in an alkaline medium versus a standard electrode at 25 °C. (Botte G., et al., 2005). The final cell reaction indicates that ammonia will be electrolysed into hydrogen gas, nitrogen gas and water if at least 1,6 V will be applied to the system in standard conditions. The formation of nitrogen gas is undesired in the experiment since the objective of the work is to preserve nitrogen in the system.

According to Nernst equation, $E = E^0 - \frac{RT}{zF} \cdot lnQ$, the final cell potential depends on the reaction quotient, which is defined as the relative concentrations of the reactants and products present in the solution at a certain point of time as the reaction proceeds. (Chemistry LibreTexts, 2017). This only adds to the overall difficulty of predicting the reactions happening in the reaction cell since the precise concentrations of the substances are unknown and not all the compounds can be identified from the struvite precipitation reject water. The reduction potentials used to predict the reactions happening at cathode and anode are measured in standard conditions: temperature of 25 °C, pressure of 1 atm and 1 M solutions. The reduction potentials, which makes the predicted overall cell potentials merely theoretical.

1.5. Previous use of electrochemistry in urine treatment

Nutrient recovery technology is driven by the goal of recovering nutrients from substances, which otherwise would be a wasted or released into the atmosphere. Several studies are conducted and new methods, incorporating currently available technologies in an innovative way are developed. For example, a biochemical reactor was constructed to recover nutrients and produce hydrogen gas from the reject water of sludge treatment. The reactor was a combination of an electrolytic cell, where the compartments are separated by a cation exchange membrane, and an air stripping system. During the air stripping, dissolved ammonia is converted to gaseous and bubbled through hydrochloric acid (HCl), where ammonia gas reacts with the acid to form ammonium chloride (NH₄Cl). (Wu X., Modin O., 2013).

The researchers found that the hydrogen gas production was very effective, $96 \pm 6\%$, but very little ammonia could be stripped using the generated hydrogen gas. However, with a subsequent air stripping, up to 79% of ammonia was removed.

Another study was conducted using similar technology, where electrochemical stripping was used for nitrogen recovery, except in this case, from raw urine. The set-up consists of a three-chamber two-membrane electrochemical stripping cell - an electrolytic cell with cation exchange membrane, which was connected to another cell compartment and separated by ammonia membrane. The third compartment is used for ammonia trapping in an acid solution. (Tarpeh W., Nelson K., 2016). The researchers found that 50% of nitrogen was recovered from the system and the losses could possibly be accounted for by chloramine formation. Most of the nitrogen was present in the third trap cell, however, some of it was still present at the anodic and cathodic compartments.

2 AIMS AND SCOPE

The aim of this thesis work is to explore the possibilities and feasibility of taking nutrient recovery and reuse from urine even further than precipitation of struvite. The reject waters from struvite precipitation are electrolysed and analyzed for their nutrient content, in particular – nitrogen.

Testing of struvite precipitation was previously conducted in TAMK (Kloet M., 2016). Then the project of capturing nitrogen from reject waters of struvite precipitation using various technologies, such as willow biochar and halloysite mixed with LECA pebbles, was carried out. The process yielded in a maximum of 18% of nitrogen recovery. (Puurunen L., 2016). The scope of this work is to test whether nitrogen can be more efficiently concentrated the solution using electrolysis.

3 MATERIALS AND METHODS

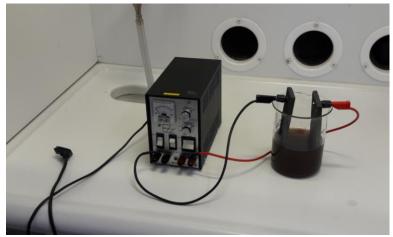
In order to evaluate whether or not electrolysis is an effective method of concentrating nutrients in the solution, several analyses need to be conducted from the samples collected during electrolysis. Four (4) main stages are defined in the process – initial, where the solution is not electrolysed, the electrolyte of 30 minutes, the electrolyte of 1 hour and the electrolyte of 1,5 hours. In some analyses, in order to acquire more data, the electrolysis was carried out for 2 hours.

The analyses, which need to be conducted in order to describe and understand the changes happening in the solution throughout the electrolysis include the total nitrogen (TN) analyses, ammonia-nitrogen measurements, ion chromatography, pH, temperature, and conductivity. Any observations related to the changes in color, odor or other perceivable factors are documented as well.

3.1. Electrolysis

From the theory of electrolysis and previous studies conducted using electrochemistry for nutrient recovery, a simple set-up of a glass beaker, two (2) electrodes, and a power supply was chosen. The volume of the struvite precipitation reject water, which is electrolysed, was decided to be kept at 300 ml due to the safety reasons, since it could not be determined with certainty what gases will evolve from the solution due to the unknown chemical composition of the liquid.

The equipment used in the electrolysis, and the experimental set-up are demonstrated in PICTURE 1. The power supply has operational voltage of up to 30 volts and current of up to 2 amperes. The electrodes purchased for the experiment are carbon electrodes with embedded inlets for banana plug wires. The black wire is connected to the negative terminal of the battery, making the electrode a cathode and the process at the electrode reductive. The red wire is connected to the positive terminal of the power supply, making the electrode and the process at the electrode reductive. The red wire is connected to the positive terminal of the power supply, making the electrode and the process at the electrode compartment – oxidation.



PICTURE 1. Experimental set-up.

A set of safety guidelines should be followed while conducting the electrolysis. The setup should be kept under a hood at all times, when the electrolysis is active, since, as was mentioned previously, the gases, which evolve during the process cannot be identified and may be toxic, such as chlorine gas (Martin J.G., White C.W., 2010). All sources of ignition should be removed from the hood, where the electrolysis experiment is conducted since hydrogen gas is predicted to form and be released from the system, which arises a risk of explosion. (FCHEA, Hydrogen Safety Fact Sheet).

Due to the unknown chemical composition of the reject water from struvite precipitation, the required cell potential cannot be calculated, since the standard reduction potential values cannot be obtained. The operational voltage was chosen to be 15 V and operational current 2 A, which should cover the demand for the potential difference for all the chemical processes happening in the electrolytic cell.

The samples for such analyses as pH and conductivity can be collected using Pasteur pipettes without interrupting the process of electrolysis, since the amounts of sample, which needs to be collected for these analyses is minuscule. If larger volumes of samples are required, for example for ion chromatography or total nitrogen analyses, the electrolysis should be interrupted after the desired time passes and initiated all over, since electrolyzing significantly smaller amounts of samples can cause an unwanted bias in the results.

3.2. Analyses

3.2.1 Nitrogen measurements

Altogether, three (3) different nitrogen analyses were conducted: total Kjeldahl nitrogen, total nitrogen, and ammonia-nitrogen measurement.

The samples are analyzed for nitrogen using Total Kjeldahl Nitrogen (TKN) method (Hoegger, 1998). An appropriate modification to the analysis for determination of organic and inorganic nitrogen from wastewater was adapted from the standard SFS 5505. The set of necessary equipment for the TKN analysis is presented in PICTURE 2.



PICTURE 2. Set of apparatus required for TKN analysis.

The digester unit, Büchi Digest System K-437, is shown on the top of PICTURE 2, together with the gas scrubber, Büchi B-414. The distillation unit, Büchi K-314, is shown on the bottom left and the titrator, Metrohm 876 Dosimat plus with a stirrer, Metrohm 801, is shown on the bottom right. The scrubber is filled with sodium carbonate (Na₂CO₃) solution, which neutralizes poisonous fumes formed in the process of digestion. (Büchi, 2017). Initially, it was planned to analyze all the samples for nitrogen using the Kjeldahl method, however, the distillation unit started to malfunction and eventually broke, so the final analyses had to be performed using an alternative method – HACH total nitrogen.

The necessary materials and equipment for the total nitrogen (TN) HACH analysis include HACH apparatus, HT 200 S digester and a reagent kit LCK 138 and are demonstrated in PICTURE 3.



PICTURE 3. Devices and reagents required for HACH total nitrogen analysis.

The LCK 138 Total Nitrogen reagent kit is meant for the determination of TN concentration from water and wastewater in the range of 1 to 16 milligrams per liter (mg/l). The pH of the sample should be within a range of 3 to 12 and the temperature should be from 15 to 25 °C.

The samples should be diluted so, that the total nitrogen concentration does not exceed 16 mg/l or is not under 1 mg/l. Concentration of TN measured from struvite precipitation reject water using Kjeldahl method is 2,33 g/l, so the sample should be ideally diluted in the ratio of 1:250, resulting in the estimated concentration of 9 mg/l ($\frac{2330\frac{mg}{l}}{250}$ = 9,32 mg/l).

For NH₃-N measurement a 'Thermo Scientific' high-performance ammonia ion selective electrode (ISE) was used. The electrode preparation should be carried out according to the manual, provided by the manufacturer. It is noted that the presence of air bubbles inside the electrode body affects the gas exchange process, which is fundamental to the operation of the ammonia ion selective electrode. Hence, before measurements, it is crucial to ensure that there are no air bubbles present. (High-Performance Ammonia ISE, 2010).

The calibration curves should be prepared in two ranges: 0 to 100 ppm (low-level calibration curve) and 0 to 1000 ppm (high-level calibration curve). The ammonia standard solutions are supplied together with the electrode. pH of the solution, where ammonia ISE is submerged into should be over 11 for all the nitrogen to be in ammonia form. (High-Performance Ammonia ISE, 2010). All the readings are given in millivolts.

3.2.2 pH, conductivity, and temperature

pH and conductivity are measured with Toledo laboratory meters. The meters were calibrated before each measurement according to the manufacturer's instructions. In order to measure conductivity, the samples should be diluted beforehand, since their conductivity exceeds the measurable range. The samples were diluted 1:40, which was determined experimentally.

It was noticed, that temperature affected both pH and conductivity, which is why, before the measurements, the samples were allowed to cool down to the room temperature after being collected from the electrolysis vessel. (Ashton J., Geary L., 2006). (Ashton C., Barron J., 2005).

The temperature was measured using a simple thermometer with an accuracy of $\pm 0,1$ °C. The temperatures were taken immediately after the samples were collected from the electrolysis vessel.

3.2.3 Ion chromatography

Ion chromatography was carried out in TAMK chemistry laboratory according to the standard ISO 10304-1:2007: Water quality – Determination of dissolved anions by liquid chromatography of ions. The anions of interest in the conducted chromatography analysis are chloride (Cl⁻), fluoride (F⁻), nitrate (NO₃⁻), nitrite (NO₂⁻), phosphate (PO₄²⁻) and sulfate (SO₄²⁻). A standard calibration solution was prepared by drying salts, containing the anions, which need to be determined and preparing a stock solution out of the ovendried salts. (ISO 10304-1:2007, p.3).

The number of the dilutions of the standard calibration solutions is 10. The dilutions include the standards with the ion concentrations of 0,5 mg/l, 1 mg/l, 2 mg/l, 5 mg/l, 10 mg/l, 20 mg/l, 25 mg/l, 50 mg/l, 75 mg/l and 100 mg/l. Such a wide range of the ion concentrations in calibration solutions is needed in order to match the concentrations of the ions in samples analyzed. The samples themselves are diluted 1:10, 1:20, 1:50 and 1:100 to increase the likelihood of the ion concentrations in the samples to be within the calibration range.

A fresh eluent for the ion chromatograph is prepared according to the instructions provided in the manual of the apparatus. An eluent recommended for the chromatograph "Dionex ICS-1000" with a column "Dionex Ionpac AS14A 4mm" is a mixture of 0,8 M Na₂CO₃ and 0,1 M NaHCO₃. (Dionex IonPac AS14A Manual, 2002, p.14).

The chromatograph itself is operated via Chromeleon software, where the desired settings for the analysis method are set. The chromatograph is demonstrated in PICTURE 4. The chromatograph has an auto-sampler device connected to it, allowing the samples to be inserted all at once and the methods switch automatically, as the auto-sampler delivers new samples for the chromatography injections.



PICTURE 4. Ion chromatograph with a computer with Chromeleon software.

When the samples are diluted, they should be transferred to vials for the analysis through syringe filtration. The pore diameter of the filter is 45 μ m. After the sample vials are filled, they should be capped with a special cap, so that no air layer or air bubbles are left in the vial. The capped vials are then loaded into the autosampler cassettes. The sequence of the samples in the cassettes should be carefully recorded.

There always must be at least two (2) vials with UHP water in the beginning of the sequence and at least two (2) in the end to flush the column. Fresh eluent should be allowed to run through the system for at least 30 minutes before the method is initiated. It was decided to insert vials with UHP water to the middle of the sample sequence as well, to flush the column in-between different sample sets and avoid cross-contamination of results.

The sample codes used during the IC with the explanations and necessary information on the sample dilutions and concentrations are demonstrated in TABLE 1.

Sample code	Explanation	Concentration/ dilution
S1		0,5 mg/l
S2		1 mg/l
S3		2 mg/l
S4		5 mg/l
S5	Standard solutions	10 mg/l
S6		20 mg/l
S7		25 mg/l
S8		50 mg/l
S9		75 mg/l
S10		100 mg/l
IS-1		1:10
IS-2	Initial compla	1:20
IS-3	Initial sample	1:50
IS-4		1:100
E30-1		1:10
E30-2	20 minute electrolyte	1:20
E30-3	30-minute electrolyte	1:50
E30-4		1:100
E1-1		1:10
E1-2	1 hour algotrolyta	1:20
E1-3	1-hour electrolyte	1:50
E1-4		1:100
E15-1		1:10
E15-2	1.5 hour alastralista	1:20
E15-3	1,5-hour electrolyte	1:50
E15-4		1:100

TABLE 1. IC sample codes, their explanations, and dilution factors.

4 RESULTS AND DISCUSSION

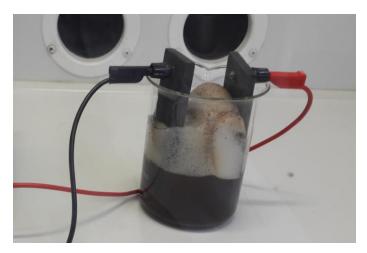
It was observed that the colour of electrolyte changes as with the duration of the electrolysis. The color differences between the samples are presented in PICTURE 5.



PICTURE 5. Colour changes throughout electrolysis.

As it can be seen from PICTURE 5, the color of the reject water from struvite precipitation becomes lighter as the electrolysis proceeds.

In addition to color changes, decreases in volume with time were observed. The estimated volume decrease rate is 30 ml/30 min, which is 60 ml/h. The decreases in the volume of liquid, however, could not be measured precisely, since a thick layer of foam was forming above the anodic and cathodic compartments of the cell. The foam, which formed during the electrolysis, periodically collapsed leading to the dissolution of substances trapped in the foam back into the electrolyte. The foam formed above the compartments is demonstrated in PICTURE 6.



PICTURE 6. Foam formed throughout the electrolysis.

As soon as the power supply was plugged in and turned on, and the current started passing through the solution, several bubbles started forming on both electrodes. The formation of foam and bubbles indicates that gases were being released from the anodic and cathodic compartments of the electrolytic cell.

The odor of the solution became stronger, the longer the solution was electrolysed. The odor had a characteristic smell of ammonia. Also, it was noticed, that after the electrolysis, there is a scent of chlorine gas present in the hood, as well as some other strong and overwhelming odor, reminding of hydrogen sulfide.

4.1. Nitrogen analyses

4.1.1 Total Kjaldahl nitrogen

It was planned to conduct the total nitrogen analyses using Kjeldahl method for the analysis of the initial sample and its' electrolytes. However, the distillation unit of the apparatus started to malfunction and the total nitrogen could not be analyzed from the electrolyte samples using the Kjeldahl method. The initial sample, however, was analyzed before the equipment broke and the results can be used to validate the accuracy of the HACH total nitrogen measurements. The results of the TKN analysis of the initial sample, which is the raw effluent from struvite precipitation, is presented in TABLE 2.

Sample	Total Nitrogen, g/l
Sample 1	2,60
Sample 2	2,10
Sample 3	2,13
Sample 4	2,49
	1

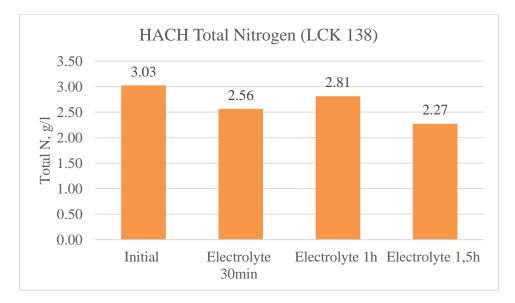
TABLE 2. Total Kjeldahl nitrogen of the struvite precipitation reject water.

Average: 2.33

The four (4) samples analyzed are all replicas of the same sample. The average concentration of total nitrogen measured with the Kjeldahl method is 2,33 g/l.

4.1.2 HACH total nitrogen

Since the apparatus for TKN analysis became unavailable, a substitute method had to be found, which is a determination of the total nitrogen with HACH. The total nitrogen concentrations were measured from samples diluted 1:250 in milligrams per liter (mg/l). In order to account for the dilutions, the final results were multiplied with a factor of 250 and then converted to grams per liter (g/l). The results of the analysis are demonstrated in GRAPH 1. The data table from the TN measurements is presented in Appendix 1.



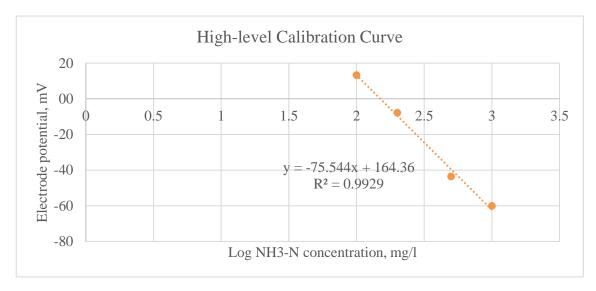
GRAPH 1. Total nitrogen of struvite precipitation reject water and its' electrolytes.

From GRAPH 1 it can be seen that the concentration of total nitrogen decreases as electrolysis proceeds. That can be due to the nitrogen assuming gaseous form and evaporating from the solution. Interestingly, the total nitrogen concentration of 1-hour electrolyte is higher than that of 30-minute electrolyte, which can be due to the fact that some of the nitrogen gas got trapped in the foam, forming over the anodic and cathodic compartments, and then dissolved back into the solution, as the foam collapsed.

4.1.3 Ammonia-nitrogen measurements

Ammonia measurements with an ISE required preparation of calibration solutions and calibration curves. Both low-level and high-level calibrations were carried out, however, only the high-level calibration was used for the result interpretation, since the concentrations of ammonia nitrogen were rather high even in the diluted samples.

The values for the calibration curve are presented in Appendix 3 and the high-level calibration curve is shown in GRAPH 2.



GRAPH 2. High-level calibration curve.

As a general observation, the electrode potential reaches more negative values with the higher concentrations. The equation's regression coefficient is 0,99, which is very close to 1, indicating that the trendline fits the results nearly perfectly and the calibration curve is valid. The calibration curve, in particular, it's equation, is used to determine the concentration of NH₃-N from the millivolts measured. The equation is the following: y = -75,544x + 164,36

$$log[NH3 - N] = \frac{(Electrode \ potential \ (mV) \ - \ 164,36)}{-75,544}$$

Electrode potential $(mV) = -75,544 \cdot log[NH3 - N] + 164,36$

The results of the electrode potential measurements from the struvite precipitation reject water and its' electrolytes are presented in TABLE 3. The full table with the initial and adjusted pH values, and the temperatures can be found in Appendix 4.

Duration of elec- trolysis, min	mV	log[NH3-N]	Undiluted [NH3-N], g/l
0	-69,4	3,09	2,49
30	-78,1	3,21	3,24
60	-87,9	3,34	4,37
90	-92,0	3,39	4,95
120	-95,2	3,44	5,46

TABLE 3. Ammonia – nitrogen measurements with an ISE.

The logarithm of NH₃-N concentration is calculated with the equation obtained from the calibration curve. The concentration of ammonia nitrogen is further calculated with the logarithm rule, by elevating 10 to the power of the logarithm of NH₃-N concentration. For example, the initial solution:

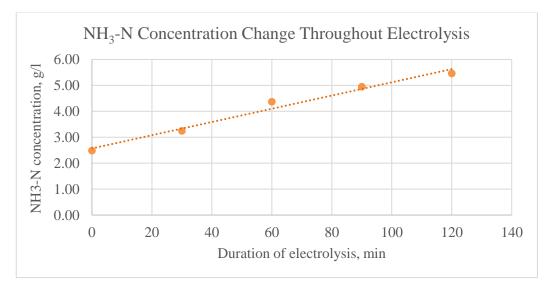
$$log[NH_3 - N] = \frac{(-69,4 - 164,36)}{-75,544} = 3,09$$

 $[NH_3 - N] = 10^{3,09} = 1242,67 \ mg/l$

Since the sample was diluted 1:2 :

Undiluted
$$[NH_3 - N] = 1242,67 \frac{mg}{l} \cdot 2 \cdot 0,001 \frac{g}{mg} = 2,49 \ g/l$$

In order to evaluate the results, the values of $[NH_3 - N]$ concentration are plotted versus the duration of the electrolysis on GRAPH 3.



GRAPH 3. NH₃-N concentration changes of the solution throughout electrolysis.

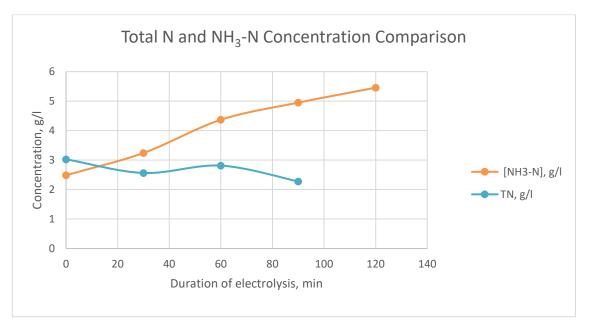
The concentration of ammonia-nitrogen increases the longer the electrolysis proceeds.

4.1.4 Nitrogen recovery: discussion

Based on the HACH total nitrogen results, the amount of nitrogen in grams per liter (g/l) reduces with the duration of electrolysis. This can be due to the formation of the nitrogencontaining gases, such as chloramine (NH₂Cl). Chloramine can be formed from ammonia reacting with sodium hypochlorite. In the section 1.4 it was hypothesized that there are sodium ions already present in the solution, and hypochlorite could form from chlorine gas reacting with the hydroxide ions. (Comninellis C., Chen G., 2009, pp. 183-187). The reaction of chloramine production is the following: NH₃ (aq) + ClO⁻ (aq) \rightarrow NH₂Cl (g) + OH⁻ (aq). The formation of chloramine was previously investigated in the context of ammonia electrolysis and it was demonstrated that various forms of chloramine indeed form during the electrolysis of ammonia. (Gendel Y., Lahav O., 2011). One of the general observations, supporting the statement about nitrogen escaping in the form of chloramine is the presence of a characteristic odour of amine in the solution and in the hood throughout the electrolysis.

As was discussed in the section 1.4, nitrogen could have escaped the system as a dinitrogen gas. (Botte G., et al., 2005). Nitrogen gas forms as a result of ammonia electrolysis. In that case, structural modifications are required for the nitrogen to remain in the system or be collected outside the system. A gas collection system can serve as such a modification. (Ball D., 2011, pp. 303-309).

As a result of testing ammonia concentrations with an ISE, that the concentrations of ammonia increase with the duration of the electrolysis. The concentration of ammonia nitrogen based on the measurements in the 1,5-hour electrolyte is 4,95 g/l, which exceeds the TN concentration of the same electrolyte solution, which is 2,27 g/l. The comparison of the concentrations is demonstrated in GRAPH 4. The ammonia concentration calculation was carried out based on the calibration curve, which had to be extrapolated over the rage. The extrapolation was done because the electrode potentials measured from already diluted solutions indicated higher concentrations of ammonia nitrogen than the most concentrated calibration standard available (1000 ppm = 1000 mg/l = 1 g/l). This could have led to overestimated and thus results. (O'Haver T., 2008).



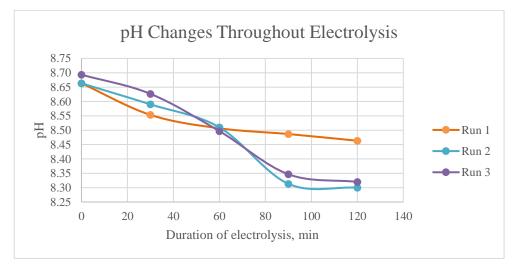
GRAPH 4. Comparison of TN and NH₃-N concentration changes throughout electrolysis.

Unfortunately, the concepts of TKN and TN could not be fully utilized to validate the results, since the electrolyzed samples could not be analyzed using the Kjeldahl method due to the mentioned malfunction of the apparatus. If both nitrogen analyses (TKN and TN) were carried out, together with the data from ion chromatography on nitrate and nitrite concentrations, the results of TN and TKN could have been checked. (Buckwell A., Nadeu E., 2016).

This validation of the initial sample analysis method can be done. The TKN of the initial sample is 2,33 g/l, nitrite concentration is 36,6 mg/l and nitrate concentration is 7,05 mg/l. The TN is the sum of the TKN, nitrate and nitrite concentrations, which theoretically should equal to 2,37 g/l. The TN measured in practice is 3,025 g/l, which suggests that some measurements were underestimated in the TKN analysis or chromatography, or overestimated in case of the TN measurements with HACH. Although, the samples analyzed with the chromatograph were not analyzed immediately after collection, which could lead to a nitrogen dissipation from the struvite precipitation reject water. This is possible through bacterial decomposition of nitrogen contained in its' organic forms to urea and ammonia. Urea can be further decomposed through enzyme activity and ammonia could volatilize from the solution. (Tchobanoglous G., Schroeder E., 1985, p.73, 183). More detailed testing is required to confirm the nature of nitrogen losses. (Lockyer D.R., Whitehead D.C., 1990).

4.2. pH

The pH values measured during the electrolysis of the reject water from struvite precipitation are presented on GRAPH 5. The raw data tables for the pH, conductivity and temperature measurements are presented in Appendix 2.

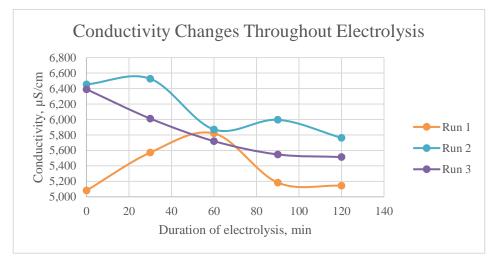


GRAPH 5. pH changes of the solution throughout electrolysis.

As it can be seen from the graph, in all the three (3) runs, the pH decreases the longer the electrolysis proceeds. Practically it means, that there are more protons, H^+ (aq), present in the solution, consecutively decreasing the pH. (Gould S.E., 2012). The decrease in the pH can be explained by consumption of hydroxide ions (OH⁻), which can happen based on a reaction presented in the section 1.4, where hydroxide ions are oxidized to form oxygen gas and water. The hydroxide ion consumption stops, when the pH reaches its plateau stage after 1,5 hours of electrolysis. This could indicate that the chloride concentration became high enough to inhibit the hydroxide consumption and, according to the Nernst equation and the theoretical half-reactions, initiate the production of chlorine and oxygen gases through oxidation of chloride.

4.3. Conductivity

The conductivity measurements were conducted three (3) times from the different runs. The electrolyte solutions and the initial samples had to be diluted since the values exceeded the measurable range of the instrument. A dilution factor of 40 was experimentally determined. The values measured from the diluted samples were then multiplied by a factor of 40 in order to account for the dilution. The results are presented in GRAPH 6.



GRAPH 6. Conductivity changes of the solution throughout electrolysis.

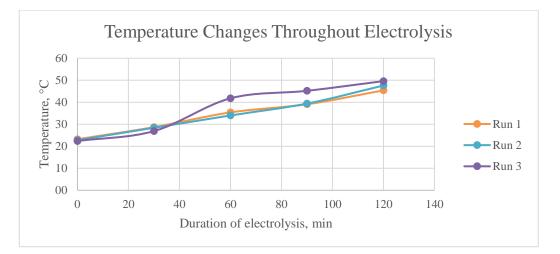
As it can be seen from the graph, there is no particular trend in the changes of conductivity. The conductivity of a solution is defined as the ability of that solution to pass electric current. In the solution, cations and anions are responsible for conducting electricity. The factors that affect the conductivity of a solution are the concentration, the mobility of ions, the valence of ions and the temperature of the solution. (Conductivity, Theory and Practice, 2004).

The temperatures of the samples analysed can be found from Appendix 2, where the collected raw data is presented. The data shows, that the conductivity values are unlikely to have been influenced by the temperature since all the samples were allowed to cool down to the room temperature before the measurements. The temperature differences between the samples are minor.

Gradual dissolution of the electrodes into the electrolyte is a likely factor, which influenced the conductivity values. It was studied that inorganic carbon affects the electrical conductivity of water, such as lime dissolution into lake waters. (Lake access, 2006). Also, some material seemed to have deposited onto the electrodes, which could account for the changes in conductivity. Trapping of gaseous nitrogen, chlorine and other substances in the foam could affect conductivity measurements since fewer species are present in the solution for the electricity conduction. (Conway B., et al., 1994, pp. 220). The changes in conductivity throughout the electrolysis did not provide conclusive data, due to the fact, that there is no clear correlation present in the results.

4.4. Temperature

The temperature was measured together with pH and conductivity at 30-minute intervals. GRAPH 7 shows the temperature values measured throughout electrolysis.



GRAPH 7. Temperature changes of the solution throughout electrolysis.

Significant temperature increases of the solution are observed. In 2 hours, the solution's temperature increased by over 20, almost 30 °C. The heat is a form of energy, which is lost from the system. If the electrolysis is implemented commercially on a big scale, heat energy can be recovered and utilized further, for example, for heating the building, which would minimize the net energy losses, since the heat is being reused. Turbine expanders can serve as a potential tool for the recovery of thermal energy. (Greeff I.L. et al., 2003).

4.5. Ion chromatography

The chromatograms of the standard solutions (S1 - S10) are demonstrated in FIGURE 2.

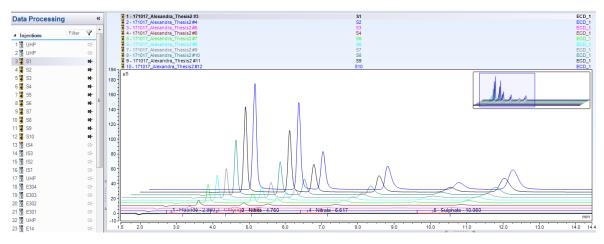


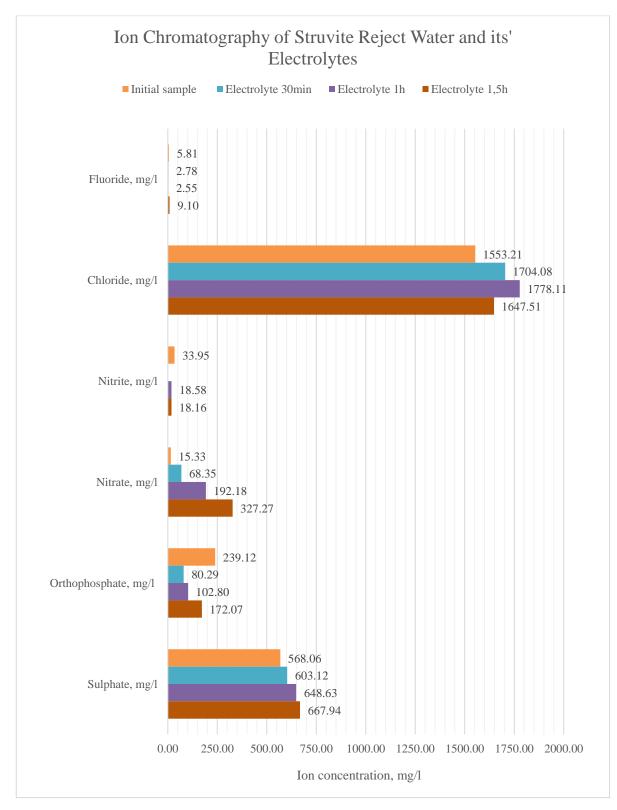
FIGURE 2. Chromatograms of standard calibration solutions S1 - S10.

The chromatograms show that all the six (6) ions, which were analyzed have eluted within the time set for one method and the peaks are distinct. On the figure, there are 10 chromatograms overlaid over each other. The dilutions of each standard solution are noticeable via the height differences of the peaks – the higher the peak is, the higher is the concentration of the ion in the measured solution.

After the peaks were identified and calibration set-up was carried out, Chromeleon – the apparatus' software, was able to calculate all the ion concentrations in milligrams per liter (mg/l) for every sample in the sequence.

The elution order of the ions corresponds to that described in the ISO 10304-1:2007 European Standard for anion determination by ion chromatography but the ion retention times slightly vary. That can be due to the different eluent used in the process than the one mentioned in the standard. The eluent used for the analysis was prepared according to the instructions of the device manufacturer. The retention time of fluoride ion is approximately 2,9 minutes, of chloride: 4 - 4,2 minutes, of nitrite: 4,8 - 4,9 minutes, of nitrate: 6,6 minutes, of orthophosphate: 8,6 minutes and the retention time of sulfate is 10,1 minutes.

The results of ion chromatography are presented in GRAPH 8. A summary data table and full analysis summary sheets can be found from Appendix 5. Sometimes the peaks did not elute properly, or the ion concentration was out of the measurable range, so the values can be missing or the average value may not be too representative.



GRAPH 8. Average ion concentrations measured by ion chromatography.

The changes in fluoride concentration do not follow a particular trend. After 30 minutes of electrolysis and after 1 hour of electrolysis the concentration of fluoride decrease, when after 1,5 hours of electrolysis the measured concentration is even higher than in the initial sample. The fluoride concentration in the 1,5h electrolyte, however, may not be reliable,

since only one peak eluted from the 4 samples analyzed, so the values could not be averaged.

The concentration of chloride in all the samples is approximately the same, which means that chlorine gas was not freed during electrolysis, or if it was, then in very small amounts. If chlorine gas was freed, it could also have been trapped in the foam, forming over the electrodes and dissolved back into the solution. These chloride concentrations are exceptionally high due to the fact, that magnesium chloride salt was added to urine for struvite precipitation. (Kloet M., 2016).

The changes in the nitrite concentration cannot be evaluated since a considerable number of peaks did not elute and show on the chromatogram. This can be due to the fact, that the nitrite concentrations in the samples are rather low. There is a slight pattern of the nitrate concentration decreasing with time, but no definite conclusion can be made since there is not enough data available.

The nitrate and sulfate concentrations clearly increase with time. The concentrations of nitrate are rather low, thinking that the TN concentration of the samples was measured to be around 3 mg/l. Thus, it can be noted that nitrogen in the solution is present in other forms than nitrate.

The concentration of orthophosphate in the samples, similarly to the concentrations of fluoride, does not follow any definite trend. The concentration of orthophosphate in the initial sample is the highest, after 30 minutes of electrolysis is decreased by more than a 50%, then after an hour of electrolysis it slightly increases and after 1,5 hours, it again increases by 60%. However, orthophosphate measurements could have been unreliable, since on FIGURE 2 the peaks of the different orthophosphate concentrations eluted without significant differences in heights.

4.5.1 Ion chromatography: discussion

Ion chromatography was able to clarify the trends in concentration changes of certain ions throughout the electrolysis. For example, nitrate concentration in the samples clearly increases with the duration of the electrolysis. It was concluded, however, that most of the

nitrogen is present in another form than nitrate in the solution, since the nitrate concentrations are insignificant, compared to the TN concentrations measured. The findings are consistent with the analyses conducted on urine previously, such as the Biourea project. (Viskari E.L. et al., 2017, pp.39-41).

Chloride ion concentration stayed approximately the same throughout the electrolysis. If some chlorine gas was formed, the amount was insignificant, or the gas was trapped in the dense layer of foam formed above the anodic compartment. Chlorine gas could have dissolved back from the foam into the solution, which could explain why the chloride concentrations remained the same. (Conway B., et al., 1994, pp. 219-223). Formation of hypochlorite, in this case, could not have been vigorous due to the unchanged concentration of the ion. Thus, not a big fraction of nitrogen could have escaped the system via the formation of chloramine. (Comninellis C., Chen G., 2009, pp. 183-187). Interestingly, the decrease of the chloride concentration is observed after 1 hour of electrolysis, which could signify that the chloride concentration became high enough for the chloride oxidation reaction to start happening according to the Nernst equation. The reaction is outlined in section 1.4.

The concentration of sulfate ions in the solution increased with the duration of the electrolysis. This is consistent with the relationship $C_1V_1 = C_2V_2$, which demonstrates that in a closed system, if the volume of the solution decreases, the concentration of the ions in that solution should increase. The volume of the solution decreased due to water evaporation. (Quansys Biosciences, 2012).

The trends in concentration changes of fluoride and phosphate ions are not clear since the concentrations of these ions fluctuated from one set of samples to the other. The sulphate ion measurement could have been unreliable as a result of autooxidation. In order to measure sulfate without any positive bias, the pH of the solution should have been adjusted to over 10. (ISO 10304-1:2007, p.2).

The nitrite concentration results obtained from the chromatography analysis were rather inconclusive since the peak for nitrite concentration did not elute on the chromatograms of several samples, so the machine did not detect any nitrite in the samples. The chances of nitrite not eluting properly are very low since the eluent prepared is suitable for the ion in question. (Dionex IonPac AS14A Manual, 2002, p.14). The lack of results could be simply due to the absence of the ion from the samples.

4.6. Power consumption

The power consumption can be calculated from current and voltage, using FORMULA 1.

$$P(W) = I(A) \cdot V(V) \tag{1}$$

With that formula, considering that the current applied to the electrolytic cell is 2 amperes and the potential difference across the cell is 15 volts, the power requirement is 30 Watts, which over a period of an hour equals to 30 Wh or 0,03 kWh. This is for a cell of a volume of 300 milliliters. If the system was commercially applied, the power requirements would grow as the volume of the electrolyte increases.

The dependency of the required power on the volume of the electrolyte could be an interesting aspect to test. If supposedly, the power requirement doubled as the volume doubles, then a 300-liter tank would already require a 30 kWh power, which is equivalent to thirty (30) coffee-makers running simultaneously for one hour. (Estimating Appliance and Home Electronic Energy Use, Energy.gov).

Before thinking whether or not electrolysis could be a feasible and cost-effective option, the electricity requirement should be evaluated and the optimal electricity demand tested. The process can end up harming the environment if environmental impacts of the electricity production used for electrolysis are too large. Testing the required electricity input and potential difference needed across the cell, could result in better preservation of nitrogen in the solution. Lower current and voltage could influence nitrogen volatilization from the liquid.

4.7. General discussion

Overall, the volume reduction recorded is 60 milliliters in 1 hour, which contributes to the objective of the research – volume reduction for the logistic benefit. The volume reduction could be significant if the electrolysis was carried out for a longer period than 2 hours. The volume of the reject water from struvite precipitation decreased by nearly 50% in 2 hours of electrolysis, considering that the initial amount of the non-electrolyzed solution is 300 milliliters.

The volume reduction without following ion concentration increase in the solution implies that the substances were escaping the solution in a gaseous form. That can be proven by the relationship $C_1V_1 = C_2V_2$. From the relationship, it follows that if the new volume (V₂) is smaller, then the new concentration should increase (C₂). (Quansys Biosciences, 2012).

Some improvements could be done to the method in order to conclude more definitely whether or not electrolysis or electrochemistry can be applied as a tool for nitrogen recovery from the struvite precipitation reject water. For example, additional analyses should be added to the procedure. The gases, evolving from the system could be analyzed with a gas analyzer. The TN and TKN measurements should be carried out several times to obtain more representative and reliable results and understand what happens to the nitrogen concentrations throughout the electrolysis and in which forms the nitrogen is primarily present in the solution.

Another important aspect to analyze is the foam evolving during the electrolysis. As it was hypothesized, some substances, which evolve from the solution are being trapped in the foam. Foam prevents efficient electrolysis by limiting the presence of oxidants in the solution, such as chloride and thus facilitating the electrolysis of water over other processes. (Conway B., et al., 1994, pp. 219-223). This validates the findings that chlorine and nitrogen gases could be trapped in the foam and then dissolved back into the solution as the electrolysis rate slows down and the foam collapses. The study opens up one limitation to the electrolysis process - foam formation, which can be suppressed by addition of soap sorbents. In addition to that, the foam can be suppressed using foam suppression devices. (Conway B., et al., 1994, pp. 220).

Fresh samples in duplicates could be analyzed by ion chromatography, since the length of the sample storage and freezing the samples could have led to unreliable results. The limiting factor for this work was time the since sample collection alone could take over 3 hours, not mentioning the analyses themselves. The nitrate measurements are considered to be accurate after freezing, unlike phosphate, which deteriorates when frozen. (Chapman P., Mostert S.A., 1990).

Capturing hydrogen gas, which is produced during electrolysis, could make the design more sustainable. As was hypothesized, there was hydrogen forming on the cathode. Hydrogen gas can be collected to be further utilized as a fuel. (Hydrogen Basics, 2017).

Nitrogen recovery and capture could be made more efficient with the structural modifications to the experimental set-up. By analogy with the research discussed in section 1.5, the set-up for effective nitrogen capturing would require an ammonia selective membrane and an acid trap. Ammonium could be trapped in phosphoric acid (H₃PO₄), producing ammonium phosphate (NH₄)₃PO₄, where both phosphorus and nitrogen can be used as fertilizers. Ammonium phosphate or monoammonium phosphate (MAP) has been used as a fertilizer for several years. (IPNI, NSS-9, Monoammonium Phosphate (MAP)). If the production of MAP was possible as a result of electrolysing the struvite precipitation reject water with an ion-selective membrane, one of the products of the process could be a ready-made fertilizer. If nitrogen escapes the system in a gaseous form, the technology for collecting nitrogen gas can be developed and implemented into the electrochemical design. Nitrogen gas can be further dissolved in the acidic medium, such as phosphoric acid, to produce the same MAP fertilizer.

5 CONCLUSION

There is a need for developing innovative technologies, which would provide solutions for water treatment as well as nutrient recycling and recovery. One of the common substances for the research and development in the area of nutrient recovery is urine. Human urine is rich in nitrogen and phosphorus – the two key nutrients required for fertilization and growth, which could be recovered and reused. Phosphorus removal via struvite precipitation has been well explored – the removal rates and the process efficiency are high. The reject water from the precipitation of struvite contains nitrogen, which could potentially be recovered. Capturing nitrogen from the reject water of struvite precipitation solution was tested previously. The aim of the work was to explore whether it is possible to reduce the volume of the solution at the same time concentrating the nutrients in it.

Electrolysis was effective in terms of the volume reduction and no large nutrient losses were observed. The total nitrogen concentration of the solution decreased with the duration of the electrolysis. Structural modifications to the process, such as the addition of an acid trap for ammonia gas, collecting evolved gases and utilizing heat produced throughout the process, could enable more efficient nitrogen recovery and lead to more sustainable design. Addition of a trap with phosphoric acid enables a possibility for production of a ready-made fertilizer monoammonium phosphate (MAP).

In conclusion, it can be said that the electrolysis and electrochemistry could be a feasible method for nutrient recovery and possibly nutrient capturing from the struvite precipitation reject water after certain modifications and cost analysis. This thesis work was effective in exploring the basics behind the process, recognizing the potential for further research and suggesting further research directions.

REFERENCES

12.2017, Compound summary for CID 1176 – Urea, PubChem Open Chemistry Database, last accessed: 28.12.2017, https://pubchem.ncbi.nlm.nih.gov/compound/urea#section=Top.

17.02.2017, Electrolysis Concepts Chemistry Tutorial, AUS_e-TUTE, last accessed: 28.12.2017, http://www.ausetute.com.au/elecysis.html.

19.04.2017, Hydrogen Basics, Alternative Fuels Data Centre, US Department of Energy, last accessed: 28.12.2017, https://www.afdc.energy.gov/fuels/hydrogen_basics.html.

2006, Lake access, Seeing below the surface, Electrical Conductivity: Measuring salts in water, last accessed: 17.01.2018, http://www.lakeaccess.org/russ/conductivity.htm.

2012, Quansys Biosciences, Dilutions: Explanations and Examples of Common Methods, last accessed: 19.01.2018, http://www.quansysbio.com/wp-content/uploads/2012/10/Di-lutions-v2.pdf.

2014, Electrolysis, Chemistry Libre Texts, National Science Foundation, last accessed: 28.12.2017, https://chem.libretexts.org/Core/Analytical_Chemistry/Electrochemis-try/Electrolytic_Cells/Electrolysis.

2017, Büchi – Products & Solutions, Scrubber K-415, last accessed: 27.12.2017, http://www.buchi.com/en/products/kjeldahl-dumas/scrubber-k-415.

Ashton C., Barron J., 2005, The effect of temperature on conductivity measurement. TSP-07, Issue 3, Reagecon Diagnostics Ltd, Ireland.

Ashton C., Geary L., 2006, The Effects of Temperature on pH Measurement. TSP-01-2, Reagecon Diagnostics Ltd., Ireland.

Ball D., 2011, Introductory chemistry, 6.6 – Gas Mixtures, Saylor Foundation, last accessed: 19.01.2018, https://www.saylor.org/site/textbooks/Introductory%20Chemistry.pdf.

Blumhof S., 13.10.2010, Removing Nitrates with Ion Exchange, Water Technology – solutions for industrial water management, last accessed: 28.12.2017, https://www.wa-tertechonline.com/removing-nitrates-with-ion-exchange/.

Botte G., Benedetti L., Gonzalez J., 2005., Electrolysis of Ammonia: an in-Situ Hydrogen Production Process, Ohio University.

Buckwell A., Nadeu E., 2016, Nutrient Recovery and Reuse (NRR) in European agriculture, A review of the issues, opportunities, and actions, The RISE Foundation, Brussels, Belgium.

Chapman P., Mostert S.A., 1990, Does freezing of nutrient samples cause analytical errors?, South African Journal of Marine Science, 9:1, 239-247, DOI: 10.2989/025776190784378763.

Chemistry LibreTexts, 7.7.2017, Nernst Equation, last accessed: 26.01.2018, https://chem.libretexts.org/Core/Analytical_Chemistry/Electrochemistry/Nernst_Equation.

Chislock, M. F., Doster, E., Zitomer, R. A. & Wilson, A. E. (2013) Eutrophication: Causes, Consequences, and Controls in Aquatic Ecosystems. Nature Education Knowledge 4(4):10., last accessed: 28.12.2017, https://www.nature.com/scita-ble/knowledge/library/eutrophication-causes-consequences-and-controls-in-aquatic-102364466.

Clark J., 2013, The electrochemical series, last accessed: 28.12.2017, https://www.chem-guide.co.uk/physical/redoxeqia/ecs.html.

Cohen P., Geffner S., 1996, Chemistry: A Contemporary Approach, Amsco School Publications Inc., USA.

Comninellis C., Chen G., 2009, Electrochemistry for the environment, Chapter 7: Drinking Water Disinfection by In-line Electrolysis, Springer Science & Business Media, USA.

Conductivity, Theory and Practice, 2004, Booklet on conductivity measurements, Radiometer Analytical SAS, last accessed: 18.12.2017, http://www.analytical-chemistry.uoc.gr/files/items/6/618/agwgimometria_2.pdf.

Conway B., Murphy O., Rose T., Rudd E., 1994, Proceedings Volume 94-19, Proceedings of the Symposium on water purification by photocatalytic, photoelectrochemical and electrochemical processes, Electrolysis, The Electrochemical Society Inc., USA.

Dana A., Elishav O., Bardow A., Shter G., Grader G., 10.06.2016., Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis, Angewandte Chemie (International Ed. In English), last accessed: 28.12.2017, https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5089635/.

Estimating Appliance and Home Electronic Energy Use, Energy.gov, US Department of Energy, last accessed: 27.12.2017, https://energy.gov/energysaver/estimating-appliance-and-home-electronic-energy-use.

Gendel Y., Lahav O., 2011, Revealing the mechanism of indirect ammonia electrooxidation, Faculty of Civil and Environmental Engineering, Technion, Haifa 32000, Israel.

Gould S.E., 2012, What Makes Things Acidic: the pH scale, Scientific American, last accessed: 17.01.2018, https://blogs.scientificamerican.com/lab-rat/what-makes-things-acid-the-ph-scale/.

Greeff I.L., Visser J.A., Ptasinski K.J., Janssen F.J.J.G., 2003, *Energy*, Volume 29, Issue 12, Pages 2045-2060, Using turbine expanders to recover exothermic reaction heat – flow sheet development for typical chemical processes, Elsevier Ltd.

Harris D.C., 2007, Quantitative Chemical Analysis, Appendix H: Standard Reduction Potentials, 7th edition, W.H. Freeman and Company, USA.

Helmenstine A.M., 2017, What Is the Chemical Composition of Urine?, Compounds and Ions in Human Urine, Thoughts.Co – Science, Tech, Math, last accessed: 19.01.2018, https://www.thoughtco.com/the-chemical-composition-of-urine-603883.

High Performance Ammonia Ion Selective Electrode, 2010, User Guide, Thermo Scientific, last accessed: 27.12.2017, https://assets.fishersci.com/TFS-Assets/LSG/manuals/D01250~.pdf.

Hoegger R., 1998, Büchi Training papers, Nitrogen determination according to Kjeldahl, Büchi Laboetwchnik AG.

Hydrogen Safety, Fact sheet on hydrogen properties and safety, FCHEA Fuel Cell & Hydrogen Energy Association, last accessed: 27.12.2017, https://www.ar-hab.org/pdfs/h2_safety_fsheet.pdf.

IonPac AG14A Guard Column, IonPac AS14A Analytical Column, 2002, Product Manual, Thermo Scientific, Dionex Corporation, last accessed: 27.12.2017, https://tools.thermofisher.com/content/sfs/manuals/4363-Man-031678-03-IonPac-AS14A-Nov02.pdf.

ISO 10304-1:2007, Water quality – determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate., CEN European Committee for Standarization.

Kimball J., 7.10.2016, The Nitrogen Cycle, Kimball's biology pages, last accessed: 28.12.2017, http://www.biology-pages.info/N/NitrogenCycle.html.

Kloet M., 2016, Optimization of Struvite Production from Urine, Bachelor's thesis, TAMK – Tampere University of Applied Sciences.

LCK 138 Total Nitrogen, TN_b, 1-16 mg/l, Instruction manual, HACH Lange, last accessed: 27.12.2017, https://es.hach.com/asset-get.download.jsa?id=25593611195.

Lockyer D.R., Whitehead D.C., 1990, Volatilization of Ammonia from Cattle Urine Applied to Grassland, Elsevier Ltd.

Martin J.G., White C.W., 2010, Chlorine Gas Inhalation: Human Clinical Evidence of Toxicity and Experience in Animal Models, Proceedings of the American Thoracic Society.

Miso, A., Spuhler, D., 2009, Fertiliser from urine (Struvite), SSWM, last accessed: 27.12.2017, https://www.sswm.info/content/fertiliser-urine-struvite.

Nutrient Source Specifics 9, Monoammonium Phosphate (MAP), IPNI: International Plant Nutrition Institute, last accessed: 19.01.2018, https://www.ipni.net/publica-tion/nss.nsf/0/2F200FA9C8C946F0852579AF00762904/\$FILE/NSS-09%20Monoammonium%20Phosphate.pdf.

O'Haver T., 2008, last updated 2017, Worksheets for Analytical Calibration Curves, The University of Maryland, last accessed: 17.01.2018, https://terpconnect.umd.edu/~toh/models/CalibrationCurve.html.

Puurunen L., 2016, Nitrogen Recovery from Struvite Precipitation Reject Water, Bachelor's thesis, TAMK – Tampere University of Applied Sciences.

SDG - Sustainable Development Goals, 2015, United Nations, last accessed: 27.12.2017, http://www.un.org/sustainabledevelopment/sustainable-development-goals/.

SFS 5505, Jäteveden epäorgaanisen ja orgaanisen typen määritys. Modifioitu kjeldahlmenetelmä, 1998, Suomen ympäristökeskus.

Tarpeh W., Nelson K., 2016, Electrochemical Stripping to Recover Nitrogen from Urine, Department of Civil & Environmental Engineering, University of California, USA.

Tchobanoglous G., Schroeder E., 1985, Water Quality, Characteristics, Modelling, Modification, Addison-Wesley Publishing Company Inc., USA.

Total Nitrogen in Wastewater, ASA Analytics, last accessed: 28.12.2017, http://www.asaanalytics.com/total-nitrogen.php.

US EPA Environmental Protection Agency, Nutrient Pollution, last accessed: 27.5.2016. https://www.epa.gov/nutrientpollution/problem.

Viskari E.L., Vilpas R., Lehtoranta S., Pakula S., Tuukkanen K., 2017, Biourea - Erilliskerätyn virtsan lannoitepotentiaali, kokeelliset tutkimukset ja elinkaaritarkastelu, Loppuraportti, Käymäläseura Huussi ry.

WHO, 2006, WHO guidelines for the safe use of wastewater, excreta and greywater, Volume 4, Excreta and greywater use in agriculture, s.l.: World Health Organisation.

Wu, X. ; Modin, O, 2013, Ammonium recovery from reject water combined with hydrogen production in a bioelectrochemical reactor, Bioresource Technology, vol. 146 pp. 530-536.

APPENDICES

Sample	Dilution	TN concentra- tion, mg/l	TN concentration with dilution, g/l	Average TN, g/l
Initial 1	1:250	12,2	3,05	
Initial 2	1:250	12,0	3,00	3,025
Electrolyte 30min - 1	1:250	10,2	2,55	
Electrolyte 30min - 2	1:250	10,3	2,58	2,563
Electrolyte 1h - 1	1:250	11,1	2,78	
Electrolyte 1h -2	1:250	11,4	2,85	2,813
Electrolyte 1,5h -1	1:250	9,07	2,27	
Electrolyte 1,5h - 2	1:250	9,11	2,28	2,273

Appendix 1. HACH total nitrogen data table.

pН	pH, average	T, °C	Conductivity , µS/cm	Conductivity average, µS/cm	Dilution for conductivity	T for measurements, °C
8,66			27,9			
8,67	7 8,66	23,2	126,6	127,0	1:40	21,6
8,66	6		126,6			
8,56	9		140,3			
8,55	5 8,55	28,7	138,9	139,3	1:40	21,3
8,55	5		138,7			
8,51	1		145,3			
8,50	0 8,51	32,4	145,5	145,5	1:40	21,9
8,51	1		145,7			
8,48	8		129,3			
8,49	9 8,49	35,1	129,6	129,6	1:40	22,2
8,49	9		129,9			
8,46	9		129,5			
8,46	6 8,46	36,4	128,6	128,6	1:40	20,5
8.47	1					

Appendix 2. Raw data collected throughout the measurements.

1(3)

Electrolysis, Run 2	Run 2					
pH	pH, average	T, °C	Conductivity , µS/cm	Conductivity average, µS/cm	Dilution for conductivity	T for measurements, °C
8,67			61,2			
8,64	4 8,66	22,8	161,4	161,3	1:40	22,1
8,68	8		161,4			
8,59	9		164,2			
8,59	9 8,59	28,4	162,5	163,2	1:40	21,4
8,59	9		162,8			
8,51	-		147,4			
8,52	2 8,51	34,0	147,2	146,8	1:40	21,7
8,50	0		145,7			
8,31	1		150,4			
8,31	1 8,31	39,4	149,6	149,9	1:40	22
8,32	2		149,7			
8,3	0		144,2			
8,30	0 8,30	47,6	142,2	144,1	1:40	21,7
8,30	0		145,8			

2(3)

45

Electrolysis, Run 3	un 3					
рH	pH, average	T, ℃	Conductivity , µS/cm	Conductivity average, µS/cm	Dilution for conductivity	T for measurements, °C
8,69			160,6			
8,70	8,69	22,4	158,9	159,8	1:40	22,4
8,69			159,8			
8,62			151,0			
8,63	8,63	26,9	151,3	150,3	1:40	22,3
8,63			148,6			
8,51			142,5			
8,49	8,50	41,8	143,6	143,0	1:40	22,1
8,49			142,9			
8,34			138,7			
8,36	8,35	45,2	139,3	138,7	1:40	22,0
8,34			138,1			
8,33			138,0			
8,31	8,32	49,6	137,8	137,9	1:40	22,4
8,31			137,8			

3(3)

46

Ammonia concentration, ppm	mV	pН	T, °C	log NH3-N concentration
100	13,3	12,69	22,1	2,000
50	31,4	12,72	22,1	1,699
20	58,5	12,71	21,8	1,301
1	102,3	12,85	21,9	0,000
1000	-60,0	12,33	22,2	3,000
500	-43,5	12,42	22,4	2,699
200	-7,8	12,59	22,4	2,301
100	13,3	12,69	22,1	2,000

Appendix 3. Data for ammonia ISE calibration curve.

Duration of electrolysis, min		pH initial	pH adjusted Dilution	Dilution	T	ຸ, °C	m٧		log[NH3-N]	[NH3-N], mg/l	Undiluted [NH3-N], mg/l
	0	8,67	12,43		1 2	23,0		-69,4	3,09	1242,67	1242,67 2485,34
	30	8,59	11,88		1:2	24,3		-78,1	3,21	1620,02	3240,04
	60	8,51	11,95		1:2	23,3		-87,9	3,34	2183,97	4367,93
	90	8,31	11,94		1:2	24,2		-92,0	3,39	2474,68	4949,36
	120	8,30	12,13		Ň	24,3		-95,2	3,44	2728,21	5456,43

Appendix 5. Ion chromatography summary sheets and table.

			Sum	mary			
Seque	nce Details						
Vame.		171017_Alexan	dra_Thesis2		Created On:	17/Oct/17 14:12:48	
Direct					Created By:	kemia	
Data V		ChromeleonLo	cal		Updated On:	18/Oct/17 09:35:11	
No. of	Injections:	33			Updated By:	kemia	
By Co	mponent	Fluoride					
		011					
No.	Injection Name	Ret.Time	Area	Height	Amount	Rel.Area	Peak Type
		min	µS*min	μS	mg/l	%	
		ECD_1	ECD_1	ECD_1	ECD_1	ECD_1	ECD_1
		Fluoride	Fluoride	Fluoride	Fluoride	Fluoride	Fluoride
1	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	2.860	0.061	0.582	0.354	31.26	BMB
4	S2	2.860	0.125	1.210	0.724	31.31	BMB
5	S3	2.860	0.286	2.657	1.664	31.73	BMB
6	S4	2.863	0.718	6.965	4.178	32.80	BMB
7	S5	2.870	2.473	24.760	14.382	33.87	BMB
8	S6	2.873	3.402	33.875	19.783	33.89	BMB
9	S7	2.877	3.948	39.068	22.960	33.86	BM
10	S8	2.890	7.780	73.751	45.239	32.90	BM
11	S9	2.903	13.162	114.987	76.540	31.22	BM
12	S10	2.913	17.436	142.761	101.392	29.98	BM
13	IS4	2.860	0.023	0.242	0.136	0.79	BMB
14	IS3	2.863	0.024	0.216	0.138	0.40	M
15	IS2	2.863	0.014	0.065	0.084	0.08	M
16	IS1	2.870	0.018	0.069	0.107	0.05	M
17	UHP	2.864	0.017	0.038	0.100	10.41	BM
18	E304	2.860	0.008	0.076	0.045	0.31	BM
19	E303	2.867	0.014	0.055	0.079	0.22	M
20	E302	2.860	0.016	0.074	0.091	0.09	M
21	E301	2.877	0.014	0.064	0.084	0.04	M
22	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23	E14	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
24	E13	2.870	0.009	0.054	0.051	0.13	M
25	E12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
26	E11	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
27	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	E154	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29	E153	2.883	0.031	0.080	0.182	0.47	М
30	E152	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31	E151	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
32	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

	Summary	/		
Sequence Details				_
Name:	171017 Alexandra Thesis2	Created On:	17/Oct/17 14:12:48	
Directory:		Created By:	kemia	
Data Vault:	ChromeleonLocal	Updated On:	18/Oct/17 09:35:11	
No. of Injections:	33	Updated By:	kemia	
By Component	Chloride			

by cu	mponent	Chionde					
No.	Injection Name	Ret.Time	Area	Height	Amount	Rel Area	Peak Type
		min	uS*min	μŠ	mg/l	%	
		ECD 1					
		Chloride	Chloride	Chloride	Chloride	Chloride	Chloride
1	UHP	4.083	0.005	0.028	0.038	22.16	BMB
2	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	4.093	0.046	0.357	0.344	23.64	BMB
4	S2	4.094	0.098	0.756	0.730	24.56	BMB
5	S3	4.097	0.190	1.468	1.421	21.09	BMB
6	S4	4.097	0.459	3.592	3.426	20.94	BMB
7	S5	4.104	1.541	12.422	11.511	21.11	BMB
8	S6	4.100	2.163	17.321	16.160	21.55	BM
9	S7	4.103	2.536	20.375	18.944	21.75	M
10	S8	4.110	5.400	44.361	40.339	22.84	M
11	S9	4.117	10.099	83.194	75.437	23.95	M
12	S10	4.120	14.287	117.023	106.727	24.56	M
13	IS4	4.107	2.348	17.663	17.539	79.16	BM
14	IS3	4.130	4.851	31.492	36.234	81.65	M
15	IS2	4.240	14.939	106.869	111.593	84.77	BMB
16	IS1	4.227	5.560	106.082	41.536	15.15	M
17	UHP	4.097	0.028	0.186	0.209	16.95	MB
18	E304	4.103	1.862	14.039	13.908	72.84	BMB
19	E303	4.133	4.559	29.460	34.055	74.81	M
20	E302	4.230	13.512	98.370	100.934	77.46	MB
21	E301	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22	UHP	4.100	0.016	0.118	0.123	100.00	MB
23	E14	4.103	2.057	15.583	15.365	69.25	BMB
24	E13	4.127	4.705	30.986	35.146	71.78	M
25	E12	4.230	13.658	99.107	102.027	73.88	BM
26	E11	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
27	UHP	4.097	0.022	0.183	0.168	100.00	BMB
28	E154	4.107	1.965	14.758	14.682	61.44	BMB
29	E153	4.233	4.582	28.092	34.231	69.03	M
30	E152	4.220	11.799	86.851	88.139	65.13	BM
31	E151	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
32	UHP	4.097	0.018	0.111	0.132	100.00	BMB
33	UHP	4.110	0.007	0.053	0.052	100.00	BMB

1(4)

			Sum	mary			
Seque	nce Details						
Name:		171017_Alexan	dra_Thesis2		Created On:	17/Oct/17 14:12:48	
Directe					Created By:	kemia	
Data V		ChromeleonLo	cal		Updated On:	18/Oct/17 09:35:11	
No. of	Injections:	33			Updated By:	kemia	
By Co	mponent	Nitrite					
		611					
No.	Injection Name	Ret.Time	Area	Height	Amount	Rel.Area	Peak Type
		min	µS*min	μS	mg/l	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	500
		ECD_1	ECD_1	ECD_1	ECD_1	ECD_1	ECD_1
	UHP	Nitrite	Nitrite	Nitrite	Nitrite	Nitrite	Nitrite
1	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	4.760	0.023	0.160	0.295	11.85	BMB
4	S2	4.760	0.052	0.334	0.662	13.02	BM
5	S3	4.763	0.115	0.737	1.473	12.78	BMB
6	S4	4.767	0.297	1.899	3.791	13.55	BMB
7	S5	4.770	1.000	6.432	12.778	13.70	BMB
8	S6	4.770	1.400	8.853	17.883	13.94	MB
9	S7	4.770	1.636	10.276	20.897	14.03	MB
10	S8	4.777	3.326	21.048	42.492	14.06	MB
11	S9	4.787	5.964	37.535	76.198	14.14	MB
12	S10	4.790	8.148	51.121	104.103	14.01	M
13	IS4	4.767	0.025	0.117	0.316	0.83	MB
14	IS3	4.787	0.057	0.156	0.726	0.96	M
15	IS2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16	IS1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18	E304	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19	E303	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
20	E302	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
21	E301	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23	E14	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
24	E13	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
25	E12	4.787	0.078	0.310	0.992	0.42	MB
26	E11	4.803	0.136	0.685	1.732	0.34	М
27	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	E154	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29	E153	4.920	0.025	0.135	0.315	0.37	M
30	E152	4.793	0.072	0.354	0.921	0.40	М
31	E151	4.817	0.159	0.784	2.032	0.39	М
32	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

	Summary	/		
Sequence Details				
Name:	171017 Alexandra Thesis2	Created On:	17/Oct/17 14:12:48	
Directory:		Created By:	kemia	
Data Vault:	ChromeleonLocal	Updated On:	18/Oct/17 09:35:11	
No. of Injections:	33	Updated By:	kemia	
By Component	Nitrate			

No.	Injection Name	Ret.Time	Area	Height	Amount	Rel.Area	Peak Type
	injood of it tall to	min	uS*min	μS	mg/l	%	
		ECD 1	ECD 1	ECD 1	ECD 1	ECD 1	ECD 1
		Nitrate	Nitrate	Nitrate	Nitrate	Nitrate	Nitrate
1	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	6.617	0.023	0.089	0.358	11.72	BMB
4	S2	6.634	0.050	0.202	0.788	12.65	BMB
5	S3	6.640	0.098	0.421	1.535	10.86	BMB
6	S4	6.637	0.250	1.072	3.918	11.42	BMB
7	S5	6.624	0.822	3.603	12.885	11.26	BMB
8	S6	6.617	1.105	4.910	17.313	11.01	BMB
9	S7	6.613	1.279	5.700	20.045	10.97	BMB
10	S8	6.597	2.609	11.806	40.880	11.03	Rd
11	S9	6.583	4.769	21.942	74.726	11.31	Rd
12	S10	6.567	6.786	31.309	106.320	11.67	MB
13	IS4	6.657	0.015	0.052	0.236	0.51	BMB
14	IS3	6.643	0.009	0.046	0.141	0.15	M
15	IS2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16	IS1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17	UHP	6.634	0.059	0.027	0.932	35.95	BM
18	E304	6.660	0.042	0.180	0.654	1.63	BMB
19	E303	6.660	0.091	0.388	1.429	1.50	M
20	E302	6.660	0.217	0.966	3.406	1.25	BMB
21	E301	6.660	0.437	1.976	6.844	1.13	BMB
22	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23	E14	6.653	0.118	0.496	1.846	3.97	BM
24	E13	6.653	0.240	1.059	3.756	3.66	M
25	E12	6.650	0.620	2.776	9.708	3.35	BM
26	E11	6.640	1.290	5.807	20.216	3.20	M
27	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	E154	6.654	0.198	0.862	3.095	6.17	BMB
29	E153	6.933	0.426	1.798	6.679	6.42	M
30	E152	6.643	1.012	4.580	15.857	5.59	BM
31	E151	6.633	2.224	10.278	34.849	5.38	BM
32	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Summary							
Sequence Details							
Name:	171017 Alexandra Thesis2	Created On:	17/Oct/17 14:12:48				
Directory:		Created By:	kemia				
Data Vault	ChromeleonLocal	Updated On:	18/Oct/17 09:35:11				
No. of Injections:	33	Updated By:	kemia				
By Component	Orthophosphate						

No.	Injection Name	Ret.Time	Area	Height	Amount	Rel.Area	Peak Type
		min	μS*min	μS	mg/l	%	
		ECD_1	ECD_1	ECD_1	ECD_1	ECD_1	ECD_1
		Orthophosphate	Orthophosphate			Orthophosphate	Orthophosphate
1	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4	S2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
5	S3	8.623	0.075	0.156	2.601	8.32	BMB
6	S4	8.600	0.138	0.340	4.788	6.31	BMB
7	S5	8.574	0.397	1.059	13.740	5.43	BMB
8	S6	8.563	0.536	1.446	18.586	5.34	BMB
9	S7	8.567	0.612	1.672	21.223	5.25	BMB
10	S8	8.553	1.208	3.437	41.860	5.11	BMB
11	S9	8.543	2.157	6.370	74.754	5.12	BMB
12	S10	8.530	3.033	9.126	105.106	5.21	BMB
13	IS4	8.600	0.099	0.231	3.438	3.34	BMB
14	IS3	8.597	0.136	0.330	4.702	2.28	M
15	IS2	8.587	0.318	0.822	11.032	1.81	BMB
16	IS1	8.577	0.453	1.191	15.692	1.23	BMB
17	UHP	8.717	0.041	0.068	1.413	24.65	BMB
18	E304	8.593	0.025	0.073	0.871	0.98	Rd
19	E303	8.600	0.044	0.128	1.518	0.72	Rd
20	E302	8.577	0.123	0.273	4.270	0.71	MB
21	E301	8.577	0.210	0.494	7.274	0.54	MB
22	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23	E14	8.580	0.031	0.092	1.060	1.03	Rd
24	E13	8.573	0.051	0.154	1.760	0.77	Rd
25	E12	8.577	0.167	0.387	5.772	0.90	MB
26	E11	8.573	0.294	0.689	10.176	0.73	MB
27	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	E154	8.597	0.052	0.148	1.815	1.64	Rd
29	E153	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
30	E152	8.570	0.253	0.593	8.783	1.40	MB
31	E151	8.563	0.459	1.120	15.904	1.11	MB
32	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Summary							
Sequence Details							
Name:	171017_Alexandra_Thesis2	Created On:	17/Oct/17 14:12:48				
Directory:		Created By:	kemia				
Data Vault:	ChromeleonLocal	Updated On:	18/Oct/17 09:35:11				
No. of Injections:	33	Updated By:	kemia				

t

ву со	mponent	Sulphate					
No.	Injection Name	RetTime	Area	Height	Amount	Rel Area	Peak Type
V U.	injection Name	min	µS*min	uS	mg/l	Nel Area	Peak type
		ECD 1					
		Sulphate	Sulphate	Sulphate	Sulphate	Sulphate	Sulphate
1	UHP	10.047	0.014	0.047	0.180	62.61	BMB
2	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	S1	10.060	0.042	0.117	0.523	21.53	BMB
4	S2	10.060	0.073	0.220	0.914	18.45	BMB
5	S3	10.057	0.137	0.401	1.712	15.23	BMB
6	S4	10.090	0.328	0.963	4.090	14.99	BMB
7	S5	10.050	1.068	3.157	13.310	14.63	BMB
8	S6	10.047	1.431	4.240	17.838	14.26	BMB
9	S7	10.050	1.648	4.888	20.534	14.13	BMB
10	S8	10.040	3.325	9.967	41.434	14.06	BMB
11	S9	10.030	6.012	18.294	74,928	14.26	BMB
12	S10	10.017	8.474	25.940	105.607	14.57	BMB
13	IS4	10.057	0.449	1.325	5,599	15.15	BMB
14	IS3	10.063	0.865	2.552	10.777	14.56	M
15	IS2	10.060	2.332	6.986	29.065	13.23	BMB
16	IS1	10.053	4.752	14.453	59.219	12.95	BMB
17	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18	E304	10.063	0.425	1.248	5.296	16.63	BMB
19	E303	10.060	0.944	2.785	11.769	15.50	M
20	E302	10.060	2.487	7.457	30.996	14.26	BMB
21	E301	10.054	5.412	16.534	67.450	13.96	BMB
22	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23	E14	10.057	0.495	1.451	6.168	16.66	BMB
24	E13	10.060	1.003	2.964	12.498	15.30	M
25	E12	10.057	2.635	7.896	32.842	14.25	BMB
26	E11	10.050	5.585	17.054	69.599	13.85	BMB
27	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	E154	10.064	0.509	1.484	6.341	15.91	BMB
29	E153	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
30	E152	10.057	2.605	7.813	32.468	14.38	BMB
31	E151	10.053	5.780	17.670	72.036	13.99	BMB
32	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33	UHP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

51

Sample	Fluoride, mg/l	Chloride, mg/l	Nitrite, mg/l	Nitrate, mg/l	Orthophos- phate, mg/l	Sulphate, mg/l
Initial sample	5,81	1553,21	33,95	15,33	239,12	568,06
Electrolyte 30min	2,78	1704,08	-	68,35	80,29	603,12
Electrolyte 1h	2,55	1778,11	18,58	192,18	102,80	648,63
Electrolyte 1,5h	9,10	1647,51	18,16	327,27	172,07	667,94

The values presented in the table represent average ion concentrations based on the ion chromatography of the struvite precipitation reject water and its' electrolytes.